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Physical Properties of Iron-Nitride Films Epitaxially Grown on Silicon (001) by Sputtering and Assessment of Giant Magnetic Moment in the Alpha'-Iron-Nitride Phase

Marilee Ann Brewer
Materials Sciences Division

December 1997
Ph.D. Thesis
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Marilee Ann Brewer
Ph.D. Thesis
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December 1997

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A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy in

Materials Science by

Marilee Ann Brewer

Committee in charge:

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December 1997
Physical Properties of Iron-Nitride Films Epitaxially Grown on
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by

Marilee Ann Brewer

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JOURNAL PUBLICATIONS


CONFERENCE PRESENTATIONS

"Magnetic and Physical Microstructure of Fe$_{16}$N$_2$ Films Grown Epitaxially on Si(001)"
M.A. Brewer, C.J. Echer, K.M. Krishnan, T. Kobayashi and A. Nakanishi

"Epitaxial Fe$_{16}$N$_2$ Films Grown on Si(001) by Reactive Sputtering"
M.A. Brewer, K.M. Krishnan and C. Ortiz

"Substrate Preparation Effects on Nucleation and Surface Profiles of Diamond Thin Films"
M.A. Brewer and K.M. Krishnan

"Simple and Inexpensive Microwave Plasma Assisted CVD Facility"

U.S. PATENT

"Pretreatment Process for Forming a Smooth Surface Diamond Film on a Carbon-Coated Substrate"
Zhu Feng, Marilee Brewer, Ian Brown, Kyriakos Komvopoulos

FIELDS OF STUDY

            Dr. Ian G. Brown

Prof. James S. Speck

1994-1997  Ph.D. dissertation research on epitaxial growth of iron-nitride magnetic films, including investigation of claimed giant magnetic moment of $\alpha''$-Fe$_{16}$N$_2$, growth of FeN films on silicon by sputtering, structural, electronic and magnetic characterization using TEM, XRD, vibrating-sample magnetometry, electron energy-loss spectroscopy, and others. Performed experiments on FeN at LBNL's Advanced Light Source synchrotron including X-ray absorption spectroscopy and magnetic circular dichroism.

Dr. Kannan M. Krishnan
ABSTRACT


by

Marilee Ann Brewer

Intense scientific and technological interest in iron nitrides has persisted since saturation magnetizations much larger than that of α-Fe (1708 emu/cm³) were reported for the metastable α"-Fe₁₆N₂ phase (2300 emu/cm³) grown by MBE on lattice-matched substrates. Most attempts at growing α" using technologically-relevant deposition processes and substrates have resulted in only a modest enhancement in moment, and are complicated by competition from more stable FeN phases. Furthermore, conventional band theory calculations for α" (1780 emu/cm³) do not predict a “giant” magnetic moment.

We have grown several phases of FeN on Si(001) by lattice matching on Ag underlayers. Optimization of reactive N₂ sputtering parameters has led to the growth of α-Fe, γ'-Fe₄N and α'-Fe₉N films. Annealing of N-disordered α'-Fe₉N films resulted in partial transformation to N-ordered α"-Fe₁₆N₂. Quantification of X-ray diffraction peak intensities determined that the α'/α" mixtures contained 48 vol% α" (remaining α'). Selected-area diffraction (SAD) in the TEM determined that the orientation relationships of the α, α', and α" phases were FeN(001)||Ag(001)||Si(001) and FeN[100]||Ag[110]||Si[100], while the in-plane orientation of γ'(001) was FeN[110]||Ag[110]||Si[100]. Electron energy-loss spectroscopy (EELS) determined that the FeN films were stoichiometrically correct and there was no significant change in N content with annealing.

Vibrating-sample magnetometry of the α' and α'/α" films measured a saturation magnetization of 1780 emu/cm³ for both phases; there was no change in the magnetization with increasing N order and no giant moment. Mössbauer spectroscopy of the α'/α" films confirmed the presence of three chemically-inequivalent iron sites with the expected occupancy ratio for FeI:FeII:FeIII of 1:2:1. X-ray magnetic circular dichroism (XMCD) was used to resolve the orbital and spin contributions to the magnetic moment; unlike iron, α'-Fe₉N may possess a non-negligible orbital angular momentum. It was concluded that Fe₁₆N₂ does not possess a giant moment when grown by sputtering on Si; however, defects inherent in sputtered films grown on lattice-mismatched substrates may inhibit achievement of perfect nitrogen ordering and, subsequently, giant moment. Nonetheless, Fe₁₆N₂ shows a dramatic enhancement in saturation magnetization compared to pure iron.
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CHAPTER I:
AN INTRODUCTION TO IRON NITRIDE

Motivation

In the industry of magnetic recording for computer data storage, there is continued interest in ferromagnetic materials with high saturation magnetization for use in inductive recording heads (write heads) for high density storage disks. Iron has the highest intensity of magnetization of the elements (1708 emu/cm$^3$, or emu/cc) and, until recently, the highest magnetization achieved (1950 emu/cc) was in an expensive alloy of Fe$_{65}$Co$_{35}$ used for pole pieces of electromagnets. In 1972, T. K. Kim and M. Takahashi of Tohoku University in Japan reported making iron nitride films with magnetization as high as 2100 emu/cc. They evaporated iron in a nitrogen atmosphere to produce polycrystalline iron nitride films, the main phase of which was $\alpha$-Fe$_{16}$N$_2$ with a magnetization of 2196 emu/cc. Kim and Takahashi were unable to reproduce their experiments, but advances in thin film techniques such as molecular beam epitaxy and ion implantation have caused renewed activity in this area, especially in Japan. Presently Y. Sugita and colleagues at Hitachi are claiming magnetizations of 2310 emu/cc in single-crystal Fe$_{16}$N$_2$ films deposited on In$_{0.2}$Ga$_{0.8}$As(001). Similar high magnetizations have been reported for this material, but have not been satisfactorily confirmed so far. Theoretical calculations based on the band structure of Fe$_{16}$N$_2$ give values for the magnetization around 1780 emu/cc, far below Sugita's claims, but consistent with the magnetizations reported by several other workers. Possible sources of the enhanced moment have not been elucidated. If the giant moment of Fe$_{16}$N$_2$ can be confirmed and reproduced, its use in magnetic recording heads would allow disk information storage to approach 10 gigabits per square inch, far greater than today's storage density. Magnetic properties relevant to iron nitride will be defined in Chapter II, and Appendix A contains definitions of the units of magnetism for Gaussian (cgs emu) and SI (rationalized mks) units. Gaussian units will be used throughout this dissertation.

The materials used in magnetic recording heads have recently received
much attention due to the perpetual demand for increased information storage which requires ever-increasing disk-drive areal densities. The recording heads that are used in high-performance disk drives typically consist of separate magnetoresistive read and inductive write heads. The function of the write head is to create regions of alternating magnetization (magnetic "bits") in the thin-film recording medium at a density which fulfills design requirements (around 3.0 μm by 0.2 μm for state-of-the-art devices), and to write this information at very high frequencies (around 150 MHz).\(^{18}\) NiFe (permalloy) has been the industry-standard pole material for thin-film heads for over a decade, but increasing recording densities and data rates have begun to push NiFe to its limit. For high-density storage, medium coercivities in excess of 2500 Oe create high flux demands on the head material. The head must produce a field roughly twice as large as the coercivity of the medium for effective writing.\(^{18}\) Permalloy has a saturation magnetization \(M_s\) of 860 emu/cc, but the gap between the head and the medium reduces the field at the medium substantially, along with other head losses. High \(M_s\) alloys, such as FeN,\(^{19,20}\) FeTaN\(^{21-23}\) and FeAlN,\(^{24,25}\) each with saturation magnetizations of about 1720 emu/cc, are being actively studied for writing on future generations of high-coercivity media (up to 5000 Oe). Evolution in write-head materials continues to provide for a unique environment for magnetic materials work.

To record information on high-coercivity media, the key materials requirements for recording heads are high saturation magnetization \(M_s\) (greater than 1720 emu/cc), low coercivity \(H_c\) (around 1 Oe) high permeability \(\mu\) at high frequencies (around 3400 at 200 MHz), low saturation magnetostriction \(\lambda_s\) (around \(10^{-6}\)) and high electrical resistivity (greater than 100 \(\mu\Omega\cdot\text{cm})\).\(^{20,26,27}\) Good tribological properties, corrosion resistance, and thermal stability are also required.\(^{20}\) How well \(\alpha''-\text{Fe}_{16}\text{N}_2\) meets these requirements is only beginning to be investigated. Its potential as a write-head material is based on the claims of a giant magnetic moment; the verification, explanation, and application of which are the primary purposes of this work.

The important parameters deduced from magnetic measurements are the magnetic moment per unit mass and the average magnetic moment per
atom, expressed in Bohr magnetons \(1 \mu_B = 9.27 \times 10^{-21} \text{ erg/Oe}\). If the volume occupied by each atom is known, the magnetic moment per atom can be related to the intensity of magnetization, \(\mathbf{M} = \mathbf{m}/V\), in which \(\mathbf{m}\) is the magnetic moment (magnetization) expressed in ergs/oersted units, \(V\) is the volume in cm\(^3\), and \(\mathbf{M}\) is the magnetization per unit volume in erg/Oe-cm\(^3\) or emu/cc. In pure iron, for example, the magnetic moment per atom is 2.2 \(\mu_B\), mainly due to two unpaired electrons in the \(3d\) band. The estimated band structure can be used to calculate the magnetic moment, which can then be compared to experiment. This has been a point of contention for Fe\(_{16}\)N\(_2\), which is claimed to have a much higher moment than the band theory of metals predicts, or even allows. The magnetization of 2310 emu/cc reported by Sugita, et al., corresponds to an average iron moment of 3.2 \(\mu_B\), but band theory predicts an upper limit of 2.7 \(\mu_B\) for the average atomic moment in a crystal.

Another issue that casts doubt on these results is that quantitative magnetic measurements are extremely difficult on thin films, since the film volume, mass and/or density are not easy to determine precisely. Researchers at Carnegie Mellon have confirmed the giant moment,\(^4\) however, their bulk samples are multiphase and the volume content of each phase may not be determined accurately either. Magnetization determinations are usually hampered by the fact that Fe\(_{16}\)N\(_2\) is not a thermodynamically stable phase, and most deposition techniques lead to multiphase films. If the magnetization is correct, perhaps the film surface has an unexpected influence on the moment, or some unaccounted orbital stabilization occurs.\(^{28}\) With these inconsistencies, Fe\(_{16}\)N\(_2\) may have an uphill battle to prove true its magnetic characteristics and its worth as a high performance head material. The real interest lies in the fundamental reasons for a giant magnetic moment, and more experiments are necessary to understand the true nature of the giant moment observed by Sugita and others.

**Review of \(\alpha''\)-Fe\(_{16}\)N\(_2\) research**

**The phases of iron nitride**

It is well known that the nitrogenation of Fe produces a remarkable range of magnetic properties in the different FeN phases. For example, the
Curie temperature of the HCP ε phase varies very strongly (from 670 K to 25 K) as a function of composition with a maximum at Fe$_{78}$N$_{22}$. Another striking example is the difference in properties of the γ and γ' phases. γ-FeN (nitrogen austenite), the N-disordered FCC phase, is non-magnetic while γ'-Fe$_4$N, the N-ordered FCC phase, is ferromagnetic with $M_s = 1340$ emu/cc.$^{29}$ It is still not entirely clear why ordering of the non-magnetic nitrogen atoms leads to strong ferromagnetic behavior.

The crystal structure of Fe$_{16}$N$_2$ was first studied by K. H. Jack at Cambridge in 1951,$^{30,31}$ but magnetic properties were not measured by any workers at that time. Jack called it α"-Fe$_{16}$N$_2$ rather than Fe$_9$N because it has a tetragonal cell with ordered nitrogen interstitials which is based on a normal, body-centered iron (α-Fe) unit cell, doubled in all three directions (Figure 1).
To form the metastable compound, Jack first heat-treated face-centered iron (γ-Fe) in a nitrogen atmosphere, since the solubility of nitrogen is negligible in α-Fe but not in γ-Fe (Figure 2). He then quenched it to yield a distorted body-centered martensitic phase called nitrogen martensite (α'-Fe₆N). This was then annealed to produce samples containing a majority of the ordered α''-Fe₁₆N₂ phase by volume, according to X-ray powder photos.

Figure 2. Fe-N phase diagram. Upper scale, weight percent N; lower scale, N atoms per 100 Fe atoms.³⁰

There are four phases of the iron nitrides, shown in Figure 2, whose structures were determined by Jack;³⁰,³² three stable phases and one metastable phase. ε-Fe₂N has the hexagonal structure in the range 2 < x ≤ 3 and transforms into the orthorhombic structure just above x = 2, at which point
nonmagnetic $\zeta$-Fe$_2$N is formed. The magnetic moment decreases with decreasing $x$ from about 2 $\mu_B$ at $x = 3$, dropping sharply to about 0.2 $\mu_B$ at $x = 2$. The crystal structure of $\gamma'$-Fe$_4$N is simple cubic composed of FCC iron ($\gamma$-Fe) with the N atom at the body center (Figure 3). There are two inequivalent iron sites; FeI at the corners and FeII at face centers. The magnetic moments on the FeI and FeII sites are 2.98 $\mu_B$ and 2.01 $\mu_B$, respectively, and experimental measurements give an average moment of 1.8 $\mu_B$. $\alpha''$-Fe$_{16}$N$_2$ is the metastable phase which forms a body-centered tetragonal (BCT) structure consisting of three iron sites, FeI, FeII and FeIII (see again Figure 1), with calculated magnetic moments of 2.27 $\mu_B$, 2.25 $\mu_B$, and 2.83 $\mu_B$, respectively. These moments imply an average magnetic moment of 2.4 $\mu_B$/Fe atom, significantly lower than the highest values claimed. It is clear, however, that the presence of nitrogen can cause a significant enhancement of the magnetic moment of Fe.

The effect of nitrogen on magnetization in the iron nitrides

Magnetic moments result from unequal populations of electrons in the 3$d$ spin-up (majority) and spin-down (minority) sub-bands. Iron is normally strongly ferromagnetic since it has a completely full majority sub-band and a partially filled minority sub-band, like cobalt or nickel. An expansion between iron atoms in one direction enhances exchange-splitting and, hence, increases the moment. The central role of the N atom, which gives rise to a net enhancement of magnetic moment in most of the iron nitrides, is believed to be due to the expansion of the Fe lattice. Calculations for a hypothetical BCT Fe (expanded BCC Fe) without nitrogen reveal an enhancement of the
moment due to the magnetovolume effect which, given the expansion along the c-axis, contributes to the anisotropy observed in Fe16N2. Upon insertion of the nitrogen, however, the moment is reduced on certain Fe sites.

In the last section it was stated that the magnetic moments of Fe atoms in Fe4N and Fe16N2, which reflect the local densities of state, are considerably different depending on the site. From the description of the structures above, it can be noted that the Fe atoms that are most distant from the N atoms (Fel for Fe4N and Felll for Fe16N2) have the largest moments. The 3d levels, especially the down-spin state of the nearest neighbor (NN) Fe atoms to the N atoms, are lowered through the hybridization with a part of the N 2p state, and in turn the 3d down-spin states of the next NN Fe atoms are raised. The result is that the electrons of the down-spin states transfer from the next NN Fe atoms to the NN Fe atoms. The large moments of the Felll sites, then, are attributed to the shortage of down-spin electrons (rather than the receipt of up-spin electrons). In effect, the N atoms promote electron hopping, thereby reducing the exchange-splitting that gives rise to ferromagnetism.

Qualitatively, then, a lower concentration (deficit) of N atoms in Fe4N and Fe16N2 leads to a larger average magnetic moment if the expansion is ideally maintained. Most calculations using currently accepted theories indicate, however, that the moment is dominated by the lattice expansion and not the hybridization, so the effect of adding N to an expanded lattice is expected to be small. The hybridization of N 2p and Fe 3d states may be reflected in the fine structure of certain absorption techniques, such as X-ray absorption which is discussed in Chapter VI. Additionally, the magnetic moment of Fe atoms in the α' martensite phase increases monotonically with increasing concentration of N up to 11.1 at% (equivalent to Fe16N2). It is likely that the expansion of the Fe lattice and the hybridization of N and FeL are inseparable.

In addition to the concentration of nitrogen, the magnetic moment in FeN is also affected by the order of nitrogen in the Fe lattice. The disordered nitrogen martensite phase (α'-Fe8N) has a lower moment than the ordered phase (α"-Fe16N2), for example, 2.6 μB compared to 2.9 μB. The lattices of α' and α" are similarly expanded for the same nitrogen concentration (up to 12
at% N, there is less than a 1% difference in the lattice parameters),\(^{32}\) so the significant change in moment is unexpected. This phenomenon is only observed by those who have measured the giant moment\(^{3,4,6}\) and, to date, has not been adequately explained.

**Synthesis of Fe\(_{16}N_2\)**

There are several approaches to obtaining the \(\alpha'^-\)Fe\(_{16}N_2\) phase. Bulk \(\alpha'^-\) can be obtained by quenching the high-temperature austenite phase after a N\(_2\) or N\(_2\)/NH\(_3\) heat treatment above 600 °C.\(^{4,28,30,34}\) Thin-film \(\alpha'^-\) can be obtained either by ion implantation of nitrogen into an iron single crystal,\(^{35,36}\) or by thin film deposition.\(^{3,15,16,37,38}\) All methods initially result in the \(\alpha'\) phase.

<table>
<thead>
<tr>
<th>Reference</th>
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<th>(\sigma_s) (emu/g)</th>
<th>(\mu_B) per Fe atom</th>
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<tr>
<td>Kim and Takahashi(^1)</td>
<td>sputtering (glass)</td>
<td>296±14</td>
<td>2.9±0.2</td>
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<td>Komuro, et al.(^39) and</td>
<td>molecular beam epitaxy (GaAs, In(_0.2)Ga(_0.8)As)</td>
<td>310±10</td>
<td>3.2±0.1</td>
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<tr>
<td>Sugita, et al.(^40)</td>
<td></td>
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<tr>
<td>Nakajima and Okamoto(^14)</td>
<td>N(^+) implantation (MgO)</td>
<td>256</td>
<td>2.5</td>
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<tr>
<td>Takahashi, et al.(^15)</td>
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<td></td>
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<td>Ortiz, et al.(^16)</td>
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<td>Fe-powder nitrogenation (bulk)</td>
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<td>&gt;270</td>
<td>—</td>
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<td>Sakuma,(^12) Matar,(^41)</td>
<td>band theory calculations (bulk)</td>
<td>240</td>
<td>2.4</td>
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<td>and Coehoorn, et al.(^9)</td>
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<tr>
<td>(\alpha)-Fe</td>
<td>(bulk)</td>
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<td>2.2</td>
</tr>
<tr>
<td>(\gamma)-Fe(_4)N</td>
<td>(bulk)</td>
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<td>2.2</td>
</tr>
<tr>
<td>Fe(<em>{65})Co(</em>{35})</td>
<td>(bulk)</td>
<td>240</td>
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which is subsequently annealed for a few hours below 200 °C to obtain $\alpha''$. The bulk form has not shown notable moment enhancement, which may be due to $\alpha''$ precipitate stress. Most thin film processes have resulted in mixed phases of iron and iron nitrides, but all have enhanced magnetic moment with respect to $\alpha$-Fe. Within the martensitic concentration range (6-12 at% N), the thermodynamically stable $\alpha$-Fe and $\gamma$-Fe$_4$N phases, in ratios given by the phase diagram (Figure 2), compete with the metastable martensites. It is generally true that annealing $\alpha''$ for very long periods or at temperatures above 250 °C leads to a decrease in moment due to conversion of Fe$_{16}$N$_2$ to Fe$_4$N and Fe, often with a loss of nitrogen. Single crystal Fe$_{16}$N$_2$ has only been achieved in thin-film form by Sugita's group on lattice-matched In$_{0.2}$Ga$_{0.8}$As using MBE. Recent results for Fe$_{16}$N$_2$ are summarized in Table I and compared to $\alpha$-Fe and Fe$_{65}$Co$_{35}$.

The usual issues of heteroepitaxy (discussed in Chapter III) apply to the growth of Fe$_{16}$N$_2$ films. Since Fe$_{16}$N$_2$ is a metastable phase, it is difficult to obtain if it is not lattice-matched to the substrate as well as deposited within a small range of sputtering parameters. Buffer layers such as Fe or Ag have been used successfully on MgO and GaAs to achieve (001) epitaxy of Fe$_{16}$N$_2$. Silver ($a = 4.08$ Å) is lattice-matched with Fe$_{16}$N$_2$ ($a = 5.72$ Å and $c = 6.29$ Å) when Ag[110]//Fe$_{16}$N$_2[100]$, and is used to planarize the surface for the Fe$_{16}$N$_2$ deposition as well as providing a lattice-matched surface. GaAs(001) (5.65 Å) is nearly matched to Fe$_{16}$N$_2$(001), however, it still requires a buffer layer of Fe (2.87 Å) to avoid a reaction between FeN and GaAs. MgO (4.21 Å) is highly mismatched with FeN and requires a thick (t > 500 Å) buffer layer of Ag to obtain Fe$_{16}$N$_2$. It is sometimes necessary to use an Fe seed layer to grow Ag(001) on mismatched substrates to avoid any Ag(111) component, since Ag has a low energy (16 mJ/m$^2$) for stacking faults compared to Fe. For growth on Ag/Si(001), it is necessary to remove the native oxide with a dilute HF acid etch, but no Fe seed layer is required to achieve Ag(001) growth.$^{42,43}$ Different approaches to Fe$_{16}$N$_2$ growth are also contained in Table I. These and other factors are discussed in the third chapter. Fe$_{16}$N$_2$ thicknesses range from 100 to 1000 Å for films with the highest magnetic moments. For thicker films the Fe$_{16}$N$_2$ moment is only mildly enhanced,$^3$ although the reason for this
has never been studied. It should be noted that calculations for the Fe$_{16}$N$_2$ moment have consistently been for the bulk phase, and that the anisotropic effects of surfaces which clearly affect the moment have not been taken into account. This point was taken up by Sugita's group to lend support to their claims of a giant moment in their 250-Å Fe$_{16}$N$_2$ films.

Pressure and gas environment in the deposition chamber also play crucial roles in stabilizing Fe$_{16}$N$_2$ films. A base pressure of at least 10$^{-7}$ Torr and a deposition pressure around 10$^{-3}$ Torr for sputtering are usually required to avoid competing phases. An argon environment with 10% N$_2$ is a common deposition environment for sputtering. NH$_3$ has been added by some workers$^{4,37,38}$ but it is unclear how the presence of ammonia or hydrogen helps to stabilize the Fe$_{16}$N$_2$. The presence of oxygen and/or carbon tends to destabilize Fe$_{16}$N$_2$; O and C are more easily incorporated into Fe films compared to N, and can substitute for N on interstitial sites. A clean system is important for this reason, although ultrahigh vacuum is not required. No study has been done on the effect of C and O impurities on the M$_s$ of Fe$_{16}$N$_2$, however, the greater presence of C and O in sputtered films compared to MBE-grown films (due to the relatively lower vacuum normally used in sputtering chambers) may explain the higher M$_s$ for MBE-grown Fe$_{16}$N$_2$.

**Characterization of Fe$_{16}$N$_2$**

In the study of Fe$_{16}$N$_2$ there are several important properties that should be analyzed based on the relevant issues. Since Fe$_{16}$N$_2$ is a metastable phase, the competing phases γ, α, and sometimes ε may be present in the films. Usually X-ray diffraction (XRD) can identify the phases present and their epitaxial orientation, and can also be used to determine volume content of the phases if the integrated X-ray peak intensities (related to the various atomic structure factors) and XRD experimental setup are carefully considered. A comprehensive XRD study is presented in Chapter III. In order to characterize the magnetic properties of Fe$_{16}$N$_2$ in a mixed-phase sample, the magnetic properties of each phase must be known in the pure form. That is, the stable phases must be grown individually to determine their contribution to the saturation magnetization of a mixed-phase film. In Chapter
transmission electron microscopy (TEM) is applied to characterize the orientation relationship between film layers and the substrate, while phase purity and distribution can be measured using micro-diffraction, which has a probe size around 200 Å. This technique can show small amounts of other phases which may not be revealed in the XRD spectrum. The morphology is analyzed using dark-field TEM imaging and high-resolution TEM. With electron energy-loss spectroscopy (EELS) the stoichiometry of Fe and N for each phase can be measured, along with impurities such as oxygen. Together with the XRD and magnetic-property analyses, this information can be used to determine whether the structure of individual phases is ideal and, if not, how this might affect the magnetic properties. Finally, saturation magnetization is measured using vibrating-sample magnetometry (VSM), as is coercivity and overall hysteresis behavior (Chapter IV). A complete analysis of the magnetization requires a knowledge of the film volume. Since the film areal width is much greater than its thickness (approximately 1 cm versus $10^{-5}$ cm), an accurate measure of the thickness is paramount. TEM imaging of a cross-sectional specimen is the method used to determine this value accurately.

Figure 4 shows an XRD spectrum of 650 Å Fe$_{16}$N$_2$ grown on 800-Å Ag/Si(001). The important peaks for (001) epitaxial Fe$_{16}$N$_2$ are at the Bragg
angles $\theta_B = 29.3^\circ$ and $14.2^\circ$. The 2θ peak at $58.6^\circ$ is shared by the N-disordered phase, $\alpha'(002)$, and the N-ordered phase, $\alpha''(004)$. The $\alpha''(002)$ superlattice peak (indicative of nitrogen ordering which doubles the unit cell of $\alpha'$) is at $28.3^\circ$. Other 2θ peaks appearing in Figure 4 include Ag(002) at $44.3^\circ$ and Si(004) at $69.4^\circ$. The corresponding VSM measurement of this sample (under a 10 kOe external field applied parallel to the film plane) is shown in Figure 5. The shape of the hysteresis loop is indicative of a relatively soft magnet (coercivity $H_c = 500$ Oe) with a saturation magnetization of 1780 emu/cc.

Mössbauer spectroscopy can give quantitative information on the electronic structure of Fe in a solid by resolving chemically inequivalent Fe sites in terms of valence, orbital symmetry and local magnetic moments. To compare magnetization measurements between different research groups and against calculations for Fe$_{16}$N$_2$, the chemical structure must be the same in all cases, and is assumed to be that proposed by Jack in 1951. A Mössbauer spectrum can be decomposed into several sextets, each with a different hyperfine field, $H_{hf}$ (kOe), representing a different magnetic environment. Thus, Fe$_{16}$N$_2$ will have three hyperfine fields (one each for FeI, FeII, and FeIII) which are all different from the one field of $\alpha$-Fe (FeIV), as shown in Figure 6. The spectrum of Figure 6(a) corresponds to a mixture of Fe$_{16}$N$_2$ and $\alpha$-Fe, while Figure 6(b) is the reconstructed spectrum of pure Fe$_{16}$N$_2$. The spectra of Sugita, et al., do not agree with these results, having one hyperfine field for Fe$_{16}$N$_2$ similar to pure Fe, and three for the disordered nitrogen martensite. Since the magnetic moment originates from the polarization of 3d electrons, while the hyperfine field comes from that of 1s, 2s,
and 3s electrons, Sugita claims that their experimental results cannot be said to be contradictory. In Chapter V the Mössbauer technique and its application to our FeN films is discussed.

A relatively new technique, X-ray magnetic circular dichroism (XMCD), could elucidate the issue of whether Fe$_{15}$N$_2$ possesses a giant moment by addressing one possible source of the discrepancy between experiment and theory; whether or not the orbital contribution to the moment is negligible. XMCD spectroscopy has the ability to separate the spin and orbital contributions to the moment in a way that is element specific and uses X-ray absorption spectroscopy (XAS) with the incident light modified to have circular polarization. Figure 7 is an example of XMCD spectroscopy for a pure Fe film on a thin parylene substrate. The MCD spectra [Fig. 7(b)] is the difference spectrum between two XAS spectra [Fig. 7(a)] measured with either the magnetic field parallel or antiparallel to the beam propagation direction. A sum-rule analysis of the MCD spectrum leads to the spin and orbital contributions to the magnetic moment. This technique is applied to FeN films on Si (Chapter VI) with interesting results.

It is apparent from this brief introduction that the giant moment measured by Sugita and others might not be explained by the presence of
Fe₁₆N₂ alone. Even if the 2310-emu/cc magnetization is excessive, however, it is clear that an enhanced magnetization of at least 1780 emu/cc does occur in this phase, and its potential as a recording-head material is intact. Some major issues for Fe₁₆N₂ include analysis of the electronic structure and the effects of nitrogen ordering and concentration on the magnetic moment, stemming from both lattice expansion along the c-axis and hybridization of nearest-neighbor iron atoms with nitrogen atoms. Contributions to the moment from other FeN phases, interactions between phases, or from impurities must be ruled out or identified. Magnetic moment and phase composition measurements on thin films must be performed carefully, as well as corroborated with other measurement techniques. Further, the magnetic moment may have a significant unexpected contribution from orbital angular momentum. To shed light on the question of giant moment in Fe₁₆N₂, this dissertation will address many of these issues by applying a novel growth process, extensive structural and chemical characterization, and direct and indirect magnetic measurements. The variety of issues described above illustrates the complexity of magnetism in Fe₁₆N₂, and fuels ongoing research in Japan and the U.S. as well as Europe.

Figure 7. L₂₃-edge XAS and MCD spectra of iron: (a) the transmission XAS spectra of Fe/parylene thin films taken at two opposite saturation magnetizations; (b) the MCD and its integration calculated from the spectra shown in (a). The p and q shown in (b) are the integrals needed in the sum-rule analysis.⁴⁵
References
CHAPTER II:
MAGNETISM AND ELECTRONIC STRUCTURE
IN TRANSITION METALS AND THE IRON NITRIDES

Electronic structure and the origin of magnetism

With the ongoing research and abundance of applications in the magnetic materials industry today, it is surprising that current quantum mechanics incompletely explain even the most common ferromagnet, iron. Research in magnetism has experienced a surge in the last few years since atomic-scale growth and characterization methods have produced structures with interesting, new magnetic behavior. The study of magnetoelectronics focuses on the properties of mobile magnetic electrons, and may soon provide the key to a complete understanding of itinerant magnetism in metallic materials, which has so far remained elusive. Until then, only approximations and assumptions can simplify the study of this narrow but significant group of materials.

Besides a small nuclear component, all magnetic properties of a solid are due to its electrons, in particular, the outer-shell electrons of its atoms or ions. In a free atom or ion, every electron has intrinsic spin (quantum number \( s \)) as well as orbital angular momentum (quantum number \( \ell \)), with each quantum number contributing its associated magnetic moment. Fundamental electrostatic interactions are isotropic, that is, they do not couple the direction of magnetization to any spatial direction. They therefore fail to provide an adequate description of the magnetic anisotropic effects which are the basis of technologically important magnetic properties, such as domain wall structure, linear magnetostriction and permanent magnetic properties in general. A description of these effects requires a relativistic (wave mechanical) treatment of the electrons' motions.

The properties of electrons are determined by the Schrödinger equation [a generalization of the DeBroglie wavelength, \( \lambda = \hbar /p \) (\( p \) is momentum), to a spatially varying potential], which will not be stated here. The main result is that electron energy is quantized:
\[
E = \frac{Z^2}{n^2} k,
\]
(2.1)
in which \( Z \) is the atomic number, \( k \) is the wave number and \( n \) (an integer) is the principal quantum number. Quantum numbers are the eigenvalues (solutions) to the Schrödinger equation and permissible combinations of these quantum numbers determine the state of a free atom. Quantum numbers must satisfy the following relationships:\(^4\)

\[
\begin{align*}
    n &= 1, 2, 3, \ldots \text{ (or } K, L, M, \ldots) \\
    l &= 0, 1, 2, \ldots n - 1 \text{ (or } s, p, d, f, \ldots) \\
    m_l &= 0, \pm 1, \pm 2, \ldots \pm l \\
    m_s &= \pm 1/2.
\end{align*}
\]
Each quantum number specifies a state with a definite energy, which depends on \( n \) only. Several states exist for every value of \( n \). Pauli's exclusion principle states that there can be no more than one electron in any given state. The angular momentum quantum number \( l \) is a measure of the magnitude of the orbital angular momentum of the electron when multiplied by \( h/2\pi \) \((\hbar)\) and also of the eccentricity of the orbit. The component of angular momentum along the axis of a magnetic field is also restricted to discrete values by quantum mechanics. The magnetic quantum number \( m_l \) which represents these discrete values arises from the solution of Schrödinger's equation for a single-electron atom. It gives the component \( l_z \) of the orbital angular momentum \( l \) along the \( z \)-axis of a coordinate system, \( l_z = m_l \hbar \), in which the \( z \)-axis is defined as the axis perpendicular to the plane in which the electron orbit lies. The physical significance of this number is that when a magnetic field is applied to an atom the electron's orbital angular momentum \( l \) can only have certain values of the component parallel to the magnetic field direction, and these are given by \( m_l \). The spin quantum number \( m_s \) arises from the inclusion of relativistic effects in quantum theory, and allows two electrons to occupy very close energy states. Electron spins are constrained to lie with a fixed component either parallel or antiparallel to a magnetic field, and this orientation is represented by \( m_s \). The component parallel to the magnetic field is \( s_z = m_s \hbar \).

By Heisenberg's uncertainty principle, one can specify only one
direction of $l$, but not the precession position. For the same angular momentum, each $l$ can take $d = 2l + 1$ orientations, shown schematically in Figure 1. In zero magnetic fields these states are degenerate (have the same energy). In the vector model of the atom, the total angular momentum $j$ of an electron is simply the vector sum of its spin and orbital angular momenta, $j = l + s$, and is therefore also quantized. The possible components of the angular momentum along any specified direction are determined by the combination of $m_l$ and $m_s$, yielding $j_z = m_l \hbar$, where $m_l = j, j-1, \ldots, -j+1, -j$. For a multielectron atom (one with more than one electron in an unfilled shell) the terms $J, L$ and $S$ designate the total, orbital and spin angular momenta of all the electrons (and, thus, the atom), respectively, and $J$ can be related to $L$ and $S$ in at least two ways.

In all but the heaviest atoms (the actinides), the spin and orbital angular momenta contributions to magnetic moment are comparable. The total angular momentum $J$ can be calculated by adding the individual angular momentum due to spin sum resultant $S$ to the $L$ resultant due to orbitals. This is known as Russell-Saunders coupling which assumes only spin-spin and orbit-orbit interactions and no spin-orbit interaction for each electron. In this case one may refer to Hund’s rules to predict the ground-state configuration of the electrons in an ion with a partially filled shell:

1. The total spin $S$ of the system has the largest value consistent with the Pauli exclusion principle, $S = \Sigma m_s$.
2. The total orbital angular momentum $L$ has the largest value consistent with
the Pauli principle and with the first rule, \( L = \Sigma m_l \).

3. The angular momentum vectors \( L \) and \( S \) couple antiparallel for electron shells less than half full (\( J = L - S \)), and parallel for shells more than half full (\( J = L + S \)).

For example, the \( \text{Fe}^{2+} \) ion has six electrons in its outer shell (3\( d^6 \)). The quantum numbers are \( n = 3, I = 2, \) and \( m_l = -2, -1, 0, 1, 2 \). To maximize \( S \) in the \( d \) orbital which holds 5 electron pairs, there are 5 spin up (+1/2) and one spin down (-1/2) electrons, giving a total spin of \( S = 5/2 - 1/2 \), or 2 per atom. To maximize \( L \), the unpaired electron is assumed to have \( m_l = 2 \) so that \( L = -2 + -1 + 0 + 1 + 2 + 2 = 2 \). For a more-than-half full orbital, \( J = L + S = 4 \). Unfortunately, this does not lead to an accurate approximation of the atomic moment. For the first transition-metal series (3\( d \)), a spin-only approximation (\( L = 0 \)) should be used since ligand field effects will "quench" small orbital angular momentum, thus, \( J = 2 \). Under certain circumstances the plane of the orbit can move about and this can average to zero over the whole atom.\(^4\) This does not occur in the 4\( f \) series. If there is a strong spin-orbit coupling for each electron (such as in the actinides), "\( j-j \) coupling" is assumed, in which \( J = \Sigma j = \Sigma (\lambda + s) \).

**Magnetic materials**

**Magnetism**

Neither classical nor relativistic treatments can explain the complexities of magnetism for all materials. In some cases classical angular momentum can be used, but for other cases (such as ferromagnetism) the relativistic angular momentum must be used. It is generally true that the presence of a magnetic material will enhance the magnetic induction (flux), \( B \), in an applied magnetic field, \( H \).\(^5\) (Variables in bold style are vector quantities.) The relationship between magnetic induction in units of gauss (G, in cgs units, see Appendix A) and applied field in units of oersted (Oe) in a magnetic material is

\[
B = H + 4\pi M, \tag{2.2}
\]

in which \( M \) is the magnetic dipole moment per unit volume (emu/cc), or simply magnetization. Note that \( 4\pi M \) is in units of gauss. Magnetization and applied field are related by the volume susceptibility \( \kappa \) (emu/cc-Oe).
\[ \kappa = \frac{M}{H}, \quad (2.3) \]

while induction is related to the applied field by the permeability \( \mu \) (dimensionless)

\[ \mu = \frac{B}{H}. \quad (2.4) \]

Combining equations, one arrives at a relationship between the permeability and susceptibility,

\[ \mu = 1 + 4\pi\kappa. \quad (2.5) \]

The macroscopic quantity \( M \) needs to be expressed in terms of the properties of the material at an atomic level (microscopically). From electromagnetic theory, an electric current, \( I \), going round in a plane will produce an orbital magnetic moment

\[ \mu_i = I A, \quad (2.6) \]

where \( A \) is the area of the current loop. If the current is caused by a single electron rotating in a circle of radius \( r \) with an angular frequency \( \omega_0 \), then the current is \( e\omega_0/2\pi \) and the magnetic moment becomes

\[ \mu_i = -\frac{e}{2m_e} I, \quad (2.7) \]

where the angular momentum is \( I = m_e r^2 \omega_0 \). The charge of the electron is negative, thus the magnetic moment is in a direction opposite to the angular momentum. \( \mu_i \) is also quantized, so that

\[ \mu_{iz} = -\frac{e}{2m_e} I_z = -\frac{e}{2m_e} m_i \hbar. \quad (2.8) \]

The orbital moment is then an integral multiple of the quantity \( e\hbar/2m_e \), which is known as the Bohr magneton, \( \mu_B \), and has the value \( 9.27 \times 10^{-21} \text{ erg/Oe} \). Thus,

\[ \mu_{iz} = -\mu_B m_i. \quad (2.9) \]

The electron spin angular momentum \( m_s \) also generates a spin magnetic moment \( \mu_s \). The relations are

\[ \mu_s = -\frac{e}{m_e} m_s, \quad (2.10) \]
and
\[ \mu_{sz} = -2\mu_B m_s. \]  \hspace{1cm} (2.11)

Notice that for a given angular momentum the spin gives twice the magnetic moment of the orbit. The total magnetic moment per electron is the vector sum of the orbital and spin magnetic moments
\[ \mu_{tot} = \mu_l + \mu_s = -g \frac{e}{2m_e} j, \]  \hspace{1cm} (2.12)

and
\[ \mu_{totz} = -g\mu_B J_z. \]  \hspace{1cm} (2.13)

where \( g \) is the spectroscopic (or Lande) splitting factor and has a value of \( g = 2 \) for spin-only contributions and \( g = 1 \) for orbital-only contributions to the magnetic moment. The value of \( g \) lies between 1 and 2 depending on the size of these contributions. Assuming the Russell-Saunders coupling scheme, for a multielectron atom \( g \) is given by
\[ g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}, \]  \hspace{1cm} (2.14)

and the total magnetic moment per atom (in erg/Oe, or emu) is given by
\[ m = -g\mu_B J. \]  \hspace{1cm} (2.15)

Returning now to the macroscopic quantity of magnetization, we can denote the number of magnetic dipoles per unit volume as \( N_m \), and the total magnetization per atom (in erg/Oe, or emu) is given by
\[ M_s = N_m m, \]  \hspace{1cm} (2.16)

in which \( M_s \) is called the saturation magnetization since this is the maximum contribution the material can provide.

The above presentation is semi-classical and phenomenological, and does not allow for nonintegral values of the magnetic moment, which occur in some materials such as iron. A classical treatment for an isolated \( \text{Fe}^{2+} \) ion gives
\[ m = l - g\mu_B J = (2)\mu_B(2) = 4 \mu_B, \]

however, \( m = 5.4 \mu_B \) experimentally. When wave mechanics (relativistic effects) are included in quantum theory, the magnitude of the angular momentum is not an integral multiple of \( \hbar \), but rather
\[ l = \sqrt{l(l+1)} \hbar. \]

Similarly, the magnitude of the spin angular momentum is given by
\[ s = \sqrt{s(s+1)} \hbar \]

and the total angular momentum by
\[ j = \sqrt{j(j+1)} \hbar. \]

Identical corrections also apply to \( S, L \) and \( J \) in a multielectron atom. The
magnetic moment equations remain the same with these corrections applied. With these corrections, \( m(\text{Fe}^{2+}) = 4.9 \, \mu_B \), which is closer to the measured value although still inadequate.

So far we have examined only free atoms which were not subject to an applied magnetic field. The energy levels of electrons within the atom are altered by the presence of an external magnetic field. This quantized energy splitting occurs between otherwise degenerate energy states and is known as the Zeeman effect. The energy of a magnetic dipole in a magnetic field \( H \) (taken in the z-direction) is

\[
E_{\text{mag}} = -\mu_{\text{tot}} H.
\]  

When the net spin angular momentum is zero, the “normal” Zeeman effect splitting is given by

\[
\Delta E_H = \mu_B H m_f.
\]
so that a \( p \) state which has \( l = 1 \) splits into three levels, \( m_l = -1, 0, 1 \), while a \( d \) state which has \( l = 2 \) splits into five levels, \( m_l = -2, -1, 0, 1, 2 \). Each of these levels is further split in two by the "anomalous" Zeeman effect when there is a net spin angular momentum. In a zero magnetic field the two levels \( m_s = \pm 1/2 \) of the dipoles are degenerate, but split when a field \( H_z \) is applied. This splitting is given by

\[
\Delta E_s = 2\mu_B H m_s.
\] (2.19)

The complete Zeeman effect for a \( p \) state is illustrated in Figure 2.4 This effect is very important for ferromagnetic materials.

*Categories of magnetic materials*

Magnetic materials are classified according to their bulk susceptibility. Diamagnets are materials for which \( \kappa \) is small and negative, \( 4\pi\kappa = -10^{-5} \), and the induced magnetic moment opposes the applied magnetic field. Examples include copper and silver, as well as superconductors which are ideal diamagnets with \( 4\pi\kappa = -1 \). When the aligned magnetic moments strengthen the magnetic induction, this is paramagnetism, and the susceptibility is small, positive and typically in the range \( 4\pi\kappa = 10^{-3} \) to \( 10^{-5} \). Examples of paramagnetism are aluminum and platinum. Both effects occur only while the material is under an external magnetic field. In a ferromagnet, the material can be magnetized in the absence of an external field. The susceptibility is positive, much greater than 1, and typically can have values \( 4\pi\kappa = 50 \) to \( 10,000 \). Examples of ferromagnets are iron, cobalt and nickel as well as several rare earth metals and their alloys. The temperature dependence of susceptibility and magnetization in paramagnets and ferromagnets is discussed in Appendix B.

*Quantifying magnetic behavior: The hysteresis loop*

The most common way to represent the bulk magnetic properties of a ferromagnetic material is by a plot of magnetization \( M \) for various field strengths \( H \). This is known as a hysteresis loop and a typical plot is shown in Figure 3.5 Plots of magnetic induction \( B \) against \( H \) are also used but contain the same information since \( B = H + 4\pi M \). In its initial state a ferromagnet is not
magnetized. Application of a field $\mathbf{H}$ causes the magnetization to increase in the field direction. If $\mathbf{H}$ is increased indefinitely the magnetization eventually reaches saturation $\mathbf{M}_s$. This represents the condition where all the magnetic dipoles within the material are aligned parallel to the magnetic field. It is an intrinsic material property and is not dependent on microstructure. When the field is reduced to zero after magnetizing the material to saturation, the remaining magnetization is called the remanence, $\mathbf{M}_r$. The magnetization can be reduced to zero by applying a reverse magnetic field of strength $\mathbf{H}_{ci}$, which is known as the intrinsic coercivity. (The nomenclature $\mathbf{H}_c$ is the field strength at which the magnetic induction $\mathbf{B}$ is reduced to zero.) Coercivity is strongly dependent on the condition and history of the sample. The field required to saturate the material is $\mathbf{H}_s$, and depends on hindrances to domain wall motion and domain rotation, which is briefly discussed in Chapter IV. All of these factors combine to form the overall hysteresis-loop shape.

The suitability of ferromagnetic materials for applications is determined principally from characteristics shown by their hysteresis loops. For example, materials for transformer applications need to have high permeability ($\mu = \mathbf{B}/\mathbf{H}$) and low hysteresis losses (in W/kg, requiring low conductivity materials). Materials for electromagnets need to have low remanence and coercivity in order to ensure that the magnetization can easily be reduced to zero as needed. Permanent magnet materials need high remanence and coercivity in order to retain the magnetization as much as possible.
The band theory of metals and its application to ferromagnetism

The electronic structure of magnetic solids can be described within the broad band theory of solids. When atoms are brought together to form a solid, the positions of the energy levels are greatly modified compared to the free atom case in which the Pauli exclusion principle allows a maximum of two electrons with opposite spin for each energy level in an atom. When two atoms approach so closely that their electron clouds begin to overlap, the Pauli principle now applies to the two atoms as a unit and prevents them from having, say, a single 1s level with four electrons. The 1s level must split into two levels with two electrons in each. When N atoms form a solid, each level of the free atom must now split into N levels. Outer electrons (the 3d and 4s electrons in transition metals) are the first to overlap as atoms approach and

![Figure 4. Splitting of electron energy levels as the interatomic distance d decreases.](image)

![Figure 5. Density of levels in the 3d and 4s bands (schematic).](image)
these levels are split first (Figure 4\textsuperscript{5}). For a finite solid, the massive number of levels in a band are so closely spaced that they almost form a continuum of allowed energy. To describe magnetic materials we are interested in the density of levels in the band, \( N(E) \), or the energy difference between levels (Figure 5). Density-of-states (DOS) calculations give important information about orbital overlap and exchange splitting in magnetic materials. Figure 6\textsuperscript{3} shows the DOS for BCC Fe in which the majority (spin-up) and minority (spin-down) electron densities have been separated. Calculations such as this can also separate contributions from different orbitals.
In transition metals, the $3d$ and $4s$ bands overlap in energy (Figure 55), but the $4s$ levels are more widely spaced since there is only one $4s$ level per atom with a capacity of 2 electrons, as opposed to five $3d$ levels per atom with a capacity of 10 electrons. Within the simple rigid band model, the extent to which these levels are occupied by electrons depends on the number of $(3d + 4s)$ electrons in the atom, and determines the magnetic properties of the metal. Filled energy levels cannot contribute a magnetic moment, because the two electrons in each level have opposite spin and thus cancel each other out. If one electron reverses its spin, however, a spin imbalance of 2 is created, and a magnetic moment appears. The force creating this spin imbalance in a ferromagnet is the exchange force. Spin imbalance requires that one or more electrons be raised to higher energy levels, which means that the levels cannot be too widely spaced or the exchange force will not be strong enough to effect a transfer (hence, $4s$ electrons are assumed to make no contribution). Experimental results indicate that the exchange force cannot keep one half-band (all spin-up or all spin-down) full of electrons if the other half-band is less than about half full.

Cullity has summarized the criteria for the existence of ferromagnetism in a metal:

1. The electrons responsible must lie in partially filled bands in order that there may be vacant energy levels available for electrons with unpaired spins to move into. This rules out inner core electrons.
2. The density of levels in the band must be high, so that the increase in energy caused by spin alignment will be small. This rules out valence electrons since the density of levels in the valence band is low.
3. The atoms must be the right distance apart so that the exchange force can cause the $d$-electron spins in one atom to align the spins in a neighboring atom. Of the transition elements, which have incompletely filled inner shells with a high density of levels, only Fe, Co, and Ni meet this last requirement. Many of the rare earths are ferromagnetic below room temperature; their spontaneous magnetization is due to spin imbalance in their $4f$ bands.

This last criterion can be demonstrated in the Bethe-Slater curve shown in Figure 75 in which the ratio of the radius of an atom to the radius of its $d$-
Ferromagnetic orbital affects the exchange integral $J_{ex}$, where

$$E_{ex} = -2J_{ex} \sum m_s \sum m_{sj} \quad (2.20)$$

is the Heisenberg exchange interaction (discussed below). Positive values of $J_{ex}$ indicate that ferromagnetic ordering occurs (parallel spins) and for negative values of $J_{ex}$ antiferromagnetic ordering occurs (alternating spins resulting in a net magnetic moment of zero).

**Figure 7.** Bethe-Slater curve (schematic).  

**Magnetic interactions in FeN Models**

When atoms are brought together in a solid, the interaction between two atoms is basically defined by the interaction of their electrons. Different types of chemical bonding define the details of magnetic interactions in solids. Most transition-metal compounds possessing covalent bonding appear to be antiferromagnetic insulators. Exchange interaction usually increases as covalency grows. In nonconducting d-metal compounds, interatomic exchange is caused by spin dependence of covalent bonding between magnetic cation and non-magnetic anion atoms. On the other hand, metallic compounds usually reveal ferromagnetic properties.

Quantum magnetic theory has set out to explain exchange interactions in solids, particularly the reason for the existence or absence of local magnetic moments in various atoms and the nature of exchange bonding which leads to the observed type of magnetic ordering, and to provide correct values of magnetic moments and magnetic ordering temperatures for any magnetic crystal. Exchange interactions have been considered in the framework of one of two approaches; the localized electrons approach, in which spin moments of purely ionic origin are situated in crystal lattice sites, and the itinerant electrons approach, in which the “band” itinerant electrons are considered to
be "correlated" (mutually dependent) by the exchange effects. In the second case, the number of electrons with "up" and "down" directions of spin become unequal, and thus a magnetization of the crystal appears. The localized model is best applied to ionic (electron transfer) and covalent (electron sharing) bonding configurations, whereas the delocalized model applies best to metallic (free electron) bonding configurations.

In the localized model, an exchange of electrons occurs in which atoms share magnetic information without relinquishing their states. The interaction energy of the atomic magnetic moments due to this kind of exchange can be written in the form

\[ E = -AJ_1J_2 \] (2.21)

where each \( J \) is the total angular momentum of that atom's electron configuration, and the magnitude and sign of the coefficient \( A \) depend on the details of the configurations. This interaction is called the Heisenberg exchange. Local magnetic moment models are characterized by atomic correlation (as opposed to electronic correlation in itinerant models). The interaction between the atoms is not strong enough to destroy the atomic character of the local electronic configuration. These models are useful in describing magnetism in materials containing rare earth or actinide atoms, they let us calculate temperature-dependent effects, and they are natural for discussing spin waves (magnons), even in cases where the magnetism is itinerant.

Itinerant magnetism in solids is based on the notion of a homogeneous electron gas in which electrons interact with each other in a constant external potential and are not bound to individual atoms. At low electron densities the electron spins align in the same direction to produce magnetic order. The only contribution to the magnetic moment is due to electron spins; orbital moments are neglected. Just as in the case of localized magnetism, however, this magnetic order is attributable to the Pauli principle. As before, correlation tends to decrease the amount of magnetic order.

Itinerant models naturally describe magnetism in metals. All the core electrons are localized, but they are spin paired; the filled shells contribute no net moment. Only the valence electrons contribute to the magnetism, and they
are clearly itinerant. This holds true for the transition metals as well. Although the 3d electrons in materials like iron and nickel are spatially localized, their hopping is fast enough that one can ignore their orbital magnetic moments. Itinerant magnetism explains very well the nonintegral values of the angular momenta of 3d-transition-metal atoms in crystals.²

Not all magnetic properties of transition metals can be adequately described by one or the other of the two above models. Noninteger values of saturation magnetic moments per atom, large bonding energies, and a considerable linear contribution to the specific heat are not consistent with the Heisenberg (localized) model. On the other hand, the Curie-Weiss susceptibility of ferromagnetic metals and the observed temperature-dependence of magnetization cannot be explained in terms of the itinerant electron model. Developments in the localized model combined with improved description of electron-transfer effects led to Anderson's superexchange theory, which is quite good when applied to antiferromagnetic compounds of transition metals. Extensive study of correlation effects within the itinerant electron model gave rise to the spin-fluctuational theory, which helps explain ferromagnetic properties of transition metals.⁷

**Calculated electronic structures and magnetizations of γ'-Fe₄N and α'-Fe₁₆N₂**

Many researchers have performed calculations using the itinerant electron approach to obtain the magnetizations of the iron nitrides. Calculations for α' have been carried out by several groups in an attempt to verify the giant magnetic moment reported by Sugita and coworkers.⁸ Calculations for Fe₄N are usually performed alongside calculations for Fe₁₆N₂, since Fe₄N is thermally stable and the experimental magnetizations are well established. An accurate magnetization calculated for Fe₄N lends support to the validity of the model used.

The crystal structure of Fe₄N is simple cubic with iron in FCC positions and nitrogen at the body center. Two distinct iron sites are present, Fel on the corners and Fell at face centers. Mössbauer and neutron diffraction data indicate that magnetic moments at these sites are 3.0 μ_B for Fel [1(a)] and 2.0 μ_B for Fell [3(c)]⁹. (See Chapter V for a discussion of Mössbauer
spectroscopy.) Fe$_{16}$N$_2$ is body-centered tetragonal (BCT), consisting of 2x2x2 unit cells of the BCC Fe lattice expanded along the c-axis. It can be described as an $\alpha^\prime$-martensite with an ordered distribution of nitrogen atoms in the deformed octahedral interstices, while in the $\alpha^\prime$-martensite, the nitrogen atoms occupy the same Fe octahedral interstices with a disordered distribution. Three inequivalent iron sites are present in $\alpha^\prime$ according to their distance from the N atoms; Fel [4(e)], Fell [8(h)] and Felll [4(d)]. Felll has the highest local moment and is furthest from nitrogen.

Two problems arise as a result of the experimental data of Sugita, et al. One is the establishment of the local magnetic moments in $\alpha^\prime$, and the other is the determination of the mechanism responsible for the occurrence of such moments, if they indeed result in a giant average moment. Many calculations have been carried out by various workers to elucidate these issues. All of the models so far have assumed the local spin density (LSD) functional theory, that is, only metallic (itinerant) and no ionic bonding is present. The most common model is the linearized muffin-tin orbital (LMTO) band-structure calculation. This is based on an atomic spheres approximation (ASA) and is semi-relativistic. In one study the resulting local moments in Fel, Fell, and Felll were 2.27 $\mu_B$, 2.25 $\mu_B$, and 2.83 $\mu_B$, respectively, giving an average moment of 2.39 $\mu_B$/Fe atom for the atomic radii used. To include the orbital contribution to the moment, a total-energy electronic structure calculation was carried out by Min using LMTO plus a spin-orbit interaction within perturbation theory. This indicated that the orbital contribution is minor, only 0.06-0.08 $\mu_B$/Fe atom. The iron moments were calculated to be 2.13, 2.50, and 2.85 $\mu_B$ for Fel, Fell and Felll, respectively, with the average moment hence 2.50 $\mu_B$. Although most authors use the same set of interatomic distances for $\alpha^\prime$ as defined by Jack, variations arise in the results of these calculations when different atomic radii are used for Fe or N. This leaves some doubt when directly comparing the calculations, but several authors have used more than one set of radii with similar results.

Using a full-potential linearized augmented plane-wave (FLAPW) method, Coehoom and coworkers attempted to determine if the ASA approximation is valid for Fe$_{16}$N$_2$, since the atomic spheres have a large...
overlap. They neglected the orbital contribution based on Min's work, and determined that the non-spherical atoms did not significantly affect the local moments. Their results for \( \text{FeI}, \text{FeII}, \text{and FeIII} \) were 2.04, 2.33, and 2.82 \( \mu_B \), respectively, for an average of 2.37 \( \mu_B \). LSD calculation results are summarized in Table I.\(^{15}\) The results of similar calculations for \( \text{Fe}_4\text{N} \) are summarized in Table II.\(^{15}\)

Table I. Theoretical and experimental data on local and averaged magnetic moments in \( \text{Fe}_{16}\text{N}_2 \) in \( \mu_B \) per atom. The interstitial magnetic moment is the magnetization residing outside the \( \text{Fe} \) and \( \text{N} \) spheres, with radii of 1.15 and 0.74 Å, used in the FLAPW method. All calculated results exclude any orbital contribution. vBHJ indicates that the local spin-density approximation as formulated by von Barth and Hedin\(^{16}\) and as parametrized by Janak\(^{17}\) has been used. The other references\(^{18,19}\) do not state which exchange-correlation potential has been chosen.\(^{15}\)

<table>
<thead>
<tr>
<th></th>
<th>FLAPW vBHJ(^{15})</th>
<th>Expt.(^8)</th>
<th>ASW(^{18})</th>
<th>LMTO(^{19})</th>
<th>LMTO vBHJ(^{11})</th>
<th>LMTO vBHJ(^{13})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe[4(e)]</td>
<td>2.04</td>
<td>2.30</td>
<td>1.96</td>
<td>2.27</td>
<td>2.13</td>
<td></td>
</tr>
<tr>
<td>Fe[8(h)]</td>
<td>2.33</td>
<td>2.37</td>
<td>2.41</td>
<td>2.25</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>Fe[4(d)]</td>
<td>2.82</td>
<td>2.74</td>
<td>2.91</td>
<td>2.83</td>
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<tr>
<td>N[2(a)]</td>
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<tr>
<td>Interstitial</td>
<td>-0.0006</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average/atom</td>
<td>2.37</td>
<td>3.5</td>
<td>2.44</td>
<td>2.42</td>
<td>2.39</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Using a similar APW method, Sawada\(^{22}\) optimized the atomic positions of Jack's structure, based on a minimum-energy configuration, and recalculated the hyperfine fields of \( \alpha" \). These results are summarized in Table III.\(^{22}\) (See Chapter III for the atomic positions of \( \alpha" \) and Chapter V for a discussion of hyperfine fields.) Note the great discrepancy with experimental values (on the left) for the three \( \text{Fe} \) sites. Sugita's results fit in even less; in 1991,\(^8\) two subspectra had hyperfine fields of -460 kG and -330 kG. In a later publication,\(^{23}\) Sugita's group claimed one hyperfine field (-330 kG) for \( \alpha" \) and three (-250, -310, and -360 kG) for \( \alpha' \), respectively. Coehoorn has suggested that hyperfine fields of \( \alpha" \) are somehow different in mixed phases compared to thin-film samples, so that surface calculations are much needed. It has been
Table II. Theoretical and experimental data on local and averaged magnetic moments in Fe₄N in 𝜇₅ per atom. The interstitial magnetic moment is the magnetization residing outside the Fe and N spheres, with radii of 1.15 and 0.74 Å, used in the FLAPW method. All calculated results exclude any orbital contribution. vBHJ indicates that the local spin-density approximation as formulated by von Barth and Hedin and as parametrized by Janak has been used. The other references do not state which exchange-correlation potential has been chosen.

<table>
<thead>
<tr>
<th></th>
<th>FLAPW</th>
<th>Expt.⁹</th>
<th>Expt.²⁰,²¹</th>
<th>ASW¹⁸</th>
<th>LMTO¹⁹</th>
<th>LMTO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vBHJ¹⁵</td>
<td></td>
<td></td>
<td></td>
<td>vBHJ¹¹</td>
<td></td>
</tr>
<tr>
<td>Fe[3(c)]</td>
<td>2.23</td>
<td>2.0</td>
<td>1.79</td>
<td>1.94</td>
<td>2.03</td>
<td></td>
</tr>
<tr>
<td>Fe[1(a)]</td>
<td>2.98</td>
<td>3.0</td>
<td>2.98</td>
<td>3.10</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>N[1(b)]</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>-0.01</td>
<td>-0.01</td>
<td></td>
</tr>
<tr>
<td>Interstitial</td>
<td>-0.01</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Average/atom</td>
<td>2.41</td>
<td>2.21</td>
<td>2.09</td>
<td>2.23</td>
<td>2.29</td>
<td></td>
</tr>
</tbody>
</table>

said that calculated hyperfine fields are always too positive at Fe sites in many alloys and intermetallic compounds, which may be attributed to an error in the treatment of the exchange-correlation interaction between core and valence electrons in calculations which employ the LSD approximation.²⁴⁻²⁶

Given that the above models are very similar, so are their explanations for the electronic structure responsible for the local magnetic moments. The total density of states for Fe₃N, Fe₄N and Fe₁₆N₂ are shown in Figure 8.¹¹ In both compounds the isolated structures located around -1.2 Ry are mainly due to 2s states of N. (Energy is in Rydberg functional units Ry, in which Eₙ = hcR/n², and the Rydberg constant is R = 1.097 x 10⁻⁷ m⁻¹.) The main structures around the Fermi energy, E_F, are almost completely composed of 3d, 4s, and 4p states of Fe. The Fermi energies are pinned around the

Table III. The hyperfine field for iron and nitrogen sites of Fe₁₆N₂. Units of kG are used.²²

<table>
<thead>
<tr>
<th></th>
<th>Expt.²⁷</th>
<th>Expt.²⁸</th>
<th>Jack²²</th>
<th>Optimized²²</th>
<th>FLAPW¹⁵</th>
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</thead>
<tbody>
<tr>
<td>Fe[4(e)]</td>
<td>-296</td>
<td>-246.4</td>
<td>-245.6</td>
<td>-243</td>
<td></td>
</tr>
<tr>
<td>Fe[8(h)]</td>
<td>-316</td>
<td>-245.3</td>
<td>-254.2</td>
<td>-241</td>
<td></td>
</tr>
<tr>
<td>Fe[4(d)]</td>
<td>-399</td>
<td>-345.7</td>
<td>-331.9</td>
<td>-334</td>
<td></td>
</tr>
<tr>
<td>N[2(a)]</td>
<td>-9.32</td>
<td>5.10</td>
<td>-7.58</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
minimum in spin-down electron density of states, which makes these states
stable with the help of spin-polarization. The local density of states for Fe$_4$N
and Fe$_{16}$N$_2$ are shown in Figures 9 and 10, respectively.$^{11}$ The N 2$p$
bands are found from -0.6 to -0.4 Ry below the 3$d$ bands in both
phases. This small
energy difference accounts for the interaction (bonding) of N 2$p$ states with Fe 3$d$
states, especially in the
nearest-neighbor Fe atoms to N. N 2$p$ states have an even stronger
interaction with Fe 4$s$ states (note the peaks for each are at the same
energies), but the DOS is less for 4$s$ and contributes very little to
the moment. There is a
small exchange splitting (two peaks) in this energy region as well,
but it has little influence on the magnetic
moment since it is located far below the $E_F$. The local magnetic
moment of the N atom
for both phases is less than 0.1 \( \mu_B \) with a direction opposite to the moment of Fe.\(^{11}\) The features of local densities of states of each Fe are considerably different depending on the site. The most distant Fe atoms from the N atom, Fel for Fe\(_4\)N and Fell\(_\text{II} \) for Fe\(_{16}\)N\(_2\), have the largest exchange energy splitting and an almost filled spin-up \( d \) band, while about 0.3 electron states are empty in the spin-up \( d \) band of Fel in Fe\(_{16}\)N\(_2\). The smaller exchange splitting in Fel compared to Fell\(_\text{II} \) in Fe\(_{16}\)N\(_2\) gives rise to the shift up in energy in the spin-up
band and the shift down for the spin-down band, and so about 0.3 electrons transfer from the spin-up to the spin-down band to reduce the magnetic moment at FeI sites.\textsuperscript{13}

\textit{Limitations of the density functional theory}

There is much debate regarding the nature of thin-film Fe\textsubscript{16}N\textsubscript{2}, one issue being that moment calculations of the bulk phase may not be valid for...
thin films which can be magnetically enhanced anisotropically. In addition, the local-density-functional approach may be inappropriate in describing the electronic and magnetic structures of Fe$_{16}$N$_2$, since the local-density approximation (LDA) is known to be poor for compounds with strong local bonding.$^{13}$ It is not such a bad approximation for transition-metal compounds, however, to justify the large discrepancy between theory and experiment. Density functional theory$^{29}$ includes the electron hopping in a much better approximation than do the Hubbard models. Electron exchange and correlation (the effects that lead to Hund’s rules in atoms) are included in principle, but the true functional that would give the exchange-correlation energy in terms of the charge density distribution is not known. Thus, the usual choice for real calculations (LDA) represents the itinerant limit exactly, in which a homogeneous, interacting electron gas is assumed.$^2$

Density functional theory is based on minimization of the total energy (at ground state and zero temperature). It contains the sum of four energy terms, one of which is an error term meant to include the exchange-correlation energy. The error in LDA is somewhat large for the 3$d$ transition metals with magnetically-ordered ground states; the error in the lattice constant is typically 3%.$^2$ For iron, even the best local density approximation wrongly gives the FCC phase lower energy than the BCC phase.$^{30}$ Only after adding gradient corrections to the exchange-correlation energy does one find that the ground state of the iron crystal is indeed BCC.$^{31}$ Still, LDA correctly yields the nonintegral spins of the 3$d$ transition metals.

One of the more important limitations of LDA is that it does not correctly calculate the magnetic anisotropy in bulk transition metals (or rare earths). The origin of crystalline anisotropy is the spin-orbit interaction, which dictates how the spin and orbital magnetic moments are coupled in free atoms. If the spin-orbit coupling is ignored, the LDA calculations do not give any orbital magnetic moment, because there are no terms in the exchange-correlation energy that generate orbital angular momentum.$^2$ This is reasonable when the orbital angular momentum is quenched, which occurs in transition metals as the symmetry is lowered and the degeneracy is decreased (compared to a rotationally symmetric free atom). Unfortunately, modifications of the LDA to
include spin-orbit coupling increase the numerical complexity of the calculations by an order of magnitude. In two-dimensional systems (such as thin multilayers) the calculations are less difficult. For Fe$_{16}$N$_2$, as computer power increases and improved models are implemented, the gap between theory and experiment may close, or the discrepancy between them may be finally explained.

In the meantime, a measure of the orbital contribution to the moment in Fe$_{16}$N$_2$ could determine whether these corrections are necessary and lead to a resolution of theory and experiment. As discussed in the previous chapter, X-ray magnetic circular dichroism (XMCD) can in principle measure the ratio of orbital-to-spin contribution to the average atomic moment in a magnetic material. While an increase in spin magnetic moment has been calculated for Fe$_{16}$N$_2$ relative to pure iron, changes in orbital magnetic moment have been largely ignored, based on the assumption that the orbital angular momentum is quenched in transition metal compounds as well as the limitations of LDA mentioned above. It would be interesting to measure whether this is a valid omission and whether the effect is large enough to justify a giant moment in Fe$_{16}$N$_2$. How the orbital contribution changes with the degree of nitrogen order is also important, since calculations predict no enhancement in moment due to the transformation from N-disordered $\alpha'$ to N-ordered $\alpha''$, although this was experimentally measured by Sugita and coworkers. This technique is explored in Chapter VI for both Fe and Fe$_{16}$N$_2$ films.

References

Sputtering deposition technique

Although the key issue for Fe$_{16}$N$_2$ is the verification of the giant moment, the processing technique used to produce such results plays an important role in its eventual transformation to real applications. In the past, those who have claimed a giant moment in Fe$_{16}$N$_2$ have deposited it using the rather expensive technique of molecular beam epitaxy and grown it on complex substrates such as lattice-matched In$_{0.2}$Ga$_{0.8}$As. While the epitaxial quality is very high with this approach, the question remains whether Fe$_{16}$N$_2$ can have good magnetic properties when deposited on simpler substrates using technologically relevant processes. More recently, ion beam sputtering of Fe$_{16}$N$_2$ on GaAs with Fe or Ag underlayers has resulted in a giant moment, an optimistic result for the technology transfer of Fe$_{16}$N$_2$, although most results show less enhancement in moment. With the same reasoning in mind, we have attempted to grow Fe$_{16}$N$_2$ on silicon using sputtering deposition, a standard industrial approach to thin film processing.

Since its discovery by W.R. Grove in 1852, sputtering has evolved into an important thin film deposition technique. Today it competes with other physical vapor deposition processes such as thermal and electron beam evaporation for deposition of high quality metal, alloy and oxide films. In the high-technology industry of silicon devices, it is the most common approach because it is reliable, economical, and lends itself to easy process modification for new materials and processing research.

Sputtering is the process by which a surface atom or molecule is ejected from a target surface upon impact by a fast incident particle (Figure 1). The incident particle need not hit a surface atom directly for it to be ejected, but can transfer its momentum indirectly to the target atoms which may lead to the ejection of a surface atom. At normal incidence, multiple collisions are required to produce sputtered atoms, but at lower incident angles they can be produced directly. The incident particles are usually ions, because they can be
accelerated by an applied electrical potential. For kinetic energies less than about 5 eV, incident ions will likely be reflected or absorbed on the surface. When the kinetic energy exceeds the surface atom binding energy, surface damage will occur as atoms are forced into new lattice positions. Typically a threshold incident ion kinetic energy of 10-30 eV will dislodge, or sputter, atoms from the target surface. This process can be used to "sputter etch" a target material, both to clean the surface of debris and to planarize (smooth) it. Alternatively, sputtered atoms and ions can be condensed onto a substrate placed in their path to form a thin film coating of atomic dimensions.

The sputtering yield, defined as the average number of target atoms ejected per incident ion, determines the relative sputtering rates (and, hence, deposition rates) for different materials. Sputtering yield is a function of ion energy and increases monotonically for ion energies up to about 1 keV (Figure 28). Above a few tens of keV the incident ions tend to penetrate into the sputtering target, which is a process known as ion implantation. Normal sputtering systems operate with ions having energies of a few hundred up to a few keV, with voltages in the range 500 to 5000 V. In addition to incident ion energy, sputter yield increases with decreasing angle of incidence, decreasing binding energy of surface atoms, and increasing mass of colliding particles. For example, at normal angle of incidence and the same ion energy, silver (AW = 108) has the highest yield while carbon (AW = 12) has the lowest yield. While aluminum (AW = 27) has an atomic weight similar to silicon (AW = 28), Al has the higher yield because it has a lower binding energy (74 kcal/mol) than Si (84 kcal/mol).

Figure 1. The sputtering process.
Figure 2. Variation of sputtering yield with ion energy at normal angle of incidence.\textsuperscript{8} Data from Stuart and Wehner,\textsuperscript{9} Rosenberg and Wehner,\textsuperscript{10} and Behrisch.\textsuperscript{11}

*Direct current diode sputtering*

A low pressure, glow discharge process can achieve energetic ion bombardment for sputtering. One basic process configuration, DC diode, is shown in Figure 3. A vacuum chamber is equipped with a target (the coating material source) and a substrate to be coated. Usually the target is bonded to a water-cooled metal (usually copper) backing plate with solder or conductive
epoxy to dissipate the considerable heat generated during the sputtering process. The chamber is evacuated and then backfilled with an inert gas, usually argon, to a pressure of 75 to 120 millitorr (mT). An electrical potential is applied between the target (cathode) and the substrate holder (anode). This produces a low pressure glow discharge (plasma) between the two electrodes. Grounded shields are used to prevent a discharge from forming in undesirable areas. In this type of DC glow discharge, current is carried by electrons that are collected from the plasma by an anode and by positive ions being accelerated from the plasma toward the target. To sustain the discharge there must be a continuous supply of additional ions and electrons. Some of the ions striking the target surface generate secondary electrons, which are accelerated by the cathode potential. These electrons have energies approaching the applied potential and can ionize gas atoms in the plasma, thereby sustaining the discharge.⁷

The DC diode configuration has some important disadvantages, including relatively low deposition rate (~1 Å/sec for metals), high operating
gas pressure, targets limited to electrical conductors, and substrate heating resulting from bombardment of the substrate by plasma electrons. Higher deposition rates can be produced at lower pressures (10^{-3} \text{Torr}) and voltages (50-100V) with triode sputtering, in which a heated filament is used as a secondary source of electrons for the discharge. Deposition rates and substrate temperature can be improved with magnetron sputtering, which will be discussed in a later section. While semiconductors can be DC-sputtered at very low rates, the problem of sputtering from an electrically insulating target can only be solved with the use of radio frequency sputtering.

**Radio frequency sputtering**

Electrically insulating materials cannot conduct a DC current that is applied, and therefore cannot be sputtered with this configuration. An applied negative potential will initially bombard the insulating target with positive ions, however, it will then accumulate positive charge on the surface until it repels any further positive ion bombardment.\textsuperscript{12} The solution is to use alternating current in the radio frequency range, commonly 13.56 MHz and multiples thereof. With alternating current (AC), the number of electrons that arrive at the target while it is positive equals the number of ions that arrive while it is negative. Since the electron has a very small mass relative to the ions present, it moves instantaneously upon switching. If the AC has a high frequency (in the RF range) the ion motion can't keep up with the switching speed, resulting in an effective negative bias voltage on the target and deposition rates virtually as high as in DC sputtering. All materials can be RF sputtered, however, the electromagnetic shielding needed to block the RF radiation, as well as power supplies and matching network needed to achieve a resonant RF network, add significant complexity. While RF sputtering is an alternative of similar performance to DC sputtering, both configurations have relatively low deposition rates. The addition of a magnetron cathode improves deposition rates for both DC and RF sputtering.

**Magnetron sputtering**

Magnetron cathodes can be used to increase the sputtering rate of the
target material. The sputtering rate depends on the ion flux, which in turn depends on the density of ions in the plasma. The dominant limitation on ion density is the recombination of ions with electrons, a common occurrence on vacuum vessel walls. Magnetic fields on the cathode (usually formed by a ring magnet behind the cathode metal, Figure 413) are used to form an electron trap which, in conjunction with the cathode surface, confines the electron drift currents to a closed-loop path on the surface of the target. The interaction between the magnetic field \( \mathbf{B} \) and an electron with vector velocity \( \mathbf{v} \) is to create a force \( \mathbf{F} \) on the electron, where \( \mathbf{F} = e\mathbf{v} \times \mathbf{B} \), so that \( \mathbf{F} \) is in a direction orthogonal to both the magnetic field and electron velocity vectors (Figure 5).14

As a result, there is a strong tendency for the electron to travel in an epicycloidal (planetary) motion close to the target surface where both the magnetic field strength and the electron velocity are large. Trapping of ions also occurs, but this is a much smaller effect due to the large mass and low velocities of the ions. Electron trapping both reduces ion loss by recombination on vessel walls and enhances ion generation at the target by electron collision. Thus, electron confinement to this “racetrack” results in higher current densities at lower pressures (1 to 10 mT), almost independent of voltage. Substrate heating is less since electron bombardment of the substrate is reduced, and deposition rates are ten times that of a DC diode system.

The main limitation of magnetron sputtering is the amount of power that

![Figure 4. Schematic representations of magnetron sputtering sources; (a) planar magnetron, (b) gun-type magnetron.13](image)
can be applied to the target before melting or cracking occurs. Also, target erosion is nonuniform, and utilization is only 25-45% before failure occurs at the racetrack. When magnetic materials are sputtered, a thinner target may be necessary to maintain the magnetic field strength above the target surface. RF can be used for magnetron sputtering as well as DC, but electron confinement is not as efficient due to the fluctuating electric field. In addition, most insulators conduct heat poorly and target degradation on the racetrack is more pronounced. There is still an enhancement of RF sputtering rate despite these difficulties.

\[ \frac{m_e v^2}{r} = Bev \quad \Rightarrow \quad r = \frac{m_e v}{Be} \]

Figure 5. The influence of a magnetic field on electron motion.\(^{14}\)

**Reactive sputtering**

In order to enhance the sputtering process, the sputtering plasma, which is normally made up of an inert gas such as argon, can be made chemically active with the addition of reactive gases. A reactive (N\(_2\)) sputtering system, using circular planar magnetrons for both DC and RF targets, was used in this work for iron nitride growth, and is depicted in Figure 6. In a reactive plasma, gas molecules are dissociated by electron impact, enhancing the chemical reactivity of the resulting component fragments. A reaction at the substrate surface incorporates the gas atoms into the growing film, which acts like a getter (collection) pump for the reactive gas up to the pressure at which a stoichiometric compound is formed. The rate at which the substrate getters the gas decreases substantially above this pressure, and the reactive gas...
pressure increases in the chamber. Reactions may then occur at the target surface, causing deposition of an insulating film on the target which decreases the sputtering rate. Reactions in the gas phase may cause agglomerates to form which deposit on the film as a powder coating. Titanium nitride is a good example of a metallic target (Ti) that is DC-sputtered in a reactive gas environment ($N_2$) to form an insulating compound ($Ti_3N_4$). For depositing iron nitride films, a pure iron target is sputtered in an argon plasma with up to 10% $N_2$ gas.

As well as forming new compounds from elemental targets, reactive sputtering can be used to control stoichiometry of films sputtered from

Figure 6. Schematic representation of the reactive magnetron sputtering apparatus used to grow FeN films on Si.
compound targets. Elements in a compound target sputter at different rates, especially if one of the elements is a gas in its natural state at room temperature. A molecular species ejected from the target may lose some of its gas atoms, which can be restored by sputtering in a plasma containing that gas. Oxide and nitride films are often deposited in a reactive RF plasma (made up of \( \text{O}_2 \), \( \text{N}_2 \) or \( \text{NH}_3 \) in Ar) from oxide and nitride targets. It is difficult to produce iron-nitride targets in bulk with uniform stoichiometry, so our films are produced using pure iron targets.

**Bias sputtering**

Previously it was shown that high energy bombardment of a target material results in sputtering. This concept can be applied to substrate materials as well, with different desirable results. While high energy target ions incident on the substrate would sputter the newly deposited film, lower impact energies result in net deposition and interesting changes in film properties. Bias sputtering uses an electrical bias applied to the substrate to control the amount of ion bombardment there. If the film is bombarded with target ion energies of a few eV or tens of eV, then any loosely bonded material, such as the chemically inert sputtering gas and contaminant atoms such as oxygen, can be removed. Ion bombardment also changes the initial stages of nucleation and growth of the thin film, although the mechanisms for this are unclear. Properties such as purity, resistivity and crystallinity can be affected by substrate bias.

Bias sputtering can also be used to control the topography of a deposited film. Ion bombardment at the growing film should be enough so that it is resputtered without loss of net deposition. This causes a redistribution of the deposited materials onto the sides of surface bumps and pits that would otherwise not be subject to direct deposition by the incoming sputtered atoms. The result is that rough surfaces can be made smooth (planarized) and uneven surfaces can have a film of constant thickness overall (conformal coverage). These conditions can usually be achieved using different degrees of ion bombardment.

Whether to use DC or RF bias on a substrate depends again on
whether the substrate is electrically conducting or insulating. Since a large number of conducting materials form a native oxide or other insulating compound on their surfaces, RF is more commonly used. An etch prior to the deposition step could remove an oxide layer so that DC bias could be used, but this is to no advantage. While the sputtering system that was used for FeN deposition on Ag/Si(001) did not have substrate bias, it may have been a beneficial feature for two reasons. The native oxide on silicon could have been physically etched in situ rather than chemically etched (before substrate loading). At low power, this is no more damaging to the surface than chemical etching. It may not be as uniform or as fast as chemical etching, however, the oxide would not reform (as it often does during sample loading) since the plasma etch is done in situ. A high-temperature predeposition treatment (thermal desorption) is a commonly used alternative, but this adds significant time to film processing. In addition, the silver underlayer on Si served to planarize the growing surface for FeN as well as ramp up the lattice constant (see discussion below on epitaxy); reaching these objectives may have been facilitated by the addition of substrate bias.

**Ion beam sputtering**

Instead of a glow discharge, a separate ion beam source may be used to etch the surface of a target (Figure 78). This has the advantage that the energy, direction, and current density of the ion beam may be controlled independently, and working background pressures are lower than other sputter deposition methods. Ion beam sputtering can also be used in addition to a glow discharge to clean and planarize a substrate surface prior to deposition by standard sputtering techniques. Film properties obtained using ion

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Figure 7. Schematic representation of ion beam sputtering source showing relative locations of target and substrate.
beam deposition rather than glow discharge sputtering may be improved in some systems, but deposition rates are lower and areal coverage is smaller.

Parameter and film property correlations
As with all thin film deposition processes, conditions present at the substrate during deposition have a significant influence on the electrical, optical and mechanical properties of the film. When a sputtered atom condenses on a substrate, its kinetic energy is transferred to the surface lattice. A loosely bonded atom will migrate over the surface until it finds a permanent low-energy site or is desorbed. Atoms within the lattice move to more stable positions by bulk diffusion as the film thickness builds.

Figure 8. Schematic representation of the relationship between substrate temperature and argon pressure on the structure of metal coatings deposited by sputtering using a cylindrical magnetron source. $T$ is the substrate temperature and $T_m$ is the melting point of the coating material in absolute degrees.\(^8\)
For most metals, the mobility of surface and bulk atoms is related to the ratio of the substrate temperature (T) and the melting point of the metal (Tm). In films deposited at low T/Tm values, in which atoms have insufficient energy to move from their initial position, the internal crystal structure is poorly defined and has many defects. As well as high melting temperature and substrate cooling, higher working gas pressures can lower T/Tm by reducing sputtered atom energies (Figure 8, Zone 1). Reactive gases adsorbed on the surface also reduce target atom mobility on the substrate. Higher T/Tm values enhance surface and bulk diffusion in the growing film, and produce denser columnar grains with fewer defects and defined boundaries (Zones 2 and 3). Zone T is a transition zone.

Sputtered films are usually in a state of compressive or tensile stress. In higher Tm materials deposited at low T/Tm, internal stresses dominate due to lattice mismatch between substrate and film, and due to imperfections in the film's crystal lattice. These internal stresses are increased by high working gas pressure. Thermal stress, due to the mismatch in thermal coefficients of expansion between the substrate and the thin film, predominate in higher T/Tm films. These factors and others affecting epitaxial growth will be discussed in the next section.

Due to substrate immersion in the plasma and any additional substrate bias applied, kinetic energy of sputtered atoms impinging on the substrate is typically ten times that of evaporated species. This changes the film properties significantly, and offers the opportunity to deposit films at lower substrate temperatures with sputtering than with evaporation processes. Epitaxial films are possible with some materials systems using sputtering. On the other hand, molecular beam epitaxy (MBE) produces high-quality epitaxial films at higher temperatures and lower growth rates, but the apparatus is very expensive because it requires ultra-high vacuum (UHV) around 5 x 10^-11 Torr. Note that one can carry out UHV sputtering or, alternatively, evaporation in moderate vacuum. The higher vacuum, while improving epitaxial quality, does not prevent the significant damage caused by the high-energy sputtering process. Subsurface implantation of atomic species during deposition can cause point defects (substitutional and interstitial impurities and vacancies). These set up
growth stresses in the film which may affect the magnetic properties of the target phase. This possibility will be discussed further in Chapter IV.

Sputtering has proven to be a versatile method of producing many types of films on a variety of substrates. Reproducibility of high-quality films is a noted feature of sputtering, as well as its potential to be scaled up for industrial purposes. There are several limitations to sputtering, including relatively low deposition rates (compared to evaporation) and poor step-coverage for sub-micron IC devices. In the future sputtering and other plasma processes such as CVD may be combined to enhance overall performance and versatility in thin-film deposition.

Issues for epitaxial growth

Lattice mismatch

Epitaxy is the controlled growth of a particular crystallographic orientation of the film with respect to the substrate. Quality heteroepitaxy, in which the epitaxial film and substrate are dissimilar materials, requires consideration of several factors. For achieving high-quality films, a substrate that has no chemical reaction with the film, similar thermal expansion coefficient to the film (especially for high-temperature growth), good surface quality (clean, well-polished, and without steps or with known periodic steps), and usually, a high-quality single crystal (theoretically dense, low defect density, and free of pores) is desirable. The substrate should have structural similarity with the film, and for achieving epitaxial growth, the single most important consideration is lattice mismatch, which is defined as

\[ \varepsilon = \frac{a_s - a_f}{a_s}, \]  

where \( a_s \) is the lattice parameter of the substrate and \( a_f \) is that of the film. Historically, epitaxy is possible when \( \varepsilon < 15\% \), however, for semiconductor structures much less than 1% is desirable to reduce the effects of defects such as dislocations on film properties. A more important parameter may be the density of coincidence sites, which are atomic positions that coincide on either side of the interface. Also, if the crystallographic symmetry of the substrate is higher than the film, "degenerate epitaxy" can occur, in which several discrete
epitaxial orientations are equally favorable. Assuming the film and substrate have similar structures, sometimes a simple reorientation of the film crystal with respect to the substrate will reduce mismatch, stabilize a particular epitaxial orientation, and enhance epitaxial quality. Reorientation may be accomplished by changing growth conditions such as temperature and deposition rate, or by substrate surface treatment or tilt. Lattice mismatch and epitaxial orientation were important considerations for determining an advantageous template for FeN growth on Si and other substrates. This will be discussed later in this section.

**Epitaxy growth modes**

Thin films grow according to one of three distinct “growth modes” illustrated in Figure 9: layer-by-layer [Frank-van der Merwe (FM)]; nucleation of three-dimensional clusters on a bare substrate [Volmer-Weber (VW)]; and formation of three-dimensional clusters on a microscopically thin uniform layer [Stranski-Krastanov (SK)] growth. The growth mode at thermodynamic equilibrium is largely determined by relative surface energies: if the deposited material has larger surface energy than the substrate, it will tend to form a three-dimensional structure; otherwise layer-by-layer growth is favored. When the epilayer-substrate interaction is much weaker than the epilayer-epilayer interaction, crossover from the SK to the VW growth mode occurs, in which there is

Figure 9. Various modes of growth of an overlayer on a substrate; (a) Frank-van der Merwe, (b) Volmer-Weber, and (c) Stranski-Krastanov growth. The horizontal plane indicates where the substrate ends.
no wetting layer. This is because layer-by-layer growth is never the equilibrium morphology for strained-layer systems, that is, the system is metastable with respect to cluster formation on a thin wetting layer.\textsuperscript{19,20}

For example, Ag grows on Si(001) via the SK growth mode when the Si surface is H-terminated with a 1x1 surface reconstruction (following an HF acid etch)\textsuperscript{21} and via the VW growth mode when the Si surface has a 2x1 reconstruction and no H-termination (following a short predeposition heat treatment \textit{in situ}).\textsuperscript{22} In both cases the growth mode may be different if the film orientation is altered by substrate T or other parameter changes. Fe, in turn, grows on Ag(001) by the SK mode,\textsuperscript{23} although some researchers now claim that the growth mode is VW.\textsuperscript{24} The surface energy of Fe (2.939 J/m\textsuperscript{2})\textsuperscript{25} compared to that of Ag (1.302 J/m\textsuperscript{2})\textsuperscript{26} would favor an island growth mode (that is, Fe should not form a wetting layer on Ag), although their perfect immiscibility below 911 °C\textsuperscript{26} may be the deciding factor, since in our experience Ag does not wet Fe either.

Although layer-by-layer growth is never the equilibrium state in strained-layer heteroepitaxy, kinetic constraints on mass transport often permit this growth mode.\textsuperscript{18} Relaxation of accumulated misfit-induced strain then becomes important. A critical thickness, $h_c$, exists which depends on the lattice misfit, beyond which interfacial misfit dislocations appear in the equilibrium state of a heteroepitaxial structure.\textsuperscript{20,27} Kinetic constraints involving dislocation generation and motion may permit growth of unrelaxed structures far beyond the critical thickness in some systems.\textsuperscript{28}

\textit{Substrate and underlayer selection}

Oftentimes the selection of a substrate for a particular epilayer is constrained by the requirements of the application itself, or there are shortcomings in some properties of the substrate chosen for a unique epilayer material. In these cases, a structurally similar buffer layer can be used in between the epilayer and the substrate. This layer can serve several purposes at once, including as a layer with properties intermediate between the two materials, such as intermediate lattice constant and thermal expansion. A buffer layer can also be used to block chemical reactions between the film and
substrate, which implies that it must be chemically compatible with both materials, although some reaction with the substrate may be permitted if it is confined to a region near the interface.15

Substrate selection for FeN films was based purely on the imperative to measure the magnetic properties of iron nitrides for a potential silicon-based Table 1. Substrate and underlayer candidates for α'-Fe16N2 epitaxial growth. Lattice mismatch is given for cube-on-cube (001) epitaxy, except when an in-plane rotation of 45° results in lower mismatch, which is given in parentheses.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Lattice constant (Å)</th>
<th>Lattice mismatch (%)</th>
<th>Thermal expansion coefficient at 423 K (10⁶/K)</th>
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<tr>
<td><strong>Film</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α'-Fe16N2</td>
<td>BCT</td>
<td>a=5.72</td>
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<td></td>
<td>c=6.29</td>
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<td></td>
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<td>5.42</td>
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device structure. Growth on several other substrates was attempted as well, and are discussed below. α-Fe has a BCC structure with a lattice parameter $a = 2.87 \text{ Å}$, while silicon has the diamond cubic structure with a lattice parameter $a = 5.43 \text{ Å}$. When the relative orientation of the film and substrate crystals is Fe(001)∥Si(001) and Fe[100]∥Si[100], the lattice mismatch is 5.7% (considering two Fe unit cells for every one of Si). This is a large misfit for heteroepitaxy, and the use of a buffer layer was anticipated. Because of their similar structures, α-Fe, α'-Fe₈N (BCT, $a = 2.85 \text{ Å}, c = 3.13 \text{ Å}$) and α''-Fe₁₆N₂ (BCT, $a = 5.72 \text{ Å}, c = 6.29 \text{ Å}$) have nearly identical requirements in the (001) plane for an underlayer material. γ'-Fe₄N (FCC, $a = 3.80 \text{ Å}$) can grow epitaxially on Si(001) with 1.0% mismatch if it is rotated 45° in-plane. Nonmagnetic underlayers were preferred to simplify magnetic property measurements. Also, materials known to grow epitaxially on Si(001) were favored. Table I lists possible substrate and underlayer candidates for α''-Fe₁₆N₂ epitaxial growth. Lattice mismatch is given for cube-on-cube (001) epitaxy, except when an in-plane rotation of 45° results in lower mismatch, which is given in parentheses.

For Fe₁₆N₂ growth on Si, it appears that Al, Ag, Au and Cr may be good candidates for an underlayer, since they match Fe₁₆N₂ within 1%. Pt and Pd probably both have too large of a mismatch with BCT FeN (3.2 and 4.0 %, respectively) to grow single-phase metastable martensites epitaxially. FCC structures are generally more difficult to deposit in the (001) orientation than BCC. The presence of FCC twins in (001) epitaxial films disrupts the stacking sequence of atoms and may result in a large (111) epitaxial component in the film. Since Al has a higher stacking fault energy than Ag one might expect this to suppress twin formation and therefore (111) growth. However, due to the unique Si-Al interface chemistry, Al(110)∥Si(001) epitaxy is observed, and actually Ag(001) epitaxy on Si(001) is more successful. Gold films deposited on Si(001) between room temperature and 400 °C almost always result in Au(111), therefore Au(001) growth was considered too difficult. In any case, Fe and Au are completely miscible up to 868 °C, so diffusion of Au into FeN films might inhibit establishment of a large magnetization. Cr was attempted early on, but the growth orientation was Cr(011)∥Si(001) and epitaxial quality
was poor, although the native oxide layer ($\text{SiO}_2$) on Si had not been removed. Fe underlayers have been used successfully by others on substrates other than Si, either as seed layers to secure (001) growth of subsequent FCC buffer layers\textsuperscript{2,5} or as buffer layers under FeN.\textsuperscript{2,32} This practice, unfortunately, complicates the magnetic measurements for Fe$_{16}$N$_2$ since removing the contribution to magnetization from the iron layer is strongly dependent on an accurate volume determination. MgAl$_2$O$_4$ (spinel) and NaCl substrates were tried as well because of their excellent lattice matching with FeN. FeN grown directly on spinel at room temperature resulted in $\gamma'$-Fe$_4$N after a 2-hour anneal at 150 °C. On cleaved NaCl, Ag(001) was epitaxially grown, however, subsequent FeN films grown at room temperature only resulted in $\gamma'$-Fe$_4$N after a 2-hour anneal at 150 °C. Phase competition will be discussed in the next section. Although spinel and NaCl substrates are not used for magnetic applications, their use as transparent substrates can facilitate the study of FeN, and should be considered for future studies.

Although thermal expansion coefficients of the elemental metals generally differ substantially from the semiconductor substrates, deposition temperatures are relatively low (less than 200 °C) in this case so that the contraction upon cooling may not be very significant to epitaxial quality. FeN martensites are not temperature stable, so annealing temperatures must be low as well.

Growth of Fe$_{16}$N$_2$ on MgO(001) using an Fe seed layer and Ag underlayer has been reported recently.\textsuperscript{5} In the case of GaAs and MgO, Fe seed layers are required to stabilize the (001) growth orientation of Ag.\textsuperscript{2,5} Initially, Fe seed layers were used on Si(001), followed by Ag and FeN, but usually a polycrystalline or predominately (111) Ag film resulted regardless of whether or not the substrate's native oxide was removed. Ag grown directly on Si(001) with the oxide removed resulted in high-quality Ag(001) films, as discussed below.

**Growth of individual FeN phases\textsuperscript{33,34}**

Ag(001) has a 1% lattice mismatch with $\alpha''$-Fe$_{16}$N$_2$(001) when it acquires an in-plane rotation of 45°, i.e., when Fe$_{16}$N$_2$[100]∥Ag[110]. A similar
orientation relationship can be achieved with Si(001), i.e., Ag[110]‖Si[100], but with a somewhat larger lattice mismatch of 6.4%. These orientation relationships were used sequentially to generate a template (Figure 10) for the epitaxial growth of the FeN phases with a c-axis normal. The silicon substrates were prepared using the following process: samples were etched using a standard sulfuric-acid/hydrogen-peroxide mixture (SPM or “piranha etch”, 5 minutes in 5:1 H₂SO₄:H₂O₂) to remove organic and metal contaminants; rinsed in deionized water (DI); etched in buffered hydrofluoric (HF) acid (3-4 minutes in 1:10 HF:H₂O) to remove the native oxide layer and to hydrogen-passivate the surface; rinsed in DI water (samples come out dry without any water droplets when the H-passivation is complete and the surface is hydrophobic). Substrates were loaded immediately into the vacuum chamber and were not heat treated. This procedure is expected to form a 1x1 reconstruction on the Si surface,21 as opposed to a 2x1 reconstruction resulting from short heating around 1000 °C in situ.22,35 The hydrogen termination of the 1x1 Si surface greatly improves the Ag(001) epitaxial growth, and may result in an island growth mode (Volmer-Weber)21 instead of interface followed by island formation growth mode (Stranski-Krastanov) for 2x1 Si(001),22 however, in both cases researchers measured 4:3 coincident growth in which four unit cells of Ag perfectly match 3 unit cells of Si along the [001] direction, i.e., Ag(001)‖Si(001) and Ag[110]‖Si[110]. There is currently no growth mode established for Ag(001) growth on Si(001) with the epitaxial relationship that we observed in our films (Ag[110]‖Si[100], discussed in Chapter IV), however, favorable epitaxial orientation also depends on kinetic factors, such as the deposition rate and the substrate temperature, in addition
to the substrate-epilayer surface chemistry. Given that Ag and Si are not reactive, the epilayer-epilayer interaction may be much stronger than the substrate-epilayer interaction. This would favor island growth, and is the likely growth mode for our films as well.

Epitaxial iron nitride films were deposited by conventional reactive (N$_2$) magnetron sputtering (see again Figure 6) on Si(001), with a base vacuum of at least 1.2 x 10^{-7} Torr. Silver was deposited directly on Si(001) at 100 °C by RF magnetron sputtering in argon (3 mT), with a thickness of 1000 Å and growth rates ranging from 0.3 Å/s to 5.2 Å/s. The growth of individual FeN phases (α-Fe, γ'-Fe$_4$N, and α'-Fe$_8$N) was accomplished by the optimization of substrate temperature, sputtering rates and gas flow rates. All FeN films were deposited by DC magnetron sputtering at a growth rate of 0.5 Å/s within a thickness range of 600-1000 Å. Pure α-Fe was grown at 25 °C in argon. γ'-Fe$_4$N was grown at 100 °C in a mixture of Ar and N$_2$ with a ratio of 46/5 sccm (standard cubic centimeters per minute). α'-Fe$_8$N was grown at 45 °C with an Ar/N$_2$ ratio of 46/4 sccm. The films were very sensitive to N$_2$ flow. α' films were annealed at 150 °C for 2 hours in vacuum (at least 10^{-6} Torr) to produce an optimal α'/α" mixture. In general, annealing temperatures above 150 °C resulted in phase separation of α' into γ'-Fe$_4$N and α-Fe. The growth configuration, FeN[100]∥Ag[110], was confirmed by electron diffraction of plan-view samples in a TEM, which will be discussed in the next chapter.

Mixed phases are commonly observed in the complicated Fe-N phase diagram and, consequently, γ'-Fe$_4$N and/or α-Fe either accompany or are formed preferentially to the metastable α"-Fe$_{16}$N$_2$ phase. Although growth of pure α-Fe, γ'-Fe$_4$N, and α'-Fe$_8$N films was accomplished, it was only after a small growth window was established for each phase. Single-crystal α" was not achieved, however, the volume fraction of α' and α" were carefully measured in this case. This technique is discussed in the next section, along with comments on the certainty of “pure” phases.

Phase identification and volume-fraction determination of FeN films

The analysis of crystal structures is normally performed using X-ray diffraction techniques. X-rays have a wavelength in the range 0.1 to 10 Å,
which can yield information about objects with a minimum separation distance in the same range, such as atoms (the average distance between adjacent atoms being ~ 1 Å). The X-rays are not focused on the atoms, but rather we measure the interference effects when plane waves of X-rays are scattered by atoms in a periodic array comprising a crystal lattice. Certain geometrical conditions must be satisfied to observe diffraction peaks. If we consider the scattering centers (atoms) to be a set of parallel planes which act as mirrors to reflect (diffract) the X-rays, then the distance travelled by each beam must be an integral number of wavelengths, \( n \lambda \). That is, for constructive interference of (monochromatic) scattered X-rays to occur, all beams scattered by parallel planes \( (n_h, n_k, n_l) \) must be in phase after they leave the crystal surface. This geometrical condition is satisfied when:

\[
\begin{align*}
n \lambda &= 2d_{hkl} \sin \theta, \\
\end{align*}
\]

in which \( n \) is taken to be 1 and \( d_{hkl} \) is the interplanar spacing. This is known as Bragg's law. It should be noted that the incident beam, the normal to the reflecting plane, and the diffracted beam are always coplanar. The angle between the diffracted beam and the transmitted beam is always \( 2 \theta \), which is known as the diffraction angle and is usually the parameter measured experimentally. The interplanar spacing for a cubic crystal is given by

\[
\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2},
\]

and for a tetragonal crystal by

\[
\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2},
\]

so that XRD patterns give a direct measure of lattice parameters and crystal structure in a sample.

Sometimes diffraction peaks of more than one material coincide or overlap. This is the case for certain peaks of \( \alpha \)-Fe, \( \alpha' \)-Fe\(_8\)N and \( \alpha'' \)-Fe\(_{16}\)N\(_2\). In a mixed phase sample, it is imperative that the contribution of each phase to a certain peak intensity be quantified so that magnetization data can be separated (assuming one has an independent measure of the saturation for all but one of the phases). This procedure is explained later in the chapter.
Phase identification of $\alpha$, $\gamma'$, $\alpha'$ and $\alpha''$ by XRD$^{33,34}$

As the interstitial nitrogen concentration increases in iron nitride phases, so too does the lattice constant, either uniformly or along the c-axis. Therefore, there is a peak shift in the Bragg reflection for (002) planes which identifies each phase although they are structurally very similar. The $\alpha$-Fe(002) peak is located at $2\theta_B = 65.02^\circ$, the $\alpha'$-Fe$_8$N(002) peak is located at $2\theta_B = 58.95^\circ$ (depending strongly on stoichiometry), the $\alpha''$-Fe$_{16}$N$_2$(002) peak is located at $2\theta_B = 28.34^\circ$ and the $\gamma'$-Fe$_4$N(002) peak is located at $2\theta_B = 47.82^\circ$. Since the Fe structure is identical in both nitrogen martensites, the $\alpha''$-Fe$_{16}$N$_2$(004) peak position is coincident with the $\alpha'$-Fe$_8$N(002) peak position; both are located at $2\theta_B = 58.64^\circ$. The Ag(002) peak is located at $2\theta_B = 44.28^\circ$ and Si(004) is located at $2\theta_B = 69.10^\circ$. The crystal structures of FeN films on Si(001) were characterized using a Siemens D5000 X-ray diffractometer with Cu-K$\alpha$ radiation ($\lambda = 1.54$ Å). X-ray diffraction spectra (from $\theta$-2$\theta$ scans) of $\alpha$,

![XRD patterns of FeN films grown on Ag/Si(001)](image)

Figure 11. XRD patterns of FeN films grown on Ag/Si(001); (a) $\gamma'$-Fe$_4$N, (b) $\alpha$-Fe, (c) $\alpha'$-Fe$_8$N, and (d) $\alpha'$-Fe$_8$N/$\alpha''$-Fe$_{16}$N$_2$. 
γ', α', and α'/α'' films are shown in Figure 11. The Ag underlayers, deposited at growth rates around 5 Å/s, are of good quality with strong (001) epitaxy. Fe-N films are also epitaxial but have broader peaks. A broad XRD peak implies that the crystallites contributing to the reflection have non-ideal interplanar spacings, causing discrete shifts in the peak position which cannot be resolved by the XRD instrument and appear as one broad peak.

![Figure 12. X-ray rocking curves for (a) the Ag(002) reflection and (b) the α'(002)/α''(004) reflection. Ag is deposited at 5.2 Å/s and 100 °C.](image)

This was confirmed by X-ray rocking curves measured on the annealed α'/α'' sample using a double-crystal diffractometer with Cu-Kα radiation. To generate the rocking curve, the crystal is rotated through the Bragg angle θ_B while the beam reflected by it is measured in a fixed counter with a wide slit. The width of the rocking curve is a direct measure of the range of orientation present, because each block (subgrain) of a typical mosaic crystal successively comes into reflecting position as the crystal is rotated. The full-width at half-maximum (FWHM) of the Ag(002) reflection shown in Figure 12(a) was 1.19°. The FWHM of the α'(002)/α''(004) reflection shown in Figure 12(b) was 1.63°, indicating the lower quality of the α'/α'' film. The sensitivity of the rocking-curve measurement used for Ag was 0.001°, however, this was admittedly too high for the lower-quality α'/α'' film for which the rocking curve
Table II. Experimental c-axis lattice parameters (in Å) for sputtered Ag and FeN films in Si(001). Lattice parameters were determined using the (002) reflections unless noted. Growth conditions were the same as those described in the text unless noted.

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>Film</th>
<th>Ag</th>
<th>α-Fe</th>
<th>γ'-Fe₄N</th>
<th>α'-Fe₈N</th>
<th>α''-Fe₁₆N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>α-Fe</td>
<td>4.083</td>
<td>2.852</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>γ'-Fe₄N</td>
<td>4.074</td>
<td></td>
<td>3.749</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>α'-Fe₈N</td>
<td>4.066</td>
<td></td>
<td></td>
<td>3.111</td>
<td></td>
</tr>
<tr>
<td></td>
<td>α'-Fe₈N</td>
<td>4.072</td>
<td></td>
<td>3.140</td>
<td>6.274</td>
<td>6.280 (004)</td>
</tr>
<tr>
<td>annealed 2 h</td>
<td>α'-Fe₈N</td>
<td>4.053</td>
<td></td>
<td>3.131</td>
<td>6.237</td>
<td>6.262 (004)</td>
</tr>
<tr>
<td>annealed 16 h</td>
<td>α'-Fe₈N</td>
<td>4.053</td>
<td></td>
<td>3.122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ag growth rate 1.9 Å/s)</td>
<td>α'-Fe₈N</td>
<td>4.065</td>
<td></td>
<td>3.135</td>
<td>6.266</td>
<td>6.270 (004)</td>
</tr>
<tr>
<td>annealed 2 h</td>
<td>α'-Fe₈N</td>
<td>4.053</td>
<td></td>
<td>3.122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ag growth rate 1.9 Å/s)</td>
<td>α'-Fe₈N</td>
<td>4.065</td>
<td></td>
<td>3.135</td>
<td>6.266</td>
<td>6.270 (004)</td>
</tr>
</tbody>
</table>

had a high level of noise. Only a 2° span of the FeN rocking curve is shown in Figure 12(b) to facilitate comparison between the Ag and FeN peak widths.

The c-axis lattice parameters for the Ag and FeN films were determined using the measured peak positions and the Bragg law. These are summarized in Table II. There is good agreement, within experimental error, between the ideal values (given in Table I) and the experimental values. There was a decrease in the silver lattice parameter when it was grown at a slower growth rate, indicating higher strain in the Ag film. Other changes in the Ag morphology due to growth rate are discussed later in this section. Small changes occurred in the Ag and Fe₈N lattice parameters upon annealing; shorter annealing of α'-Fe₈N decreased α' and Ag c-axis strain, while prolonged annealing increased the strain. As expected, there was a small increase in the c-axis lattice parameter upon annealing α' to form α''. The a-axis lattice parameters were not determined since the θ-2θ scan only contained (001) reflections in which h=k=0. In order to determine the in-plane
lattice constants, one could tilt the sample to the angles which satisfy the Bragg condition for peaks unique to $\alpha'$ [such as (103), (202) and (112)] and $\alpha''$ [such as (103), (105), (204), and (114)].

\textit{Determination of volume fraction in mixed $\alpha'/\alpha''$ for (001) growth}\textsuperscript{33}

Since $\alpha''$ films could not be grown single-phase, a method to measure the volume fraction of $\alpha''$ in $\alpha'$ films was established. The integrated intensity of XRD peaks is related to the scattering mass of each phase. The relative mass fractions of $\alpha'$ and $\alpha''$ can be quantified using structure factors, $F_{hkl}$, for each phase, since $I \propto |F_{hkl}|^2$. The integrated intensity in X-ray scattering is given by $I_{hkl} = A|F_{hkl}|^2 L_p P$,\textsuperscript{37} in which $A$ is a constant, $L_p$ the combined Lorentz and polarization factor, and $P$ the multiplicity factor. The Lorentz factor, $\cos \theta / \sin^2(\theta)$, is modified to $1 / \sin^2(\theta)$ since the $\cos \theta$ term is only included for randomly-oriented specimens. The polarization factor is unity for monochromatic radiation, and the multiplicity is unity for an oriented specimen. The focus now turns to calculating the structure factors for $\alpha'$ and $\alpha''$ and developing a formula to quantify the volume fraction of both phases in the film.

As has been stated previously, $\alpha''$-$\text{Fe}_{16}\text{N}_2$ has a structural resemblance to $\alpha'$-$\text{Fe}_8\text{N}$ with the same composition except for their nitrogen arrangement. The structures of both compounds are characterized by body-centered tetragonal (BCT), whose lattice is elongated along [001] by nitrogen atoms in octahedral interstices. $\alpha''$-$\text{Fe}_{16}\text{N}_2$ can be regarded as nitrogen-ordered martensite, but nitrogen atoms in $\alpha'$-martensite are disordered. Jack proposed that a unit cell of $\alpha''$-$\text{Fe}_{16}\text{N}_2$ contains 16 iron atoms and 2 nitrogen atoms at the

<table>
<thead>
<tr>
<th>Atom</th>
<th>Sites ($x = 0.25, z = 0.31$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1):(d)</td>
<td>0, 1/2, 1/4</td>
</tr>
<tr>
<td>Fe(2):(e)</td>
<td>0, 0, z</td>
</tr>
<tr>
<td>Fe(3):(h)</td>
<td>$\pm(x, x, 0)$</td>
</tr>
<tr>
<td>N:(a)</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1/2, 0, 3/4$</td>
</tr>
<tr>
<td></td>
<td>$1/2, 1/2, 1/2+z$</td>
</tr>
<tr>
<td></td>
<td>$\pm(1/2+x, 1/2+x, 1/2)$</td>
</tr>
<tr>
<td></td>
<td>$\pm(x, -x, 0)$</td>
</tr>
<tr>
<td></td>
<td>$\pm(1/2+x, 1/2-x, 1/2)$</td>
</tr>
<tr>
<td></td>
<td>$1/2, 1/2, 1/2$</td>
</tr>
</tbody>
</table>

Table III. Atomic positions in $\alpha''$-$\text{Fe}_{16}\text{N}_2$ (space group 139, I4/mmm).\textsuperscript{39,40}
sites of space group I4/mmm (Table III), given in Wyckoff notation.\textsuperscript{39,40}

The structure factors were calculated using the formula given by Cullity:\textsuperscript{37}

\[ F_{hkl} = \sum_{1}^{N} f_{n} e^{2\pi i(hu_{n} + kv_{n} + lw_{n})}, \]

which for Fe\textsubscript{16}N\textsubscript{2} becomes (with \( x = 1/4 \))

\[
F_{hkl} = f_{Fe} \left[ e^{2\pi i\left(\frac{1}{2}h\frac{1}{2} + \frac{1}{4}\right)} + e^{2\pi i\left(\frac{1}{2}h\frac{3}{4} + \frac{1}{2}\right)} + e^{2\pi i\left(\frac{1}{2}h\frac{1}{4}+\frac{1}{2}\right)} + e^{2\pi i\left(\frac{1}{2}h\frac{3}{4}+\frac{1}{4}\right)} \right. \\
\left. + e^{2\pi i\left(\frac{1}{2}h\frac{1}{4}+\frac{1}{4}\right)} + e^{2\pi i\left(\frac{1}{2}h\frac{3}{4}+\frac{1}{4}\right)} + e^{2\pi i\left(\frac{1}{2}h\frac{1}{4}+\frac{1}{4}\right)} + e^{2\pi i\left(\frac{1}{2}h\frac{3}{4}+\frac{1}{4}\right)} \right] \\
+ f_{N} \left[ 1 + e^{2\pi i\left(\frac{1}{2}h\frac{1}{2} + \frac{1}{4}\right)} \right]. \]

This simplifies to

\[
F_{hkl} = f_{Fe} \left[ e^{\pi i\left(\frac{1}{2}h\frac{1}{2} + \frac{1}{4}\right)} + e^{\pi i\left(\frac{1}{2}h\frac{3}{2} + \frac{1}{2}\right)} + e^{\pi i\left(\frac{1}{2}h\frac{1}{2} + \frac{1}{4}\right)} + e^{\pi i\left(\frac{1}{2}h\frac{3}{2} + \frac{1}{2}\right)} \right] \\
+ 2\cos(2\pi l) + e^{\pi i(h+k+l)} 2\cos(2\pi j) \\
+ 2\cos\left(\frac{1}{2}\pi(h+k)\right) + 2\cos\left(\frac{3}{2}\pi h + \frac{3}{2}k + l\right) \\
+ 2\cos\left(\frac{1}{2}\pi(h-k)\right) + 2\cos\left(\frac{3}{2}\pi h + \frac{1}{2}k + l\right). \]

From this expression, structure factors for several important reflections were generated in Table IV. For \( \alpha' \)-Fe\textsubscript{8}N, a BCC lattice was assumed, since the Fe position varies depending on whether the N site is occupied, and this has a random distribution. The sites are Fe(1)(d); (0, 0, 1/2) and (1/2, 1/2, 0), and N(a); (0, 0, 0) and (1/2, 1/2, 1/2). The nitrogen positions have an occupation of 1/8. The resulting structure-factor expression is:

\[
F_{hkl} = f_{Fe} \left[ e^{\pi i(h+k)} + e^{\pi i(h-k)} \right] + \frac{1}{8} f_{N} \left[ 1 + e^{\pi i(h+k+l)} \right]. \]

which is used for values in Table IV. The sample area was large compared to the beam size, but the thickness was smaller than the effective X-ray
penetration depth. Therefore, the integrated intensity was multiplied by the factor \( G = 1 - \exp(-2\mu t/\sin \theta_B) \), in which \( \mu \) denotes the line absorption coefficient. The resulting equation for integrated intensity is

\[
I_{\text{hkl}} = A|F_{\text{hkl}}|^2 \left( \frac{1}{\sin^2 \theta} \right) \left[ 1 - \exp \left( -\frac{2\mu t}{\sin \theta_B} \right) \right].
\] (3.9)

Subsequent calculations of the integrated intensity were based on an ideal structure in which the Bragg angles (\( \theta_0 \)) are 14.2° and 29.3° for \( \alpha''(002) \) and \( \alpha''(004) \), respectively. Atomic scattering factors for Fe and N were those reported by Cullity. The absorption factor \( G \) was calculated using \( t = 800 \) Å, however 600-1000 Å values for \( G \) only mildly affect the ratio of \( G_{\text{hkl}} \) used in the expression derived below. We would like to know the volume fraction of \( \alpha' \) and \( \alpha'' \), so we need an expression for the contribution of \( \alpha'' \) to the shared peak at 29.3° based on the \( \alpha'' \) peak height at 14.2°, since the peak height ratio can be experimentally measured. One can write an expression for the weighted contribution of both phases to the peak at 29.3° relative to the \( \alpha''(004) \) peak intensity:

\[
\frac{x_l\alpha''(004) + (1-x_l)\alpha''(002)}{xl\alpha''(002)} = \left[ \frac{I_{\alpha''(004)} + I_{\alpha''(002)}}{I_{\alpha''(002)}} \right]_{\text{expt}}
\] (3.10)

or,
in which $x$ is the mass fraction (and volume fraction if one assumes similar densities for $\alpha'$ and $\alpha''$) of $\alpha''$. The left side of the equation contains the calculated ratios while the right side contains the measured ratio of integrated intensity at $2\theta_B = 58.6^\circ$ to that at $2\theta_B = 28.3^\circ$. We calculated the ideal integrated intensity ratio, $l_{\alpha''}(004)/l_{\alpha''}(002)$, to be 5.8 for a single-crystal $\alpha''$ film. In addition, to determine the volume fractions of $\alpha'$ and $\alpha''$, we obtain the ideal $l_{\alpha'}(002)/l_{\alpha''}(002)$ integrated intensity ratio for a 50/50 wt% mixture of $\alpha'$ and $\alpha''$, since $\alpha'$ and $\alpha''$ have different scattering intensities for the same mass. Using similar parameters and values the intensity ratio was calculated to be 9.8. Using the above formula and the experimental data, the $\alpha'/\alpha''$ mixtures were estimated to be 48 vol% $\alpha''$. Longer annealing times (16 hours) did not increase this fraction.

This X-ray diffraction analysis represents a one-dimensional slice of the crystal structure; the in-plane lattice parameters and crystallography cannot be determined using $\theta$-2$\theta$ measurements. Thus, the volume fractions determined above are based on the assumption that the ratios of integrated intensities are the same in all three crystallographic directions. This has not been quantified, but is supported by the rocking curves shown in Figure 12. Good in-plane crystalline quality is an indication that variations in film structure with crystallographic direction are not significant. Also, it was assumed that the $\alpha'/\alpha''$ film was a perfect binary phase mixture, that is, composed only of the $\alpha'$ phase with no ordered N and the $\alpha''$ phase with perfectly ordered N. There is no unique way of determining the quality of the $\alpha''$, therefore, point defects due to sputtering damage or lattice-mismatch stresses may be present.

The nature of annealed $\alpha'$ films is affected by the silver morphology as well as the annealing temperature and duration. In Figure 11(c), the data represent an $\alpha'$ film grown on Ag deposited at 5.2 Å/s. An $\alpha'$ film grown under the same conditions except for the Ag deposition rate (1.9 Å/s), showed similar X-ray characteristics. Upon annealing at 150 °C for 2 hours, however, the resulting $\alpha'/\alpha''$ mixtures varied in quality and purity. Compared to the spectra
in Figure 11(d) [reproduced in Figure 13(a)], the XRD spectra in Figure 13(b) indicates a film containing a similar $\alpha'/\alpha''$ ratio mixed with a small amount of $\alpha$-Fe. It is difficult to quantify such a small volume fraction of $\alpha$-Fe, however, the scattering intensity of the $\alpha(002)$ peak is very similar to the $\alpha'(002)$ peak (since $F_{002} = 16f_{Fe}$ for BCC Fe), thus, if we compare the two peak intensities we can assume the volume fraction of $\alpha$-Fe is probably less than 5%. Although we did not rule out that $\alpha$-Fe is present in both films, the slower growth rate for Ag resulted in a morphology which stabilized the $\alpha$-Fe phase during annealing. Phase separation of $\alpha'$-Fe$_6$N into

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*Figure 13. XRD pattern of $\alpha'$-Fe$_6$N deposited and annealed as in Figure 11(d); (a) Ag deposited at 5.2 Å/s and (b) Ag deposited at 1.9 Å/s.*

*Figure 14. X-ray rocking curve for the Ag(002) reflection for an $\alpha'/\alpha''$ film grown on Ag deposited at 1.9 Å/s and 100 °C.*
$\alpha$-Fe and $\gamma'$-$Fe_4N$ may have occurred, however, there is no $\gamma'(002)$ peak present. It may be that in order to stabilize small regions that are free of N ($\alpha$-Fe), extra N was absorbed into the remaining $\alpha'/\alpha''$ structure. The difference in morphology between the Ag films may be simply that the Ag grain size is larger when the growth rate is slower, although this was not confirmed. A rocking curve of the Ag(002) reflection measured for the $\alpha'$ film grown on Ag deposited at 1.9 Å/s is shown in Figure 14. The FWHM of the Ag(002) reflection is 1.02°, indicating that the crystalline quality is slightly higher in this Ag film than in the Ag film grown at 5.2 Å/s [Figure 12(a), FWHM = 1.19°]. This higher crystalline quality would be consistent with a larger grain size. It is interesting to note that the "lower" crystalline quality for Ag is preferred to stabilize the $\alpha''$ phase during annealing.

$\alpha$-Fe, $\gamma'$-$Fe_4N$ and $\alpha'$-$Fe_8N$ have been grown individually on Ag/Si(001), and annealing of the $\alpha'$ phase resulted in an $\alpha'/\alpha''$ mixture with 48 vol% $\alpha''$. With the volume fraction of $\alpha''$ in $\alpha'$ quantified, we may proceed to the next step of measuring the magnetic properties of each phase (Chapter IV). There is still some doubt, however, whether the purity of the phases has been established. Although XRD is appropriate for characterizing the presence of certain phases and their structure, it is a technique which, for small grain sizes, measures the average lattice structure. Small areas of other phases may be present and not be detected. If a particular phase is made up of small regions with slightly varying interplanar spacings, the XRD reflections should in principal have discrete splittings. Unfortunately, XRD cannot resolve these small variations (when the grain size is less than 0.1 μm) and measures one broad peak. This is known as line broadening. A small, sharp peak that rises above the background intensity could be measured, however, a small, broad peak with the same integrated intensity (same volume fraction) might not rise above the background and would be undetected. This issue is addressed in the next chapter through the use of transmission electron microscopy (TEM). Also, we have made an assumption in our analysis that a mass fraction determination is equivalent to a volume fraction when only $\alpha'$ and $\alpha''$ are present. If there is any change in stoichiometry during annealing (for example, due to nitrogen loss), the density of the $\alpha'$ and $\alpha''$ phases may be dissimilar. Electron energy-
loss spectroscopy in the TEM will address this question in the next chapter as well.

References

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CHAPTER IV:
PHYSICAL STRUCTURE AND MAGNETIC PROPERTIES OF IRON-NITRIDE FILMS

In our study of \( \alpha''\text{-Fe}_{16}\text{N}_{2} \), the goal has been to verify and consequently explain the presence of a giant magnetic moment, while attempting to grow the phase on silicon with similar desirable properties. In the last chapter it was demonstrated that \( \alpha\text{-Fe} \), \( \gamma\text{-Fe}_{4}\text{N} \) and \( \alpha'\text{-Fe}_{8}\text{N} \) could be grown individually on \( \text{Ag}(001)/\text{Si}(001) \), and annealing of the \( \alpha' \) phase resulted in an \( \alpha'/\alpha'' \) mixture with 48 vol\% \( \alpha'' \). The (001) growth direction was confirmed by the \( \theta\text{-}2\theta \) X-ray scans; however, the in-plane orientation of the layers will be determined by the TEM analysis to follow. A more detailed analysis of the structural and chemical phase purity is still needed so that magnetic properties can be accurately measured. Although XRD is appropriate for characterizing the presence of certain phases and their structure, for small grain sizes (< 0.1 \( \mu \)m)\(^1\) it can resolve only the average lattice structure over several thousand grains. Small volumes of other phases may be present and not be detected. This is because a small average grain size causes line broadening, in which small, closely-spaced peaks are resolved as one broad peak.\(^1\) Thus, while a small but sharp peak would rise above the background noise, a broad peak with the same integrated intensity would not be resolved. To increase the detection of a small volume fraction of \( \alpha'' \), transmission electron microscopy (TEM) can be used and is presented in this chapter. Also, we have made an assumption in our volume-fraction analysis that a mass-fraction determination is equivalent to volume fraction when \( \alpha' \) and \( \alpha'' \) are the only phases present (since they have similar densities and the same stoichiometry). If there is any change in stoichiometry during annealing (for example, due to nitrogen loss), the density of the \( \alpha' \) and \( \alpha'' \) phases may be dissimilar. Electron energy-loss spectroscopy (EELS) in the TEM will address this question. With the volume fraction of \( \alpha'' \) in \( \alpha' \) quantified, we will proceed to measure the magnetic properties of each phase, including an analysis of changes in hysteresis behavior upon annealing \( \alpha' \) to form \( \alpha'/\alpha'' \), application potential of FeN films based on the magnetic properties and the possibility of a giant moment in \( \alpha'' \).
Determination of orientation relationships and physical structure: Transmission electron microscopy\(^2,3\)

A transmission electron microscope (TEM) is primarily used for its high lateral spatial resolution (often better than 2 Å) which can provide information on atomic structure and defects present in a material. A thin (< 1000 Å) solid specimen is bombarded in vacuum with a highly-focused, monoenergetic beam of electrons, which is of sufficient energy to propagate through the specimen. A series of electromagnetic lenses then magnifies this transmitted electron signal. Diffracted electrons are observed as a diffraction pattern beneath the specimen, which can be used to determine the atomic structure of the material. There are several scattering mechanisms associated with interactions between electrons and the atoms of the sample. The scattered electrons that are transmitted form a signal that is delivered (by the magnetic lenses) to a detector (usually a fluorescent screen, film plate or video camera). The detector displays the image (signal) which contains contrast from small regions of the sample and can yield information about atomic and defect structure.\(^4\) The TEM images and selected-area electron diffraction (SAD) presented in this chapter were performed on a JEOL 200CX analytical electron microscope (or AEM, Figure 1) at the National Center for Electron Microscopy (NCEM). It is capable of chemical analysis while using the microscope in scanning mode (STEM) with the attached spectrometers for energy-dispersive X-ray spectroscopy (EDS or EDXS), and electron energy-loss spectroscopy (EELS). EELS analysis of Fe:N stoichiometry and oxygen concentration will be discussed later in the chapter.

Crystallography: Selected-area diffraction and TEM imaging of FeN films

A typical selected-area bright-field image and diffraction pattern (inset) of the (001) zone axis of an annealed \(\alpha'/\alpha''\) film on Ag/Si(001) is shown in Figure 2(a). The bright-field image is taken with the objective aperture centered around the undiffracted central beam, blocking out contrast from the diffracted beams. The grain size of the film is on the order of 100 Å if one assumes that each contrasting region is a single grain, although this could not be confirmed with the AEM (see discussion of high-resolution TEM below).
The in-plane orientation relationships of α-Fe, γ-Fe₄N, α'-Fe₈N, and α'-Fe₈N/α''-Fe₁₆N₂ films were confirmed by selected-area diffraction of plan-view

Figure 1. JEOL 200CX analytical electron microscope at Berkeley National Lab. Counterclockwise from top left; EDS, light-element EDS (ultrathin Be window or UTW), TEM and SAD, EELS, high-resolution lattice image, CB diffraction, and elemental mapping.
samples in the AEM. The diffraction pattern shown in Figure 2(b) is a superposition of patterns from individual $\alpha'$-$\text{Fe}_8\text{N}$ and Ag layers. SAD patterns of thicker regions containing the Si substrate were identical. We deduced the orientation relationship to be $\text{Fe}_8\text{N}(001)\parallel\text{Ag}(001)\parallel\text{Si}(001)$ and $\text{Fe}_8\text{N}[100]||\text{Ag}[110]||\text{Si}[100]$, confirming that Ag grows with a 45° rotation with respect to the Si(001) substrate, rather than the cube-on-cube orientation of the 4:3 coincidence-site epitaxy mentioned in Chapter III. The SAD pattern in Figure 2(b) contains the bright spots of the overlapping Si, Ag and FeN lattices, in agreement with the expected epitaxial relationships, and also the weaker superlattice spots of the $\alpha''$ lattice. In the $\alpha'$ phase, N occupies the interstitial octahedral sites of the BCT Fe structure randomly, whereas in the $\alpha''$ phase the N is ordered on every-other octahedral site. This extended ordering doubles the unit cell size, and causes the emergence of superlattice reflections in both electron and X-ray diffraction.

Earlier, analysis of XRD data indicated that the $\alpha'/\alpha''$ mixture films were 48% $\alpha''$ by volume; the pure $\alpha'$ films, as expected, did not show any superlattice peaks. Selected-area diffraction in the TEM, however, showed the presence of weak superlattice reflections in both the unannealed ($\alpha'$) and annealed ($\alpha'/\alpha''$) samples. This may be

![Image](image.jpg)

Figure 2. (a) Plan-view TEM bright-field image and diffraction pattern (inset) of an annealed $\alpha'$-$\text{Fe}_8\text{N}/\alpha''$-$\text{Fe}_{16}\text{N}_2$ film and (b) diffraction pattern reflection identification for an as-deposited $\alpha'$-$\text{Fe}_8\text{N}$ film on Ag(001) underlayers on Si(001) substrates. $\text{Fe}_8\text{N}[100]||\text{Ag}[110]||\text{Si}[100]$.

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explained by the difference in the scattering lengths of the two techniques; as mentioned earlier, for small grain sizes XRD measures the average lattice structure, while TEM is a local probe of crystal structure in which small areas of α" are detected. Thus, we conclude that some α" exists in the α' film in the as-deposited state. Subsequent annealing greatly increases the volume fraction of α" in α', and hence becomes detectable by XRD.

Centered dark-field images (Figure 3) affirm the partial N ordering of the annealed α'/α" film. CDF images are taken by tilting a specific diffracted beam into the optical axis, then centering the objective aperture around it to block out other diffracted beams (and the central beam). In Figure 3(a), the α'(200)/α"(400) diffraction spot is imaged in dark field. Some contrasting (bright) regions in this image disappear in Figure 3(b), in which the α"(200) reflection is imaged (see arrows, for example). This latter reflection is not shared by the α' phase, so α' regions lose contrast. It does contain, however, the same contrast information for α" as the α"(400) reflection, and thus confirms that there are regions of pure α". The size of these regions is 10-20 Å. Generally, it appears that regions of α" are uniformly dispersed in the α' phase. It should be noted that exposure times were different for the two images; areas appearing dark in

Figure 3. Plan-view TEM dark-field images and corresponding diffraction patterns of an α'/α" film for (a) α'(200)/α"(400) and (b) α"(200) reflections. Arrows are discussed in the text.
Figure 4. Plan-view TEM bright-field images and diffraction patterns (inset) of (a) $\alpha'$-Fe$_8$N film, (b) $\gamma'$-Fe$_4$N film, (c) $\alpha'$-Fe$_8$N/$\alpha''$-Fe$_{16}$N$_2$ film after a 2-hour anneal at 150 °C, and (d) $\alpha'$-Fe$_8$N/$\alpha''$-Fe$_{16}$N$_2$ film after a 16-hour anneal at 150 °C.

Figure 3(a) but bright in Figure 3(b) are merely underexposed [in Figure 3(a)] due to the high intensity of the $\alpha'(200)$ reflection. The image in Figure 3(a) was exposed for a few seconds, whereas the image in Figure 3(b) was exposed for 90 seconds to develop contrast from the weak $\alpha''(200)$ reflection. Although no Ag was detected in this region by EDXS, it may be contributing to the CDF image of Figure 3(a) since the $\alpha'(200)$ reflection is coincident with the Ag(220) reflection. Due to its heavy atomic weight, Ag has a very high atomic scattering factor compared to Fe, so its intensity contribution to the reflection is expected...
to be large. Thus, the Fe contribution from both FeN phases may be underexposed in Figure 3(a).

Selected-area bright-field images and diffraction patterns (inset) of the (001) zone axis of \( \alpha', \gamma', \) and \( \alpha'/\alpha'' \) films on Ag/Si(001) are shown in Figures 4(a, b, and c), respectively. The average grain size of the \( \alpha' \) and \( \alpha'/\alpha'' \) films is significantly smaller than that of the \( \gamma' \) film, however, the \( \gamma' \) film has extensive oxidation [as indicated by the amorphous ring pattern in the SAD, Figure 4(b) inset] and may have been adversely affected by TEM sample preparation more than the other films. The FCC \( \gamma' \) orientation is the same as that of the Ag underlayer; \( \text{Fe}_4\text{N}[110] \parallel \text{Ag}[110] \parallel \text{Si}[100] \). The oblong shape of the \( \text{Fe}_4\text{N}(220) \) reflection [superimposed on the Ag(220) reflection which was labeled in Figure 2(b)] indicates a spread (mosaic) in the in-plane orientation of \( \text{Fe}_4\text{N} \) grains. This alludes to the 6.9% lattice mismatch present between the Ag and \( \text{Fe}_4\text{N} \) which causes strain. In general, the grain size in nitrogen martensite is rather insensitive to short annealing times; there is only a small change in the grain size in the TEM images from the pure \( \alpha' \) phase [Figure 4(a)] to the mixed \( \alpha'/\alpha'' \) film, which was annealed for 2 hours in vacuum [Figure 4(c)]. A measurable increase in grain size appears after 16 hours [Figure 4(d)], which implies that grain growth is occurring, albeit slowly. Despite this grain development there is no further increase in the volume percentage of \( \alpha'' \) in \( \alpha' \) after the 16-hr anneal compared to the 2-hr anneal, based on volume-fraction quantification performed using the procedure outlined in Chapter III. It is not clear why the extent of N ordering is limited to around 50 vol%.

It is desirable to measure the grain size of the iron nitride films to make a better assessment of the distribution of \( \alpha' \) and \( \alpha'' \) grains. This was attempted using a high-resolution electron microscope (the Topcon 002B at the NCEM). Figure 5(a) is a plan-view HREM filtered image of an \( \alpha-\text{Fe} \) film grown on Ag/Si(001). The film is nearly single crystal with some c-axis misalignment of grains, although there are no distinct grain boundaries. There is a 20-Å Ag capping layer which adds a polycrystalline ring pattern to the SAD pattern (inset), although over time this layer proved ineffectual for oxidation protection since 20 Å of Ag did not form a continuous layer over the FeN film (see again Chapter III). Note that the diagonal streak in the SAD pattern is an artifact of
Figure 5. Plan-view HREM bright-field filtered images and diffraction patterns (inset) of (a) $\alpha$-Fe film with a 20-Å Ag cap, (b) $\alpha'$-$\text{Fe}_8\text{N}$ film with a 20-Å Ag cap, and (c) $\alpha'$-$\text{Fe}_8\text{N}/\alpha''$-$\text{Fe}_{16}\text{N}_2$ film, uncapped (facing page).
the microscope. Figures 5(b and c) are plan-view HREM filtered images of $\alpha'$ and $\alpha'/\alpha''$ films, respectively, grown on Ag/Si(001). The films are also nearly single crystal with some c-axis misalignment of grains. Again, there are no distinct grain boundaries, although the rocking curve analysis showed that some dispersion exists in the c-axis orientation and the films are not perfectly single crystalline. There does not appear to be any mosaic in the film plane, which would be manifested as a radial spread (arcs) in the SAD reflections. Also, the $\alpha'$ film has a Ag capping layer while the $\alpha'/\alpha''$ film does not. It should be noted that there are lattice fringes in Figure 5(c) (lower left corner) that appear to come from Ag which has an orientation inconsistent with the diffraction pattern; the foil may have had some curvature during imaging. These “filtered” images are generated using a computer application program with a rotational filter; any intensity which is constant at a specific radius in the Fourier transform of the image (the diffraction pattern calculated from the image) is removed as amorphous background, then the inverse Fourier transform is performed to restore the image. It was hoped that the amorphous iron oxide contribution to the image could be removed in this way, but even the
filtered images unfortunately do not implicitly show the grain size.

It would be interesting to know if there are distinct grains of pure $\alpha''$ and of pure $\alpha'$ or if each grain contains regions of $N$ order and $N$ disorder within a single-crystal BCT Fe structure. The distinction between $\alpha'$ and $\alpha''$ may not be that of two separate phases but rather the end points of a continuum characterized by the degree of order. This determination can only be made with oxide-free TEM specimens, since the lattice fringes must be very clear with minimal amorphous and/or polycrystalline noise. Unfortunately, producing oxide-free TEM specimens was not possible during the course of this work. The HREM images also raise another issue regarding the $N$ order. Due to the significant point defects generally present in sputtered films, the coherence length (the distance over which a crystal is perfectly ordered) is relatively short. For the films shown in Figure 5, the coherence length is on the order of 50-100 Å (as measured by the distance between discontinuities in the lattice fringes). If $N$ disorder is viewed as a cluster of point defects within a perfectly ordered $\alpha''$ phase, this disorder may inhibit perfectly-ordered $\alpha''$ from reaching its bulk value of the magnetization. For small grain sizes like those estimated here, the grain boundaries would also contribute to a short coherence length, thereby disrupting the magnetic behavior. It is well-known that grain size can effect the coercivity, but its effect on the magnetization is not well understood in Fe-N. If the lattice effect (increased magnetization along one axis due to enhanced exchange coupling caused by lattice expansion) dominates the magnetization in Fe$_{16}$N$_2$, then this effect would be reduced by a small grain size (short coherence length). According to calculations, the lattice effect alone cannot explain the giant moment reported for Fe$_{16}$N$_2$, thus, another mechanism may be present. It is unclear how short coherence lengths affect both this unknown mechanism and the lattice effect mechanism, or what length scale is required to reach optimal magnetization. Based on the magnetization data for $\alpha''$ in the literature (see again Table I in Chapter I), optimal magnetization can only be achieved by MBE on lattice-matched substrates, while other methods and substrates are less successful. This may be due to a longer coherence length in the high-quality MBE samples. Magnetization data for our films is presented in the last section.
Phase purity and $\alpha'/\alpha''$ distribution: Micro-diffraction

Through the use of SAD, in which the condenser lens is defocused to produce parallel illumination at the specimen and a selected-area aperture is used to limit the diffracting volume, it was shown that some $\alpha''$ is present in the as-deposited $\alpha'$ films. It is possible to further reduce the diffracting volume using micro-diffraction, and therefore have greater precision in measuring the phase purity and distribution. Micro-diffraction is a technique in which the incident electron probe is focused, thus utilizing convergent illumination instead of parallel illumination. The characteristic diffraction pattern consists of "discs" instead of spots, and can sample much smaller areas of the sample than SAD. For our AEM operating in STEM mode, the probe size is 200 Å. This was previously calibrated at a magnification of 60,000 times with the condenser voltage locked at $C_2 = 5.0$ V; therefore, all micro-diffraction was performed under these conditions. This technique was performed on several of the FeN films and provided interesting results.

The probe was positioned within a random region of dark contrast on the STEM screen in bright field. Figure 6 shows two micro-diffraction patterns of the unannealed $\alpha'$-Fe$_8$N film on Ag/Si(001). Figure 6(a) contains only $\alpha'$-Fe$_8$N reflections [such as $\alpha'$(200)] but no superlattice reflections from $\alpha''$, whereas Figure 6(b) does contain the superlattice reflections [such as $\alpha''$(200)]. Figure 6(a) indicates that there exist...
regions as large as 200 Å that have no ordered nitride, while Figure 6(b) indicates that some regions as large as 200 Å contain either pure \(\alpha''\) or a mixture of \(\alpha'\) and \(\alpha''\). In the annealed sample known to contain 48 vol% \(\alpha''\) in \(\alpha'\), both micro-diffraction patterns shown in Figure 6 were similarly recorded. Qualitatively, while there was clearly a more frequent occurrence of micro-diffraction patterns containing \(\alpha''\) reflections in the annealed sample, there were still regions at least 200 Å across which contained no \(\alpha''\). This may indicate that the distance between \(\alpha''\) nucleation sites exceeds 200 Å. Micro-diffraction patterns of a \(\gamma\)-Fe\(_4\)N film were difficult to interpret due to the extensive oxidation of the specimen.

It should be noted that while XRD detected no \(\alpha\)-Fe in either of these samples, it may be present in small amounts and its diffraction pattern would be identical to \(\alpha'\) in these (001) plan-view specimens. Undetected (and therefore unaccounted-for) \(\alpha\)-Fe would result in a lower value for the saturation magnetization of the \(\alpha'\) and \(\alpha''\) phases due to the incorrect assessment of phase volume. A way to study this would be to tilt the TEM specimen to a major zone axis such as [110] or [111] so that reflections with a c-axis component could be analyzed. Since \(\alpha\)-Fe has a c-axis lattice parameter \((a = c = 2.87 \text{ Å})\) different from \(\alpha'\) \((c = 3.13 \text{ Å})\), there would be distinct reflections for each phase in the diffraction patterns if both phases were present. This experiment, however, would not conclusively establish whether \(\alpha\)-Fe was present in the films prior to room-temperature aging and TEM specimen preparation, both of which can cause some phase separation, and would not quantitatively establish the volume fraction of any \(\alpha\)-Fe present in the specimen.

**Determination of chemical concentrations: Electron energy-loss spectroscopy**

The crystal structures, orientation relationships, volume fractions and distribution of FeN phases grown on Ag/Si(001) have been determined using XRD and TEM techniques. To draw conclusions from the magnetic property data examined in the next section for these phases, the stoichiometry (chemical concentration ratio of Fe and N) must be determined as well. The
amount and uniformity of nitrogen incorporation during growth can affect film
density, phase uniformity, strain, lattice parameter and, subsequently,
magnetic properties. Especially important are changes in stoichiometry, such
as nitrogen loss, which may occur during annealing of $\alpha'$ films in vacuum to
produce $\alpha'/\alpha''$ mixtures, assuming that the vapor pressure of N in FeN is higher
than $10^{-6}$ Torr. Electron energy-loss spectroscopy (EELS) is a technique which
can determine the local elemental concentration of each atomic species
present. EELS is an absorption spectroscopy similar in many respects to X-
ray absorption spectroscopy (XAS), which will be covered at length in Chapter
VI. An in-depth treatment of EELS is given by Egerton.\textsuperscript{7} EELS derives its
information from the measurement of changes in the energy and angular
distribution of an initially monoenergetic beam of electrons that has been
inelastically scattered during transmission through a thin specimen.\textsuperscript{8} This is
the geometry routinely used in a TEM, and therefore the technique is normally
associated with this instrument. The characteristic spectral signature is the edge
profile, derived from the excitation of discrete inner-shell levels to empty states
above the Fermi level. Conservation of energy requires that the incident
electron beam lose the corresponding amount of energy and intensity
expended in exciting each inner-shell level, and these are the parameters which are
recorded in each experiment. Figure 7(a) is a schematic of

![Diagram of electron energy-loss spectroscopy](image)

Figure 7. (a) Excitation of inner shells by Coulombic interactions. (b) Energy level
diagram illustrating excitation from inner shell and valence band into the conduction
band and the creation of a corresponding electron hole.
the excitation of inner shells by Coulombic interactions, in which inelastic scattering causes atomic electrons to be excited to higher energy states (or ejected altogether) leaving behind an electron hole [Figure 7(b)].

Figure 8 is an experimental energy-loss spectrum from a thin specimen of beryllium. At zero-energy-loss is a large peak which represents the elastically scattered and phonon-scattered incident electrons that have passed through the specimen suffering either negligible or no energy losses. The "low-loss" regime (extending from 1 eV to 50 eV by convention) exhibits a series of broad spectral features related to inelastic scattering with the valence electron structure of the material. In metallic systems these peaks arise due to a collective excitation of the valence electrons, and are termed plasmon oscillations or peaks. For higher energy losses one observes a series of "edges" superimposed on a continuously decreasing background. These edges result from electrons that have lost energy corresponding to the creation of vacancies in the deeper core levels of the atom (K, L₃, L₂, L₁, M₅, and so forth, see Chapter VI). The energy needed to eject an electron amounts to the binding energy of the respective shell plus the work function to eject the electron into the continuum, which is characteristic for each element. By measuring the threshold energy of each edge the investigator can determine the identity of the atom giving rise to the signal, while the net integrated intensity for the edge can be analyzed to obtain the number of atoms producing the signal. This is the basis of quantitative compositional analysis in EELS.

Since EELS is a primary interaction event, while all other electron-column analytical techniques (such as EDXS) are the result of secondary
decay or emission processes, quantitative concentration measurement is straightforward. The number density of atoms is given by

\[ N = \frac{I_K(\beta, \Delta E)}{G I_0 \sigma_K(\beta, \Delta E) t}, \]  

(4.1)

in which \( G \) is the instrument gain, \( I_0 \) is the total number of electrons incident (passed) through the sample (the integrated intensity of the zero-loss peak), \( \sigma_K \) is the absolute cross-section in \( \text{m}^2/\text{atom} \) (for the K shell, for instance), and \( t \) is specimen thickness. \( I_K \) is the net intensity above background over an integration window of \( \Delta E \) and scattering angle \( \beta \). \( \sigma_K \) is known or calculable and \( I_K \) and \( I_0 \) are measured quantities. To find the absolute number density of atoms requires an accurate measure of film thickness and \( I_0 \). It is more convenient and common to calculate the ratio of the number densities of any two edges A and B:

\[ \frac{N_A}{N_B} = \frac{\sigma^B_K(\beta, \Delta E^B) I^A_K(\beta, \Delta E^A)}{\sigma^A_K(\beta, \Delta E^A) I^B_K(\beta, \Delta E^B)}. \]  

(4.2)

For the AEM at the NCEM, the cross-sections for many elements have been accurately measured using known standards, including those for N-K, O-K and Fe-L edges. The theoretical cross-sections used in the data-analysis software agree well with those measured experimentally, and accuracies to approximately 1 at% can be realized in ideal cases.

**Fe:N concentration ratio and oxygen content**

Quantitative analysis of N-K and Fe-L edges in electron energy-loss spectroscopy requires a consistent application of EELS collection, energy calibration, and spectrum quantification methods. Our results varied greatly depending on the background and integration widths and offsets used for the data analysis procedure, so the best method was determined and used throughout the study. Data was collected in image mode (20-30 kX magnification) using either approximately 1 eV per channel (4-5 eV resolution) or 0.5 eV/ch (2 eV resolution), with 1024 channels available. Energy calibration was based on peak position: the N-K edge position (401 eV) was chosen as the far left side (the onset) of the hydrogenic peak shape; the Fe-
$L_3$ edge position (708 eV) was chosen as the half-maximum intensity of the edge onset of the white-line peak shape. The background intensity (modeled as $AE^{-1}$) was measured over a 50-eV width below the edge, beginning 5 eV before the edge threshold (as defined by the energy calibration above) and subtracted. Then the intensity of the peak was integrated for a width of 50 eV above the edge, beginning 5 eV before the edge threshold. With this quantification setup, the application program for the EELS spectrometer (Gatan EL/P 2.1) completely calculates the N-K edge intensities above background first, then calculates the Fe-L edge contribution using the remaining spectrum. The atomic ratio then results from equation 4.2 above.

When employing cross-section standards, it is essential that the near-

![Figure 9](image)

Figure 9. Electron energy-loss spectrum for an $\alpha'$-Fe$_8$N film on Ag/Si(001). The background fit for the N-K edge (dashed line) is shown for reference. The integrated intensities of the N-K and Fe-L edges are shown at the bottom of the graph, with the dark-gray area indicating the program's integration fit using the measured cross-sections. The light-gray areas indicate the background interval (-5 to -55 eV from the edge position) and the integration integral (-5 to +45 eV from the edge position) used in the quantification. The atomic concentration ratio was calculated to be $N/Fe = 0.11$. 

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edge structure does not vary significantly between the unknown and the standard, since in many cases near-edge structure contributes substantially to the net integrated edge profiles, especially for white-line shapes. Despite having different shapes (hydrogenic and white-line, respectively), both the N-K edge and the Fe-L edge were required to use the same background integration width and the same intensity integration width (including offset from the peak position) by the spectrum quantification program. This is the primary reason for the choice of peak position in the energy calibration. Instrument calibrations performed during spectra collection were around 0.95 eV/ch (0.47 eV/ch in some cases).

Figure 9 is the EELS spectrum for an \(\alpha'-\text{Fe}_8\text{N} \) film (made into a plan-view TEM specimen). The background fit for the N-K edge is shown for reference. The integrated intensities are shown at the bottom of the graph,

\[
\frac{N}{Fe} = 0.12
\]

Figure 10. Electron energy-loss spectrum for an \(\alpha'/\alpha'' \) film on Ag/Si(001). The integrated intensities of the N-K and Fe-L edges are shown at the bottom of the graph, with the gray area indicating the program's integration fit using the measured cross-sections. The atomic concentration ratio was calculated to be \(N/Fe = 0.12\).
with the dark-gray area indicating the program's integration fit using the measured cross-sections (including a white-line correction for the Fe-L edge). The light-gray areas indicate the background interval (-5 to -55 eV from the edge position) and the integration integral (-5 to +45 eV from the edge position) used in the quantification. Note that the intervals start just to the left of the peak position, since the onset of the peak is not exactly coincident with the peak position. The atomic concentration ratio was calculated to be N/Fe = 0.11 ± 0.015, or 9.9 at% N, corresponding to Fe$_{8.1}$N. Given that the ideal value for Fe$_8$N is 0.125 (11.1 at% N), a smaller value indicates that there may be a shortage of N incorporation during growth. Figure 10 is the EELS spectrum for an α'/α'' film. The ratio was N/Fe = 0.12, or 10.7 at% N, corresponding to Fe$_{8.3}$N. It is unlikely that the α'/α'' film acquired more N during the anneal (which is carried out in vacuum), but both values are reasonable within an

Figure 11. Electron energy-loss spectrum for an γ'-Fe$_4$N film on Ag/Si(001). The integrated intensities of the N-K and Fe-L edges are shown at the bottom of the graph, with the gray area indicating the program's integration fit using the measured cross-sections. The atomic concentration ratio was calculated to be N/Fe = 0.25.
error of ±0.015 (±1.2 at%). In any case it may be concluded that a change in FeN stoichiometry due to annealing is insignificant. This implies that magnetic data for α' and α'' (extracted from pure α' and mixed α'/α'' films) may be directly compared to the expected values for their structures and to each other. Figure 11 is the EELS spectrum for a γ'-Fe₄N film. Spectrum quantification results in a value for N/Fe of 0.25 (20 at% N), which agrees with the expected value. There was more oxidation of the Fe₄N sample than of the other samples, thus, a rather thick region was used for the EELS analysis to minimize the contribution from oxygen. This causes the peaks in Figure 11 to appear weaker than those in Figures 9 and 10. Also, a smaller energy calibration (0.47 eV/ch) was used for this sample, which visually broadens the peaks shown here but has no effect on the microanalysis.

All of the samples contained a significant amount of oxygen, as indicated by the presence of the O-K edge at 532 eV (Figure 9 is a fortuitous exception). It is not clear how much oxygen results from oxidation, specimen preparation, annealing and/or film growth. What impact oxygen has on the magnetic properties in iron nitride is unknown, although much more oxygen was detected near the film surface than near the film bulk in the TEM. This was observed by collecting EELS data in several locations near or far from the thinnest area of the specimen and noting a qualitative change in the O-K edge intensity. Since the specimen is dimpled from the back side, the thinnest area is near the film surface, and this area had the most oxygen. This would imply that magnetization data, covered in the next section, would not be greatly affected by the presence of oxygen that is confined to the surface, since the “surface” is only a small percentage of the film volume measured to obtain the saturation magnetization.

Structural characterization of the films, including crystal structure, epitaxial growth orientation and stoichiometry, has demonstrated that the FeN films were produced with high quality and purity. These properties are strongly tied to the magnetic properties of the films, and their determination is crucial to reliable magnetic characterization. Another important contributor to magnetic properties is the chemical structure, that is, the bonding configuration, electronic structure and local moments of Fe and N atomic sites.
This important analysis is reserved for a separate chapter (Ch. V) in which Mössbauer spectroscopy is used to verify the expected chemical structures of the $\alpha'$ and $\alpha''$ phases.

**Magnetic properties of FeN films — Giant moment?**

With the completion of the structural characterization of FeN films, the magnetic properties can now be meaningfully analyzed. The most important question, naturally, is whether Fe$_{16}$N$_2$ has a giant magnetic moment. Since we did not produce single-phase Fe$_{16}$N$_2$ films we must rely on the volume-fraction analysis performed in Chapter III when quantifying the contribution of the Fe$_{16}$N$_2$ saturation magnetization to the total measured saturation magnetization. How our values for magnetic saturation compare with the experimental and theoretical values for all the iron nitrides is an important part of this work. The important magnetic properties of materials, such as saturation magnetization ($M_s$) and coercive field ($H_C$), are often measured using a vibrating-sample magnetometer (VSM). (See again Chapter II for definitions of magnetic properties.) The VSM was first described by Foner and is shown schematically in Figure 12. A VSM measures the magnetic moment of a sample when it is vibrated perpendicularly to a uniform magnetizing field. It is actually a gradiometer measuring the difference in

![Figure 12. Schematic diagram of a vibrating-sample magnetometer](image)
magnetic induction between a region of space with and without the specimen.\textsuperscript{11} It therefore gives a direct measure of the magnetization $M$. The detected signal, an AC signal of fixed frequency, is measured using a lock-in amplifier. A reference signal is provided for the lock-in amplifier by using a permanent magnet and a reference pick-up coil. Magnetic moments as small as $5 \times 10^4$ Am$^2$ (5 x 10$^{-5}$ emu) are measurable with a VSM, and its accuracy is better than 2\%.\textsuperscript{11} Most magnetic properties can be derived from the hysteresis loop, although values for the saturation magnetization per unit volume require the measurement of two parameters; the saturation derived from the hysteresis loop, and the volume of the material measured. In our case, the volume determination includes measures of the volume fraction of individual phases, film thickness and film area. Film area is generally assumed to be that within the sample mask area, although there can be shadow effects when sputtering near an edge of finite thickness (resulting in thinner film near the edge). Film thickness can be measured either with a profilometer or more accurately by a TEM cross-sectional sample. The latter technique was used to determine the thickness of an $\alpha'$ film, and it was assumed that the sputtering deposition rate was reproducible.

![Hysteresis Loops](image)

Figure 13. Vibrating-sample magnetometry hysteresis loops of (a) $\alpha$-Fe, (b) $\gamma'$-Fe$_4$N, and (c) $\alpha'$-Fe$_8$N epitaxial films deposited on Ag/Si(001), normalized with sample volume.
Magnetic saturation and hysteresis characteristics of FeN films

Vibrating-sample magnetometry data acquired at room temperature with the field applied parallel to the film plane and normalized with sample volume are shown in Figure 13. The diamagnetic contribution from the Si substrate was removed by subtracting a line through the origin of slope equal to that measured above saturation on the hysteresis loop. Assuming a magnetization of 1708 emu/cc for α-Fe [Figure 13(a)], the film volume was estimated from the VSM data (which is initially in emu). The film thickness was then calculated from the estimated area, and was used as a calibration for γ′-Fe₄N (including volume expansion), since the α and γ films were grown under identical sputtering conditions (growth rate and total gas pressure). The γ′ magnetization was then estimated to be 1478 emu/cc [Figure 13(b)]. The fact that this is the expected value for γ′ substantiates the use of the α-Fe calibration. These moments are based on ideal structures and densities, which are supported by the X-ray diffraction and EELS analyses but are not certain; usually sputtered films are not theoretically dense.

The magnetic properties of the α and γ phases are well established, however, for the controversial α′ and α′/α″ phases an accurate volume determination was made. Since the film areal width is much greater than its thickness (approximately 1 cm versus 10⁻⁵ cm), an accurate measure of the film thickness is paramount. The thickness of Ag and α′-Fe₈N layers were measured by cross-sectional TEM at 200 kX (Figure 14) and determined to be approximately 950 Å and t₉FeN = 650 Å, respectively. In Figure 14 the poorly-adhering Ag film has pulled away from the Si substrate, leaving a gap visible in the image. A 10-Å amorphous layer (presumed to be
native Si oxide which reformed during sample loading) has been observed at the interface of Ag and Si(001) in similarly-prepared samples,\textsuperscript{13} and may contribute to the poor adhesion. $\alpha'$ was consequently estimated to have a moment of 1780 emu/cc (Figure 13(c)]. The film thickness after annealing was assumed to be approximately the same as the as-deposited $\alpha'$. Figure 15 shows normalized SQUID magnetometry data taken at 15 K for the $\alpha'/\alpha''$ film annealed for 2 hours.\textsuperscript{2,12} (The SQUID magnetometer was used while the VSM was unavailable and provides similar data as the VSM.) We estimate that the moment of the $\alpha'/\alpha''$ film is also around 1780 emu/cc. These magnetic moments vary widely ($\pm$8 \%) depending on the volume estimates used for each film. Some concluding comments will address this issue.

Values of the coercive field ($H_c$) and saturation field ($H_s$), as well as saturation magnetization ($M_s$) for all the FeN films are summarized in Table I. Fe and Fe$_4$N films have fairly low coercivities (165 Oe and 265 Oe, respectively) compared to Fe$_8$N and Fe$_{16}$N$_2$ (450 to 500 Oe, respectively). In soft magnets, the coercivity is principally determined by pinning of magnetic domain walls during magnetization of the material. This is caused either by crystal imperfections or by uniaxial anisotropy (due to preferred orientation

![Figure 15. SQUID magnetization data for an $\alpha'$-Fe$_8$N/$\alpha''$-Fe$_{16}$N$_2$ epitaxial film deposited on Ag/Si(001), normalized with sample volume.](image)

<table>
<thead>
<tr>
<th>Film</th>
<th>$M_s$ (emu/cc)</th>
<th>$H_c$ (Oe)</th>
<th>$H_s$ (Oe)</th>
</tr>
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<tr>
<td>$\alpha$-Fe</td>
<td>1708</td>
<td>165</td>
<td>1900</td>
</tr>
<tr>
<td>$\gamma$-Fe$_4$N</td>
<td>1478</td>
<td>265</td>
<td>2100</td>
</tr>
<tr>
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<td>4900</td>
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<td>485</td>
<td>7900</td>
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</table>

95
combined with crystal anisotropy, or due to uniaxial stress).\textsuperscript{14} Certainly crystal anisotropy is important in epitaxial films, which may explain the relatively high coercivity values of these films compared to bulk Fe ($H_c = 1$ Oe). For the BCC iron film the “easy-axis” for magnetization is $\langle 100 \rangle$, which lies in the plane of the film, while for FCC $\gamma$ it is expected to be $\langle 111 \rangle$ (in bulk), which does not lie in-plane. This may be a contributing factor to the higher coercivity measured for the $\gamma$ phase compared to $\alpha$. For BCT $\alpha'$ and $\alpha''$, the easy-axis is expected to be along [001], which is clearly out-of-plane in these measurements. Shape anisotropy (determined by the relative dimensions of the film) is still the stronger force and keeps the easy magnetization direction in the plane of the film, according to VSM measurements taken with several different sample orientations relative to the field direction, in addition to in-plane and out-of-plane. (The sample orientation with the smallest hysteresis-loop area corresponds to the easy-axis direction.) Grain size is probably similar in these films since their preparation and epitaxial relationships are similar. Thus, this factor may not help explain the differences in $H_c$, although grain size and $H_c$ are proportional for single-domain particles ($d < 200$ Å for Fe).\textsuperscript{14} Note that if the grains are not magnetically isolated, there will not be single-domain behavior but perhaps multi-domain behavior (decreasing $H_c$ with increasing grain size). In general, these coercivities are far too high for magnetic recording heads, which require coercivities less than 1 Oe. There is always a trade-off between high magnetization and low coercivity. A reasonable balance has been reached using polycrystalline Fe films with N\textsuperscript{15} as well as ternary alloys of FeXN.\textsuperscript{16,17}

Besides uniaxial anisotropy, crystal imperfections such as inclusions and residual microstress can hinder domain wall motion and decrease $H_c$. Assuming that inclusions are not present in the FeN films (based on the TEM micrographs), residual microstress may be contributing to the higher coercivities. Residual microstress depends on the dislocation density and the magnetostriction of the film.\textsuperscript{14} Dislocations are present in all of the films, although in similar numbers since the lattice-mismatch conditions are similar. Magnetostriction is the strain caused by a dimensional change $\Delta l$ in a substance when it is exposed to a magnetic field, and is given by
\[ \lambda = \frac{\Delta l}{l}. \] (4.3)

Ordinary, field-induced magnetostriction is caused by the conversion of a demagnetized specimen, made up of domains spontaneously strained in various directions (isotropically), into a saturated, single-domain specimen spontaneously strained in one direction. Since the various domains are not free to deform independently, microstresses are set up. Thus, if there is an increase in magnetostriction, there is an increase in domain wall pinning since microstress impedes domain wall motion.

Studies indicate that magnetostriction varies linearly with N content in Fe (negative for zero N but crossing zero and becoming increasingly positive with increasing N), hence, magnetostriction may also be contributing to domain wall pinning in iron nitride. No studies of magnetostriction have been carried out on epitaxial iron-nitrogen films or on the effect of annealing nitrogen martensite at constant N concentration. The magnetostriction is also tied to crystal anisotropy, that is, if the lattice parameter increases in one direction, the magnetostriction may change along that axis. According to the 0-2θ X-ray scans (Chapter III), the films do not appear to be significantly stressed, and uniaxial anisotropy is expected to be more important than magnetostriction.

The applied fields required to saturate FeN films follow the same trend as the coercive fields, however, there is a significant difference between the unannealed and annealed \( \alpha' \) (Table I). Figures 16(a) and 16(b) represent VSM hysteresis loops for \( \alpha' \) and \( \alpha'/\alpha'' \) films, respectively. Annealing and the presence of N order have significantly increased \( H_s \), although \( M_s \) remains unchanged. This is a result of a change in the magnetization process. Under an applied field, magnetization changes as a result both of domain wall motion and domain rotation. Wall motion is the main process up to about the "knee" of the magnetization curve [indicated by the arrow in Figure 16(b)]. From the knee to saturation, rotation predominates; in this region work must be done against the anisotropy forces, and a rather large increase in \( H \) is required to produce a relatively small increase in \( M \). This "knee" is a rather arbitrary division applicable to a polycrystal, since domain wall motion and rotation are not sharply divisible processes.
After annealing the $\alpha'$ film to produce 48 vol% $\alpha''$ in $\alpha'$, domain rotation is more obstructed during magnetization than before annealing, based on the shift of the magnetization curve to higher applied fields [Figure 16(b)]. An increase in the anisotropy constant upon annealing may be responsible for this. This is supported by measurements of the uniaxial perpendicular (out-of-plane) anisotropy constant; for $\alpha'$-$\text{Fe}_{90}\text{N}_{10}$, $K_u$ was measured to be $6.36 \times 10^6$ erg/cc,\textsuperscript{19} and for $\alpha''$-$\text{Fe}_{16}\text{N}_{2}$, $K_u$ was measured to be $7.8 \times 10^6$ erg/cc.\textsuperscript{20} An approximation of $K_u$ can be made for our data using the simple expression\textsuperscript{14}

$$K_u = \frac{1}{2} M_s H_s.$$  \hfill (4.4)

Using the values of $M_s$ and $H_s$ given in Table I, $K_u = 4.4 \times 10^6$ erg/cc (1 erg = 1 emu/Oe) for the $\alpha'$ film and $K_u = 7.0 \times 10^6$ erg/cc for the $\alpha'/\alpha''$ film. These

Figure 16. Vibrating-sample magnetometry hysteresis loops for (a) $\alpha'$-$\text{Fe}_8\text{N}$ and (b) $\alpha'$-$\text{Fe}_8\text{N}/\alpha''$-$\text{Fe}_{16}\text{N}_2$ epitaxial films deposited on Ag/Si(001), normalized with sample volume. The arrow indicates the approximate transition from domain wall motion to domain rotation.
results agree fairly well with the measured results given above, and certainly indicate an increase in the anisotropy constant upon annealing. Although the uniaxial anisotropy is expected to favor magnetization along the c-axis, the shape anisotropy \( (2\pi M_s^2) \) is much larger \((3.1 \times 10^7 \text{ erg/cc}^{20} \text{ or } 2.0 \times 10^7 \text{ erg/cc for our } \alpha' \text{ and } \alpha'/\alpha'' \text{ films}) \) and forces the magnetization direction to be in-plane. Anisotropy is an intrinsic property, so a change in this parameter due to annealing may be a direct result of the N ordering, although measuring techniques for anisotropy tend to make this a structurally-sensitive measurement in practice.\(^{14}\)

It is interesting to note that Mössbauer spectroscopy, covered in Chapter V, determined that the easy-axis for the annealed \( \alpha'/\alpha'' \) film was 35° off the film normal, but may have been different prior to annealing. The anisotropy is therefore rather complex, neither dominated by the shape anisotropy which aligns the easy-axis with the film plane, nor the magnetocrystalline anisotropy, which aligns the easy-axis with the tetragonal c-axis of the martensite. A change in the easy-axis direction could certainly account for the change in hysteresis behavior upon annealing. A change in grain size would also affect domain rotation, however, this would generally result in a change in coercivity as well. While a small increase in coercivity with annealing did occur and may be due to the small amount of grain growth observed in the TEM, this effect may not be as important as an increase in anisotropy. It can be concluded in any event that, as is commonly the case, improving the crystalline quality through annealing has resulted in detrimental changes to all magnetic properties except the saturation magnetization, at least in terms of soft-magnet inductive-head applications. If the saturation magnetization of \( \alpha' \) had improved upon annealing when it formed \( \alpha'' \), it may have been a more beneficial trade-off; unfortunately, this did not occur and the giant moment was not confirmed for \( \alpha'/\alpha'' \) films grown on silicon.

While the VSM is sensitive enough to measure magnetization in thin films, quantifying the magnetization per unit volume is more difficult for thin films than for bulk materials. The magnetization data presented here have a relatively large error (±8%), which is not due to the moment measurement, but rather to the difficulty in determining the film volume. A combination of pho-
tolithographic techniques for depositing known film areas and cross-sectional TEM to determine film thickness on every sample would lead to a great improvement in volume accuracy. Photolithography, however, adds significant complexity to film processing, and analyzing a battery of TEM cross-sections is indeed tedious. It is possible to measure the absolute magnetic moment without knowledge of the film volume using a relatively new technique, X-ray magnetic circular dichroism (XMCD). In ideal cases, the absolute moment can be measured, however, it is more realistic to attempt to measure the relative contributions of spin and orbital angular momentum to the moment. XMCD could elucidate the issue of whether Fe\textsubscript{16}N\textsubscript{2} possesses a giant moment by addressing one possible source of the discrepancy between experiment and theory; whether or not the orbital contribution to the moment is negligible. XMCD spectroscopy, which uses X-ray absorption spectroscopy (XAS) with the incident light modified to have circular polarization, has the ability to separate the spin and orbital contributions to the moment in a way that is element specific. This technique and its application to FeN films is discussed in Chapter VI.

References


CHAPTER V:
CHEMICAL ENVIRONMENT OF IRON ATOMS IN IRON NITRIDE — MÖSSBAUER SPECTROSCOPY

The Mössbauer effect and its application to FeN films

In order to verify reports of a giant moment in Fe$_{16}$N$_2$, the structure of the films must be confirmed beyond the phase purity, lattice parameter and the extent of nitrogen ordering, as characterized by X-ray diffraction and TEM analyses. To compare magnetization measurements between different research groups and with calculations for Fe$_{16}$N$_2$, the chemical structure must be the same in all cases, and is assumed to be that proposed by Jack in 1951. The chemical structure defines not only the atomic positions in a unit cell but also the chemical environment, such as bonding, orbital symmetry and local atomic moments, for each Fe and N position. If a deviation in chemical structure could be linked to a change in the magnetic moment, this might explain the disparity in experimental results as well as the disagreement between experimental giant-moment Fe$_{16}$N$_2$ and the enhanced-moment Fe$_{16}$N$_2$ predicted by band-theory calculations. Mössbauer spectroscopy may provide such a link, and has become the hallmark analysis technique for Fe$_{16}$N$_2$. Besides giving quantitative information on the electronic structure of Fe in the solid, Mössbauer spectroscopy can resolve chemically inequivalent Fe sites in terms of valence, orbital symmetry and local magnetic properties.

The Mössbauer effect, which is the recoilless emission and resonant absorption by a nucleus of a $\gamma$-ray, was discovered by Rudolf L. Mössbauer in 1958 using the nuclear fluorescence of $\gamma$-radiation in iridium-191 and led to the award of the Nobel prize in physics in 1961. The technique was immediately applied to studies of gravitation, relativity, and certain areas of nuclear physics, but found more widespread use in the fields of solid-state physics and chemistry, metallurgy, geochemistry and biophysics. This was mainly due to the rapid discovery by other workers in 1959 and 1960 that the Mössbauer effect occurred in iron-57 at room temperature, as opposed to liquid-helium temperatures that were required for iridium-191.

The process occurring in nuclear $\gamma$-ray resonance spectroscopy is fairly
simple. Nuclei are the heavy cores of atoms and are generally considered to be composed of protons and neutrons. The number of protons in the nucleus is the atomic number of the atom, and it determines the chemical properties of the atom. For each element (atomic number), a number of different isotopes, corresponding to different numbers of neutrons in the nucleus, may be stable. These are the naturally occurring isotopes of that element, identified by their mass number (sum of protons and neutrons). Unstable radioactive nuclei undergo decay, or transformation, with the emission of various kinds of radiation.

Even stable nuclei, however, can have excited states; configurations in which the nucleus has some discrete, well-defined quantity of added energy over that present in the stable (ground state) configuration. These excited states often decay to the nuclear ground state, with the extra energy being emitted in the form of a γ-ray. Gamma-rays, which are identical in properties to X-rays, are electromagnetic radiation which can interact with electric charge and be scattered by electrons of the atom. They have no electric charge or magnetic moment and cannot be deflected by electric or magnetic fields.

Figure 1. Schematic indication of the events occurring in Mössbauer spectroscopy. The horizontal lines represent the nuclear states. The diagram shows (left) the source nucleus going from the excited state to the ground state, emitting a γ-ray. The γ-ray is subsequently absorbed (right), raising the absorber nucleus to its excited state. The resonance absorption can be detected either by the decreased transmission of the absorber or by the subsequent decay of the absorber nucleus out of the excited state.
When γ-rays pass through matter, they are absorbed or scattered primarily by occasional energetic collisions with electrons.\(^3\)

The basis of the Mössbauer effect is the emission of γ-rays by radioactive nuclei, and the subsequent reabsorption of these γ-rays by other nuclei of the same type. The nuclear absorption energies are slightly affected by the solids in which the nuclei are incorporated. Using the Mössbauer effect, these tiny energy changes can be measured, and used to deduce information about the surroundings of the nucleus.\(^3\) The nuclear decay and excitation process is shown in Figure 1.\(^3\)

The Mössbauer effect requires a γ-ray which has been emitted from a nuclide that has not undergone nuclear recoil. If recoil does occur the γ-ray energy is decreased enough that no resonance will occur with the absorber and no Mössbauer effect is possible. If the emitting nuclide is placed in a solid matrix, then, as first discovered by Mössbauer, some fraction of the decay events will occur without nuclear recoil. This fraction of events is referred to as the recoil-free fraction, or the Debye-Waller factor.\(^4\)

There are some notable advantages of the Mössbauer technique over other spectroscopies:\(^3\)

1. Since nuclear energy levels in the range involved here are so narrow and sharply defined, γ-rays from any nucleus (e.g., \(^{57}\)Fe) can only be reabsorbed by nuclei of the same type, since any other isotope will have absorption energies (corresponding to excited states) in a different energy region. Thus, experiments are absolutely specific to the particular isotope involved, and no cross-interference from other isotopes or elements ever arises.

2. Radioactive source atoms can be incorporated in the material to be studied and thus combine the advantages of radioactive tracer experiments with those of the Mössbauer technique.

3. Since the resonance absorption is a purely nuclear process, its existence is inherently independent of the long-range properties of the host (e.g., symmetry and metallic character), which sometimes interfere with the use of other resonance techniques.

4. The nuclear energy level perturbations observable using the Mössbauer
effect arise only from the first few nearest-neighbor shells of an ion. Thus, short-range interactions (10-15 Å or more) are adequate to provide sharp features in Mössbauer spectra.

5. Sample preparation is usually simple. Powders can be used as well as single crystals, with no special polishing or surface treatment in either case. Thin films can be measured using backscattering geometry (described below). Surface layers 0.1-1.0 μm thick can be easily studied, while thinner films require longer collection times.

6. The dependence of the recoil-free fraction on the properties of the host lattice allows investigation of the Debye temperature and anharmonic binding forces via the temperature dependence of the resonance intensity.

7. Although the technique is in principle limited to studying nuclei in solids, it is often possible to investigate dissolved molecules and complexes by freezing the solutions and making measurements on the resulting solid.

8. The existence of chemically, crystallographically, or magnetically inequivalent sites is generally revealed by the appearance of distinct components, arising from the different sites, in the Mössbauer spectrum. This is especially advantageous for studying the FeN phases, which often contain inequivalent Fe sites.

Experimental techniques

A Mössbauer spectrum is generally produced by varying the source γ-ray energy and measuring the (nuclear) resonance absorption as a function of γ-ray energy, as shown in Figure 2(a). The variation of γ-ray energy is almost always obtained by introducing a relative motion between the source and the specimen, giving a change of energy by the Doppler effect of \( \delta E_\gamma = E_\gamma \nu/c \). At γ-ray energies the nuclear resonance occurring in the nuclei of the absorber will result in increased absorption, and an absorption "line" will occur. This dip (or series of dips) is the Mössbauer spectrum.

There are a limited number of elements that can be studied with Mössbauer spectroscopy, since not all elements exhibit the Mössbauer effect and have the right properties for a practical radiation source. Commonly used isotopes and their ease of use are shown in Table 1. A Mössbauer-effect
source consists of a radioactive material which yields, through radioactive decay, an isomeric nuclear excited state of the element under study. This precursor radioactive nuclide must have a reasonably useful half-life of at least several months. Low cost and abundance are also considerations. The radioactive nuclide must be placed on or in a solid matrix that will provide a temperature-independent, cubic, nonmagnetic environment that yields a

Figure 2. (a) Basic arrangement for measuring a Mössbauer spectrum in transmission geometry. The source is moved to Doppler modulate the γ-ray energy. When the γ-rays have the proper energy to be resonantly absorbed, the increased absorption produces a decrease in the number of γ-rays transmitted through the absorber, and the counting rate decreases.3 (b) Mössbauer spectrometer for backscatter experiments. When the γ-rays incident on the absorber are the proper energy to be resonantly absorbed, absorber nuclei are raised into their excited states. They subsequently decay, emitting radiation that is detected by the counter.3

narrow-line monoenergetic Mössbauer γ-ray. The matrix must withstand radiation damage produced by the active nuclide. For the 57Fe experiment the best source seems to be 57Co that is electroplated onto rhodium and annealed.4
A solid matrix is essential for the precursor source because the Mössbauer effect requires a γ-ray which has been emitted from a nuclide that has not undergone nuclear recoil. In general it is found that the higher the γ-ray energy, the lower will be the fraction of recoil-free emission (or absorption) events, and the more difficult will be the observation of a Mössbauer spectrum. The recoil-free fraction can, however, be increased if the source (or absorber or both) are cooled to liquid-nitrogen or liquid-helium temperature. The opposite extreme of very low-energy γ-rays also presents a problem because of the high nonresonant scattering of these γ-rays by most solids.4

The final major requirement for a Mössbauer source is an appropriate linewidth. It has already been pointed out that a recoil-free nuclear decay yields a γ-ray with a very narrow linewidth or energy distribution. The linewidth of such a γ-ray is controlled by the Heisenberg uncertainty principle such that

\[ \Delta E \Delta t \geq \hbar, \]  

or

\[ \Gamma \tau \geq \hbar. \]  

In these expressions, \( \Delta E \) represents the distribution in energy of the γ-ray, that is, its linewidth \( \Gamma \), and \( \Delta t \) is the mean lifetime, in which \( \tau = t_{1/2}/\ln2 \), of the nuclear excited state which generates the γ-ray. From the above expressions

Table I. Elements that can be studied with Mössbauer spectroscopy.3

<table>
<thead>
<tr>
<th>K</th>
<th>Ca</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Ga</th>
<th>Ge</th>
<th>As</th>
<th>Se</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Re</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Xe</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
<td>Rn</td>
</tr>
</tbody>
</table>

Fr Ra Ac

Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

Easy to study, extensive research
More difficult to study, some research
Very difficult or limited results
it is apparent that a long mean lifetime for the Mössbauer isomeric excited state produces a $\gamma$-ray with a very narrow energy distribution and vice versa. Mössbauer-effect source prerequisites are summarized in Table II. The properties of the iron-57 Mössbauer active element are shown in Table III along with its nuclear decay scheme in Figure 3.

### Table II. Mössbauer-effect source prerequisites

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Parent radioactive source of reasonable half-life.</td>
<td></td>
</tr>
<tr>
<td>2. Efficient nuclear decay scheme producing predominately the Mössbauer isomeric state.</td>
<td></td>
</tr>
<tr>
<td>3. A well-defined, preferably single-line, solid-state matrix for the parent nuclide.</td>
<td></td>
</tr>
<tr>
<td>4. A reasonable mean lifetime for the Mössbauer isomeric excited state.</td>
<td></td>
</tr>
<tr>
<td>5. Low internal conversion of the Mössbauer isomeric excited state.</td>
<td></td>
</tr>
<tr>
<td>6. A high recoil-free fraction for the Mössbauer isomeric excited state.</td>
<td></td>
</tr>
<tr>
<td>7. Mössbauer $\gamma$-ray of reasonable (10-100 keV) energy.</td>
<td></td>
</tr>
<tr>
<td>8. Absorber nuclide of relatively high natural abundance.</td>
<td></td>
</tr>
</tbody>
</table>

### Table III. Nuclear data for the iron-57 Mössbauer-active element

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent natural abundance</td>
<td>2.14</td>
</tr>
<tr>
<td>Parent nuclide</td>
<td>$^{57}\text{Co}$</td>
</tr>
<tr>
<td>Parent nuclide half-life (days)</td>
<td>270</td>
</tr>
<tr>
<td>Mössbauer $\gamma$-ray energy, $E_\gamma$ (keV)</td>
<td>14.413</td>
</tr>
<tr>
<td>Isomeric excited-state half-life (ns)</td>
<td>97.81</td>
</tr>
<tr>
<td>Natural linewidth, $\Gamma$ (mm/s)</td>
<td>0.194</td>
</tr>
<tr>
<td>Nuclear recoil energy, $E_R$ (eV)</td>
<td>$1.956 \times 10^{-3}$</td>
</tr>
<tr>
<td>$E_\gamma / E_R$</td>
<td>$7.4 \times 10^6$</td>
</tr>
<tr>
<td>$E_\gamma / \Gamma$</td>
<td>$1.55 \times 10^{12}$</td>
</tr>
<tr>
<td>Internal conversion coefficient</td>
<td>8.21</td>
</tr>
<tr>
<td>Ground-state nuclear spin</td>
<td>$-1/2$</td>
</tr>
<tr>
<td>Excited-state nuclear spin</td>
<td>$-3/2$</td>
</tr>
</tbody>
</table>

Gamma-rays in transmission experiments are detected with conventional commercial equipment. Most commonly, gas-filled (e.g., argon) proportional counters are used for $^{57}\text{Fe}$, although NaI (sodium iodide) scintillators and solid-state Si detectors are also used. It is possible to study thick samples in situ without the preparation of a thin layer of the material, or to study thin films on bulk substrates, by using a Mössbauer spectrometer with
Backscattering geometry, such as that shown in Figure 2(b). Backscatter spectra are obtained by detecting the decay products of the deexcitation of nuclei in the specimen which have been resonantly excited by the source radiation. These decay products may be X-rays or conversion and Auger electrons, and backscatter detectors are designed to be sensitive to one or other of these radiations. Table IV gives the proportions of X-rays and conversion or Auger electrons in the case of $^{57}$Fe.

One cannot practically construct a window for conversion electrons, so detectors are constructed such that the specimen can be effectively made part of the counter wall. The crucial distinction between electron and X-ray detection is in the gas filling. A filling of argon with 10 vol% methane at atmospheric pressure absorbs most X-rays from $^{57}$Fe in about 20 mm, producing a 6-keV photoelectron. The pulse spectrum therefore shows a peak at 6 keV. A filling of He with 5 vol% methane will have a very small efficiency for X-rays or γ-rays but is easily able to absorb low-energy conversion electrons by ionization. The ionization electrons are collected by the positively charged wire, and gas amplification occurs in the normal way. The pulse produced by the amplifier is thus closely proportional to the energy lost by the electron in the gas. More recently it has become possible to detect γ-rays using both transmission geometry (transmission Mössbauer spectroscopy, TMS) and backscattering geometry (conversion X-rays, CXMS, and conversion electrons, CEMS) simultaneously.

**Interpretation of Mössbauer spectroscopy**

The two principal experimental results determinable from a Mössbauer spectrum are the hyperfine parameters and recoil-free fraction. The relative
Table IV. Summary of major events during the decay of $I = 3/2$ nuclear excited-spin states of $^{57}$Fe.\(^6\)

<table>
<thead>
<tr>
<th>$^{57}$Fe</th>
<th>Energy (keV)</th>
<th>Number (per 100) absorption events</th>
<th>Approximate maximum range in typical solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ photons</td>
<td>14.4</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>$K$ X-rays</td>
<td>6.3</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>$K$ conversion electrons</td>
<td>7.3</td>
<td>81</td>
<td>250 nm</td>
</tr>
<tr>
<td>$L$ conversion electrons</td>
<td>13.6</td>
<td>9</td>
<td>900 nm</td>
</tr>
<tr>
<td>$M$ conversion electrons</td>
<td>14.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$KLL$ Auger electrons</td>
<td>5.4</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>$LMM$ Auger electrons</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and absolute line energies are determined by electronic effects on the nuclear energy levels. These effects are generally lumped together as "hyperfine parameters," and are the isomer shift (chemical), quadrupole hyperfine interaction (electric), and dipole hyperfine interaction (magnetic). Figure 4\(^4\) is a schematic of nuclear energy level shift and splitting. ($I$ is the nuclear spin.) The overall intensity (amplitude) of the resonance spectrum depends on the recoil-free fraction (Debye-Waller factor), normally termed $f$. The recoil-free fraction is dependent on the binding of the Mössbauer-active atom in the lattice and can thus be used for studies of lattice vibrations.\(^3\)

Two other features make up the Mössbauer spectrum. First, the relative intensity of various lines of the spectrum can be analyzed to yield information on the direction between the crystal and hyperfine field axes and the direction of the $\gamma$-ray beam. The second effect, called the second-order Doppler shift, or thermal red shift, is a displacement of the entire spectrum arising from the thermally-excited vibrations of the Mössbauer ion.\(^3\) This effect is only important if the isomer shift temperature dependence is being studied. At temperatures above the Debye temperature $\theta_D$, the shift for $^{57}$Fe is -0.073 mm/s per 100 K ($\theta_D = 420$ K).\(^3\) For temperatures much lower than the Debye temperature of the lattice, the shift becomes vanishingly small and depends on the relationship between the temperature and $\theta_D$. In practice, the temperature dependence of the isomer shift (due to lattice expansion or wave function changes) introduces complications that make it difficult to determine these
corrections accurately. Temperature dependence of the isomer shift will not be studied here, although the temperature dependence of Fe site occupation and magnetization direction will be studied, which do not depend on the thermal red shift.

**Isomer shift**

The isomer shift (also called the chemical shift) arises from the electrostatic interaction of nuclear energy levels with their surrounding electronic environment. The isomer shift provides direct information about the electron density at the nucleus, and this can often be interpreted to give unequivocal information about the valence state of the ion under study. Because the $ns$ wavefunctions have a nonzero probability density at the nucleus, the electrostatic interaction will produce a slight shift in the nuclear

![Figure 4. Schematic diagram of the nuclear energy level shift and splitting as a function of (a) chemical environment, (b) electric field gradient, and (c) internal magnetic hyperfine field. $I$ is the nuclear spin.](image)

Figure 4. Schematic diagram of the nuclear energy level shift and splitting as a function of (a) chemical environment, (b) electric field gradient, and (c) internal magnetic hyperfine field. $I$ is the nuclear spin.
energy level as compared with what it would be for the “bare” nucleus, as illustrated in Figure 4(a). This interaction may be different for the nuclear ground and excited states because these two states do not necessarily have the same size, that is, $R_{ex} \neq R_{gd}$. The Mössbauer isomer shift, usually denoted by the symbol $\delta$, is given by the expression for the nuclear ground and excited states do not necessarily have the same size, that is, $R_{ex} \neq R_{gd}$. The Mössbauer isomer shift, usually denoted by the symbol $\delta$, is given by the expression for the nuclear ground and excited states do not necessarily have the same size, that is, $R_{ex} \neq R_{gd}$. The Mössbauer isomer shift, usually denoted by the symbol $\delta$, is given by the expression for the nuclear ground and excited states do not necessarily have the same size, that is, $R_{ex} \neq R_{gd}$. The Mössbauer isomer shift, usually denoted by the symbol $\delta$, is given by the expression for the nuclear ground and excited states do not necessarily have the same size, that is, $R_{ex} \neq R_{gd}$. The Mössbauer isomer shift, usually denoted by the symbol $\delta$, is given by the expression for the nuclear ground and excited states do not necessarily have the same size, that is, $R_{ex} \neq R_{gd}$. The Mössbauer isomer shift, usually denoted by the symbol $\delta$, is given by the expression for the nuclear ground and excited states do not necessarily have the same size, that is, $R_{ex} \neq R_{gd}$. The Mössbauer isomer shift, usually denoted by the symbol $\delta$, is given by the expression for the nuclear ground and excited states do not necessarily have the same size, that is, $R_{ex} \neq R_{gd}$. The Mössbauer isomer shift, usually denoted by the symbol $\delta$, is given by the expression 

$$\delta = C \left[ |\psi_{ns}(0)|_{std}^2 - |\psi_{ns}(0)|_{abs}^2 \right] \frac{\delta R}{R} \tag{5.3}$$

$$\delta = f\left[ \left( \text{electronic term} \right) \left( \text{nuclear term} \right) \right], \tag{5.4}$$

where $|\psi_{ns}(0)|_{std}^2$ and $|\psi_{ns}(0)|_{abs}^2$ represent the electronic probability density of the $ns$ electrons at the nucleus in the standard reference material and the absorber under study, respectively, and $C$ is a constant. The $\delta R/R$ term represents the normalized radius difference between the nuclear excited state and the nuclear ground state. As is always the case for all the hyperfine parameters, $\delta$ is a function of both the nuclear and electronic properties of the system. For a given nuclide, $|\psi_{ns}(0)|_{std}^2$ and $\delta R/R$ are constant, and the isomer shift may be related to the $|\psi_{ns}(0)|_{abs}^2$ once the sign of $\delta R/R$ is known. For $^{57}$Fe, $\delta R/R$ is less than zero and the isomer shift decreases as $|\psi_{ns}(0)|_{abs}^2$ increases.\(^4\)

There are two basic mechanisms by which the valence of the ion under study influences the electron density $\rho$ (contained above in $\psi_{ns}$) and effects change in the isomer shift energy. The first is a direct change in $\rho$ due to the presence or absence of valence $s$ electrons. Second, in ions of the transition elements, where valence changes occur via a change in $d$ or $f$ electron number, no direct change in $\rho$ at the nucleus is produced, because the charge densities of those electrons are negligible at the nucleus. There is, however, a substantial indirect change in the total $\rho$ arising from the altered shielding of the outermost $s$ electron shell. For example, in iron, if a $3d$ electron is removed (increasing the valence by 1), the $4s$ electrons will be pulled closer to the nucleus, and the charge density due to them will increase. Note that in this case an increase in valence, corresponding to the removal of a non-$s$ electron, results in an *increase* in total electron density at the nucleus.\(^3\)

A wide variety of studies have shown that the isomer shift for $^{57}$Fe is
highly sensitive to coordination number and oxidation state. For instance, octahedral high-spin compounds containing $3d^6$ Fe$^{2+}$ typically have room-temperature isomer shifts in the range 1.1 to 1.3 mm/s relative to natural $\alpha$-iron. In the related $3d^6$ Fe$^{3+}$ compounds the isomer shift would typically be 0.3-0.5 mm/s, a value significantly smaller than that found in Fe$^{2+}$ because of the decreased nuclear screening of the 3s electrons by the fewer 3d electrons in Fe$^{3+}$. In general a decrease in the coordination number decreases the isomer shift such that, for example, in tetrahedral Fe$^{2+}$ complexes the isomer shift is typically 0.7-0.9 mm/s. The isomer shift is also found to be dependent upon the spin-state multiplicity of an Fe$^{2+}$ or Fe$^{3+}$ complex.4

Actual behavior in compounds that are not simple ionic insulators is more complex than that described above and results from a combination of these two effects plus additional phenomena, such as back-donation and formation of conduction bands. Despite the fact that the basic interactions underlying the electronic density changes are well established, it is extremely difficult to make “first principles” calculations that accurately represent real solids. Most analyses of Mössbauer isomer shifts are still based on systematics and semiempirical calculation using comparison with compounds of relatively well-established electronic structure.3

Nuclear quadrupole interaction

In addition to the changes in nuclear energy levels produced by the isomer shift, the levels may be split by the electric quadrupole and magnetic dipole hyperfine interactions. This splitting leads to a number of possible absorption energies, and thus a number of lines in the absorption (or emission) spectrum. For $^{57}$Fe, as in Figure 4, the nuclear excited state ($I = 3/2$) and ground state ($I = 1/2$) are split to produce two absorption lines (a doublet) under the quadrupole interaction, and then (normally) six lines under the magnetic hyperfine interaction (discussed in the next section).3 Typical Mössbauer spectra for $^{57}$Fe are shown in Figure 5.3

The quadrupole coupling arises from the fact that the nucleus is not perfectly spherical, but may be ellipsoidal, either elongated (prolate or cigar-shaped) or flattened (oblate or pancake-shaped). The electrostatic forces
Figure 5. The room-temperature Mössbauer-effect spectra of (a) sodium nitroprusside, Na$_2$Fe(CN)$_5$NO·2H$_2$O; (b) iron foil; and (c) hematite, α-Fe$_2$O$_3$. The approximate 3:3:1:1:3:3 intensity ratio in the iron foil spectrum indicates that it is partially magnetized in the direction normal to the γ-ray.\textsuperscript{4}
between the surrounding ligands, which are assumed to be negatively charged, and the nonspherical part of the nuclear charge tend to make the nuclear axis point toward the ligands. This state is then the lower energy state of the quadrupole split doublet, and the state with the nuclear axis perpendicular to the ligand axis is the higher energy state.\(^3\)

In the quantum mechanical analysis, the nucleus is normally considered to have \(2I + 1\) orientations relative to an external axis, and these are described by values \(I_x\), running in steps of one unit from \(-I\) to \(+I\). Since the two “ends” of the nucleus have the same charge distributions, the coupling energies of the nucleus with the external charges are identical in the “spin-up” \(I_x = +3/2\) and “spin-down” \(I_x = -3/2\) states, and these are termed “degenerate” (two or more distinct states with the same energy). For a nuclear spin of \(I = 1/2\), the states available are \(I_x = +1/2\) and \(I_x = -1/2\); following the same analysis, these states will both have the same energy, and there will be no quadrupole splitting. Thus, the doublet observed in \(^{57}\text{Fe}\) arises from the splitting of the \(I = 3/2\) state into two levels (\(\pm 3/2\) and \(\pm 1/2\)), while the \(I = 1/2\) state remains unsplit, as in Figure 5(b).\(^3\)

For nuclear states with \(I = 3/2\) a mathematical analysis leads to the expression\(^4\)

\[
E_Q = \pm \frac{1}{4} e V_{zz} \left( 1 + \frac{\eta^2}{3} \right)^{1/2},
\]

\[
E_Q = f[(\text{nuclear term})(\text{electronic term})],
\]

for the quadrupole coupling energy \(E_Q\), where the \(\pm\) term corresponds to the fact that the \(I_x = \pm 3/2\) and \(I_x = \pm 1/2\) state energies are perturbed equally, but in opposite directions. Note that the measured quadrupole splitting, sometimes called \(\Delta\) or \(\Delta E_Q\) (the observed energy difference between the lines of a quadrupole-split doublet), is twice the value of \(E_Q\) as defined above. In the above equation, \(Q\) is the nuclear quadrupole moment, \(V_{zz} = -eq\) is the electric field gradient along the z-axis, and \(\eta = (V_{xx} - V_{yy}) / V_{zz}\) is the asymmetry parameter describing the difference in electric field gradient in the x- and y-axes. The discussion of quadrupole coupling here is valid only for \(I = 3/2\); for higher spin states the analysis is more complicated, particularly if the
asymmetry parameter is nonzero. Wertheim offers a more detailed treatment of the Mössbauer effect.

The field gradient $V_{zz}$ arises from nonsymmetric distribution of the electronic charge in the ion under study and its surrounding; the principal contributions follow:

1. In transition ions, especially iron or the rare earths, if the $d$ or $f$ electronic wavefunction has orbital angular momentum ($L \neq 0$), a large contribution to $V_{zz}$ is obtained. Since $d$ and $f$ wavefunctions can be calculated relatively accurately and $V_{zz}$ can be calculated directly from the wavefunctions, it is sometimes possible to decide if a particular electronic configuration could be the source of the observed field gradient.

2. Non-$s$ electrons participating in bonding also provide large contribution to $V_{zz}$. For example, tin organic compounds have extremely large quadrupole couplings arising from $5p$ orbitals. In metallic systems, this term would include contributions from conduction electrons.

3. The direct field gradient contribution from ligand ions is negligible in comparison to the first two terms. However, distortion of the electronic charge distribution in the outer shells of the ion under the influence of the ligand field greatly enhances the gradient actually observed at the nucleus. This phenomenon is called Stemheimer shielding, and increases the field gradient from the ligands by a factor which is about 7 for iron and about 80 for rare-earth ions.

Whether these contributions can be quantitatively separated from one another depends on how much is known about the structure from other techniques and wavefunction calculations. For example, if the contribution to $V_{zz}$ from non-$s$ and conduction electrons was known, a nonzero orbital angular momentum could account for any remaining contribution and might then be quantified.

Magnetic hyperfine interaction

The magnetic hyperfine interaction (nuclear Zeeman effect) arises from the coupling of the nuclear magnetic moment, $\mu_n$, with effective magnetic fields at the nucleus (either internal or applied). This results in splitting of the nuclear
ground and excited states (if the nuclear spin has \( I > 0 \)) into its \( 2I + 1 \) component Zeeman states. The energy of these states is given by\(^4\)

\[
E_m = -g_n \mu_n m_I H
\]

\[
E_m = f[(\text{nuclear term})(\text{electronic term})],
\]

where \( g_n \) is the nuclear g factor or gyromagnetic ratio (related to \( I_z/I \)), \( m_I \) is the component nuclear spin, and \( H \) is the magnetic field of electronic origin experienced by the nucleus. Because the selection rules for these magnetic dipole transitions require that \( \Delta m_I = 0, \pm 1 \), only six transitions are observed, as illustrated in Figure 4(c), where it is assumed that \( V_{zz} \) is zero. Figure 5(b) shows an example of magnetized \(^{57}\)Fe. The overall splitting of the spectrum is proportional to the magnetic field experienced by the nucleus and is found to be proportional to the moment at the iron site. Hence, no magnetic splitting is observed above the Curie point of a ferromagnetic material or above the Néel point of an antiferromagnetic material.\(^4\) Individual atoms can have a moment, however, due to the absence of the internal exchange field, a paramagnetic material would not show magnetic splitting (six peaks), although it may still exhibit quadrupole splitting (two peaks) and isomer shift. The electronic term in the above expression arising from the nuclear surroundings can be considered to be the sum of components arising from a number of sources\(^3\) listed below:

1. Hyperfine (hf) fields as large as 9 MG (megagauss) are produced in rare-earth ions (and actinides) by the orbital momentum of the \( 4f \) (or \( 5f \)) electrons. For most rare-earth ions, this component of the hyperfine field is proportional to the magnetic moment of the ion with a known constant. Thus a measurement of the hyperfine field determines the ion moment.

2. If the ion is in a magnetic metal or is itself magnetic, densities of the spin-up and spin-down electrons at the nucleus will not be the same, and there will be a net spin polarization. The interaction of this electron spin polarization with the nucleus is called the Fermi contact interaction and can be considered as an effective magnetic field at the nucleus. In ions with a partly filled \( 3d \) or \( 4f \) shell, the net electronic spin density is produced by core polarization of the distortion of core-level electronic wavefunctions by
the interaction with the spin of the d or f electrons. This mechanism leads to hf fields of about -220 kG/spin for iron (a total of about -550 kG for high-spin Fe\(^{3+}\), \(S = 5/2\)) and about -100 kG/spin for 4f electrons (about -330 kG for Gd\(^{3+}\), \(S = 7/2\)). The polarization of conduction electrons by magnetic ions produces hf fields as large as 1500 kG.

3. In insulating materials, hf fields as large as a few hundred kilogauss can be produced by polarization of the ion’s electrons by magnetic ligand ions.

4. Externally applied fields are also effective in producing magnetic splitting of the nuclear energy levels.

In the simplest cases, such as rare earths and iron in magnetically ordered systems, the first and second terms, respectively, dominate.\(^3\)

Using relative line intensities of the magnetic hyperfine pattern, one can measure the direction of magnetization of its components. The angular dependence of the transitions in the nuclear Zeeman effect is given in Table V.\(^9\) Here \(\theta\) represents the angle between the direction of the magnetic field at the nucleus and the propagation direction of the \(\gamma\)-radiation. Assuming isotropy of the lattice vibrations, one can derive the relative line intensities \((H_1:H_2:H_3:H_2:H_1)\) of a Zeeman hyperfine pattern in the thin absorber approximation from Table V. The relative intensities of these six transitions are given by \(3:1:1:1:3\), so that \(x\) is given by:

\[
x = \frac{H_2}{H_3} = \frac{4\sin^2 \theta}{(1 + \cos^2 \theta)}.
\]  

(5.9)

Thus, \(x\) is zero if the \(\gamma\)-ray direction is parallel to the magnetization direction, 4 if the \(\gamma\)-ray direction is normal to the magnetization, and 2 if the sample is a random powder or unmagnetized foil.

So far, the discussion of the hf splitting of the nuclear energy levels has not demonstrated how these splittings lead to the hf spectrum. As shown in Figure 4 for the 1/2 \(\rightarrow\) 3/2 transition in \(^{57}\)Fe, in general, both the nuclear ground state and excited state are split by the magnetic hf interaction. In principle, one could expect a hf absorption line from each ground-state \(I_z\) level to each excited-state \(I_z\) level. However, the character of the \(\gamma\)-ray emission, termed the multipolarity, allows transitions only between nuclear states with \(I_z\)
values differing by no more than the order of the multipolarity. Thus, for $^{57}\text{Fe}$, if the absolute difference between the $I_z$ of the ground state and the excited state is greater than 1, the transition is forbidden (for example, $-1/2 \rightarrow 3/2$). In this way the spectrum is restricted to the six lines shown in Figure 4. Occasionally, spectra do have lines at the energies appropriate to forbidden transitions, which is the result of interactions in which $V_{zz}$ is not along the magnetic hf field. The relative intensities of the transitions connecting the nuclear states are determined by the transition multipolarity, the $I$ and $I_z$ of the initial and final states, and the angle between the $\gamma$-ray direction and the z-axis.$^3$

Table V. Angular dependence of the allowed transition in the nuclear Zeeman pattern. $\theta$ is the angle between the direction of the magnetic field at the nucleus and the propagation direction of the $\gamma$-radiation.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\Delta m_s$</th>
<th>Angular dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pm 3/2 \rightarrow \pm 1/2$</td>
<td>$\pm 1$</td>
<td>$3/4 (1 + \cos^2 \theta)$</td>
</tr>
<tr>
<td>$\pm 1/2 \rightarrow \pm 1/2$</td>
<td>$0$</td>
<td>$\sin^2 \theta$</td>
</tr>
<tr>
<td>$-/+1/2 \rightarrow \pm 1/2$</td>
<td>$-/+1$</td>
<td>$1/4 (1 + \cos^2 \theta)$</td>
</tr>
</tbody>
</table>

Some of the basic features determining Mössbauer spectra can be summarized as follows:$^3$

1. Three important interactions determine the energy of the lines; the isomer shift, which moves all lines in the spectrum by the same energy, and the electric quadrupole and magnetic dipole interactions, which split the nuclear energy levels and determine the splittings of the hf lines.

2. Each of those interactions can be factored into a nuclear term, which is always the same for a given transition, and a "solid-state" or chemical term characteristic of the material under study.

3. The nuclear energy levels are determined by the hf interaction parameters; the observed spectrum is then determined by $\gamma$-ray absorption transitions connecting these energy levels, with relative intensities dependent on the transition multipolarities and absorber orientation.
4. Hf parameters significant in determining the Mössbauer spectra are dependent almost entirely on the atom under study and its first two nearest-neighbor shells.

5. The analysis has used implicitly the idea that all atoms in the sample had identical hf parameters. In cases in which inequivalent sites (i.e., classes of nuclei with different hf parameters) are present, each class contributes its own complete spectrum, and the observed spectrum is the sum of those arising from the individual sites. This point has special significance for the iron nitrides and is discussed in the next section.

The Mössbauer technique has been shown to be extremely useful in the study of certain materials, especially iron. It has the advantage that the linewidth is narrow enough that the effect is specific to the isotope being studied, and sample preparation is simple. In addition, the Mössbauer components of electronically inequivalent sites can be identified in the spectra. The next two sections deal specifically with bulk iron and epitaxial iron films containing interstitial nitrogen, and compares the predicted Mössbauer spectra with the experimental results for several structures, including our own results for $\alpha'$ and $\alpha'/\alpha''$ films.

Mössbauer spectroscopy of FeN

The sensitivity of the Mössbauer effect to the atomic scale environment has given rise to its use for the investigation of the structure and symmetry of interstitial atom sites in FeC and FeN martensites. Processes of interstitial C and N atoms, such as agglomeration, clustering, ordering, and precipitation kinetics, have been widely studied during the period since 1966. In the 1970's, improved techniques stimulated the investigation of the martensitic structure.\textsuperscript{10} Substantial differences in the phase composition, microstructure, and transformation temperatures in thin martensite films as compared with bulk martensite were first observed in 1977.\textsuperscript{11} For this reason the Mössbauer backscattering method is especially appropriate for FeN martensite films.

The usual procedure for the evaluation of experimental Mössbauer spectra is to use a least-squares-minimum computer fit to a superposition of Lorentzian lineshapes. For accurate quantitative results, however, the effects
of finite absorber thickness and differences in the $f$ factors (recoil-free fraction) of the various components (phases, nonequivalent sites, etc.) must be considered. Complex Mössbauer patterns are often encountered in FeN alloys, for instance, a sample consisting of martensite and precipitated nitrides may display a spectrum consisting of six or more sextuplet components. Frequently, lines are broadened due to metastable states and lattice relaxation caused by strains, which are inherently present in (quenched) martensite.10

Certain spectra, particularly unannealed martensite, are more complex than $\alpha$-iron. Not only are the readily distinguishable peaks broader, but within each ferromagnetic spectrum the peak width varies as a function of the magnitude of magnetic splitting of the nuclear state, that is, peaks farthest from the center of the spectrum are broader than the inner peaks. Close fits between model and experimental spectra for FeN martensites can be obtained by the following procedure: for each ferromagnetic spectrum, each individual absorption peak is broadened by convoluting it with a Gaussian curve whose width is proportional to the distance of the peak from the center of the spectrum.1

It is helpful at this point to review the bulk phases of FeN. Nitrogen atoms occupy interstitial sites in the lattice of iron. The binary phase diagram is shown again in Figure 6.12 Both FCC FeN austenite and BCT FeN martensite are interstitial solids in which the N atoms are randomly distributed on octahedral sites. FeN austenite having a N concentration higher than 2.4 wt% can be retained at room temperature. Below this concentration a partial transformation to martensite occurs. In bulk BCT FeN martensite, the nitrogen atoms occupy one set of octahedral interstices carried over from the austenite by the Bain transformation. The $c$-axes of the FeN martensite unit cells are aligned in parallel, nitrogen is negatively charged, and the interaction between nitrogen atoms is slightly attractive. In unannealed FeN martensite at room temperature, nitrogen atoms agglomerate and form local regions of ordered $\alpha''$-$Fe_{16}N_2$. Aging at 100 °C leads to decomposition of martensite to $\alpha$-iron and $\alpha''$-$Fe_{16}N_2$. Aging above 160 °C leads to the precipitation of the stable $\gamma'$-$Fe_4N$ precipitates.10

FeN austenite is retained at room temperature upon quenching alloys
Figure 6. Fe-N phase diagram. Upper scale, weight percent N; lower scale, N atoms per 100 Fe atoms.\textsuperscript{12}

which have a sufficient concentration of nitrogen. The austenite lines appear in the central part of the Mössbauer spectrum (shown in Figure 7\textsuperscript{13}) because austenite is paramagnetic. This facilitates its differentiation from other, mostly ferromagnetic, FeN phases. The spectrum of retained FeN austenite has been interpreted as a superposition of two components. The room-temperature spectra for 2.34-wt\%-N austenite consist of a single line and a doublet. These were related to Fe atoms having no nitrogen nearest neighbor (NN) and one nitrogen NN. Comparing the fits of computer-generated spectra and experimental data points, it is seen that the random distribution model [Figure 7(b)] provides a better fit than the one based on the model of separated N atoms [Figure 7(a)].\textsuperscript{10}

\(\gamma\)'-Fe\textsubscript{4}N is a stable precipitate that forms upon aging FeN martensite.
above 160 °C. The corner Fe atom and the face-center Fe atom are two inequivalent iron sites in the ratio 1:3. Correspondingly, the Mössbauer spectrum contained two components related to these two iron sites, although a later high resolution spectrum consisted of three six-line spectral components (see Figure 8) of relative spectral intensities of 1:2:1. Note the difference between FeN austenite (Figure 7) and γ'-Fe₄N (Figure 8), which arises from N stoichiometry and ordering.

Fe₄N martensite is metastable, has the BCT structure, and is ferromagnetically ordered. The low symmetry, lattice distortion, and the effect of interstitial N atoms lead to a number of magnetically inequivalent iron-atom sites. A spectrum for unannealed 2.83-wt% N martensite is shown in Figure 9(a). The computer fit of Figure 9(b) is a superposition of four hyperfine field components related to Fe atoms having first, second, and third nitrogen neighbors and one having further than third-neighbor nitrogen (see Table VI). The relative spectral intensities, calculated with the assumption of a random distribution of nitrogen on one of the three interstitial sublattices, were 0.221, 0.306, 0.298, and 0.175 for the iron-atom groups with first, second,
Figure 8. Mössbauer spectrum of $\gamma$-Fe$_4$N. The solid line is a computer fit of a superposition of three components related to inequivalent iron sites. The sites are Fe$^c$ (Fel) corner atoms and Fe$^f$ (Fell) face-center atoms, which subdivide into two groups of different quadrupole interaction.\textsuperscript{14}

third, and further nitrogen neighbor, respectively.\textsuperscript{10}

In our own work,\textsuperscript{16,17} we have generated Mössbauer spectra which support the assertion that there are three inequivalent iron atom sites in nitrogen martensite. For $\alpha'$ and $\alpha'/\alpha''$ films deposited on Si(001), CEMS were measured at 15-16 K and at 300 K with a gas-filled proportional counter which is described elsewhere.\textsuperscript{18} The Mössbauer source was $^{57}$Co of 1.85 GBq in a Rh matrix. The counter was filled with pure helium for the measurements at 15 and 16 K, and 98% He and 2% CH$_4$ for room-temperature experiments. Measurements were performed by T. Kobayashi and A. Nakanishi at Shiga University of Medical Science in Japan.

CEMS measurements were obtained for the $\alpha'$ sample at 15 K and 300 K [Figures 10(a) and 10(b), respectively]. Using a non-linear least squares method, good fit to the data was obtained by assuming three Lorentzian sextets (Table VII). In the original fitting procedure a Lorentzian doublet was
also included; however, this turned out to be unnecessary if a distribution in hyperfine fields is included in the analysis. The line width of the first sextet is narrow and typical of a nondistributed magnetic component. The isomer shift (IS), quadrupole splitting (QS), and the ratio $H_2/H_3$ of the second and third sextets are similar to each other, but their widths are much larger than the first one. Hence, an alternative way is to analyze the spectrum as composed of a

\[
\begin{align*}
1.00 & - 0.98 - \text{c}\ 
\text{c}\ 
\text{c}\ 
\text{c}\ 
0.96 & - 0.94 - \text{c}\ 
\text{c}\ 
\text{c}\ 
\text{c}\ 
0.92 \\
\end{align*}
\]

Figure 9. (a) Mössbauer spectrum of 2.83-wt%-N martensite. (b) Comparison of a spectrum for unannealed martensite with a computer-generated one based on a model of randomly distributed nitrogen atoms (line). Positions labelled 1nn, 2nn, and 3nn correspond to peaks from the first-, second-, and third-nearest-neighbor iron atoms of a nitrogen atom. Positions labelled Fe correspond to peaks from iron atoms that are further than third neighbor.\textsuperscript{13}
Table VI. Mössbauer parameters associated with iron-atom types in FeN alloys.\textsuperscript{10}

<table>
<thead>
<tr>
<th>Iron atom type</th>
<th>T (°C)</th>
<th>Isomer shift\textsuperscript{a} (mm/s)</th>
<th>Quadrupole splitting\textsuperscript{a} (mm/s)</th>
<th>Hyperfine magnetic field (kOe)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-2.34-wt%-N austenite:\textsuperscript{13}</td>
<td>20</td>
<td>-0.13</td>
<td>0.29</td>
<td>—</td>
<td>0.45</td>
</tr>
<tr>
<td>N neighbor</td>
<td>-0.13</td>
<td>0.29</td>
<td>—</td>
<td>—</td>
<td>0.55</td>
</tr>
<tr>
<td>No N neighbor</td>
<td>-0.39</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.55</td>
</tr>
<tr>
<td>Fe-2.83-wt%-N martensite:\textsuperscript{13}</td>
<td>-193</td>
<td>-0.11</td>
<td>-0.32</td>
<td>316</td>
<td>0.221</td>
</tr>
<tr>
<td>1NN of N</td>
<td>-0.11</td>
<td>-0.32</td>
<td>316</td>
<td>0.221</td>
<td></td>
</tr>
<tr>
<td>2NN</td>
<td>-0.12</td>
<td>0.12</td>
<td>346</td>
<td>0.306</td>
<td></td>
</tr>
<tr>
<td>3NN</td>
<td>-0.06</td>
<td>0.00</td>
<td>370</td>
<td>0.298</td>
<td></td>
</tr>
<tr>
<td>No N neighbor</td>
<td>-0.06</td>
<td>0.00</td>
<td>370</td>
<td>0.298</td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{16}N\textsubscript{2}:\textsuperscript{13}</td>
<td>20</td>
<td>-0.15</td>
<td>-0.17</td>
<td>288</td>
<td>0.25</td>
</tr>
<tr>
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<td>-0.17</td>
<td>288</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>2NN</td>
<td>-0.06</td>
<td>0.09</td>
<td>314</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>3NN</td>
<td>-0.09</td>
<td>-0.09</td>
<td>399</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>γ-Fe\textsubscript{4}N:\textsuperscript{14}</td>
<td>RT</td>
<td>0.24</td>
<td>0.00</td>
<td>340.6</td>
<td>1</td>
</tr>
<tr>
<td>Fe\textsuperscript{c}</td>
<td>0.24</td>
<td>0.00</td>
<td>340.6</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Fe\textsuperscript{l}</td>
<td>0.52</td>
<td>-0.22</td>
<td>215.5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Fe\textsuperscript{ll}</td>
<td>-0.15</td>
<td>+0.43</td>
<td>219.2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>ε-Fe\textsubscript{3.2}N:\textsuperscript{15}</td>
<td>22</td>
<td>0.33</td>
<td>—</td>
<td>238</td>
<td>7.33</td>
</tr>
<tr>
<td>Fe\textsuperscript{c-1}</td>
<td>0.33</td>
<td>—</td>
<td>238</td>
<td>7.33</td>
<td></td>
</tr>
<tr>
<td>Fe\textsuperscript{0.5}</td>
<td>0.24</td>
<td>298</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Isomer shift relative to pure α-Fe.

sextet with nondistributed magnetic hyperfine field (sextet one) and another sextet with a magnetic field distribution. The line width was assumed to be the natural value of α-Fe and both the H\textsubscript{2}/H\textsubscript{3} ratio and peak positions were fixed at the observed values for the first sextet. The probability versus magnetic field of the distributed component for the unannealed sample (α') at 300 K is shown in Figure 11(a). The distribution was fitted with Gaussians and two discrete peaks were resolved. Thus, three distinct sites for Fe were confirmed. Similar
Figure 10. CEMS spectra for $\alpha'$-Fe$_8$N film at (a) 15 K and (b) 300 K.
results were obtained for $\alpha'$ at low temperature. Lorentzian fitting of the three components gives site occupations as indicated in Table VII (Intensity column). It is interesting to note that the relative site occupation changes with temperature.

Table VII. Mössbauer spectral parameters (isomer shift (IS) and quadrupole splitting (QS) against pure $\alpha$-Fe, width of the Lorentzian line, and hyperfine magnetic field) for an $\alpha'$ film. Intensity (Fe atom %) gives the relative occupation of each distinct site.

<table>
<thead>
<tr>
<th>Fe Site</th>
<th>$T$ (K)</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>Width (mm/s)</th>
<th>Field (kOe)</th>
<th>I (Fe%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fel</td>
<td></td>
<td>0.18</td>
<td>-0.10</td>
<td>0.38</td>
<td>302.8</td>
<td>15.2</td>
</tr>
<tr>
<td>Fell</td>
<td>15</td>
<td>0.29</td>
<td>0.02</td>
<td>0.63</td>
<td>331.1</td>
<td>48.7</td>
</tr>
<tr>
<td>Fellll</td>
<td></td>
<td>0.22</td>
<td>-0.05</td>
<td>0.86</td>
<td>384.0</td>
<td>31.8</td>
</tr>
<tr>
<td>Fel</td>
<td></td>
<td>0.24</td>
<td>1.82</td>
<td>0.24</td>
<td></td>
<td>4.3</td>
</tr>
<tr>
<td>Fell</td>
<td>300</td>
<td>-0.04</td>
<td>-0.08</td>
<td>0.50</td>
<td>294.6</td>
<td>16.5</td>
</tr>
<tr>
<td>Fell</td>
<td></td>
<td>0.04</td>
<td>0.01</td>
<td>0.69</td>
<td>323.4</td>
<td>40.3</td>
</tr>
<tr>
<td>Fellll</td>
<td></td>
<td>-0.03</td>
<td>-0.03</td>
<td>1.02</td>
<td>369.3</td>
<td>39.0</td>
</tr>
<tr>
<td>Fel</td>
<td></td>
<td>-0.00</td>
<td>1.76</td>
<td>0.23</td>
<td></td>
<td>4.3</td>
</tr>
</tbody>
</table>

Figure 11. Probability curves for the second and third hyperfine fields for (a) $\alpha'$-Fe$_8$N film and (b) $\alpha'$-Fe$_8$N/$\alpha''$-Fe$_{16}$N$_2$ film at 300 K.

Mössbauer spectroscopy of Fe$_{16}$N$_2$ films grown on MgO(001) and Si(001)

Aging of bulk FeN martensite below 200 °C results in the formation of $\alpha$-iron and $\alpha''$-Fe$_{16}$N$_2$, which is an ordered arrangement of N atoms in the BCT matrix of martensite. A Mössbauer spectrum taken at -193 °C of 2.83 wt% N
martensite, aged 24 hr at 100 °C, is shown in Figure 12. The bars on the top of the spectrum show the positions of the outer lines from three groups of iron atoms having first-, second- and third-neighbor N atoms in the \( \alpha''\)-Fe\(_{16}\)N\(_2\) structure. The relative spectral intensities were taken as 1:2:1, corresponding to the relative number of atoms in the iron-atom groups in this structure. A plot of differences between the spectrum for an alloy aged at room temperature and a spectrum for unannealed martensite shows that the difference peaks correspond to the hyperfine fields of \( \alpha''\)-Fe\(_{16}\)N\(_2\), as they were determined for martensite aged at 100 °C. It was concluded that the changes observed in the Mössbauer spectra of FeN martensite due to room-temperature aging are a result of agglomeration and ordering of nitrogen into the \( \alpha''\)-Fe\(_{16}\)N\(_2\) structure.

![Mössbauer spectrum](image)

Figure 12. Mössbauer spectrum measured at -193 °C of 2.83-wt%-N martensite aged 24 hr at 100 °C. The bar diagrams at the top of the spectrum indicate the \( \alpha''\)-Fe\(_{16}\)N\(_2\) components.

In more recent years, Fe\(_{16}\)N\(_2\) thin films deposited on single-crystal substrates have been of technological interest, and Mössbauer spectroscopy
has been an effective tool for their study. Mössbauer data for α"-Fe₁₆N₂ are collected in Table VIII,¹⁹ along with similar data for α-Fe, α'-N-martensite and γ'-Fe₄N. The Mössbauer spectrum of α"-Fe₁₆N₂ differs from that of α'-N-martensite. The three sextets seen for α"-Fe₁₆N₂ can be assigned with certainty to the three sites Fel [4(d), 1NN], Fell [8(h), 2NN], and Felll [4(e), 3NN] only if the expected 4:8:4 relative intensities are obtained and if the signs of all the electric field gradients are known. The Mössbauer hyperfine fields $H_{hf}$ = 296, 316, and 399 kOe are assigned to Fel, Fell, and Felll, respectively.

Table VIII. Mössbauer spectral parameters [hyperfine magnetic field ($H_{hf}$) quadrupole splittings ($\Delta E_Q$) and isomer shifts (IS) against pure α-Fe at room temperature] for α"-Fe₁₆N₂, and relative population (Fe atom %). Data for other phases (α-Fe, α'-N-martensite, γ'-Fe₄N) are given for comparison.¹⁹

<table>
<thead>
<tr>
<th>$H_{hf}$ kOe</th>
<th>$\Delta E_Q$ mm/s</th>
<th>IS mm/s</th>
<th>Fe %</th>
<th>$H_{hf}$ kOe</th>
<th>$\Delta E_Q$ mm/s</th>
<th>IS mm/s</th>
<th>Fe %</th>
<th>$H_{hf}$ kOe</th>
<th>$\Delta E_Q$ mm/s</th>
<th>IS mm/s</th>
<th>Fe %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α&quot;-Fe₁₆N₂ (three sextets)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fel (4e) 4mm(1NN)</td>
<td>302</td>
<td>0.14</td>
<td>-0.15</td>
<td>325</td>
<td>0.3</td>
<td>0.1</td>
<td>418</td>
<td>0.27</td>
<td>-0.08</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>297.9</td>
<td>315.9</td>
<td>372.8</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>289.8</td>
<td>0.04</td>
<td>-0.10</td>
<td>19.4</td>
<td>321.7</td>
<td>0.16</td>
<td>0.06</td>
<td>47.2</td>
<td>400.2</td>
<td>0.15</td>
<td>-0.06</td>
<td>13.9</td>
<td>25</td>
</tr>
<tr>
<td>296</td>
<td>-0.07</td>
<td>-0.09</td>
<td>18.7</td>
<td>316</td>
<td>0.25</td>
<td>0.06</td>
<td>34.9</td>
<td>399</td>
<td>0.12</td>
<td>-0.07</td>
<td>17.9</td>
<td>20</td>
</tr>
<tr>
<td>292</td>
<td>-0.17</td>
<td>0.01</td>
<td>9.7</td>
<td>317</td>
<td>0.15</td>
<td>0.10</td>
<td>15.8</td>
<td>397</td>
<td>-0.04</td>
<td>0.07</td>
<td>9.7</td>
<td>26</td>
</tr>
<tr>
<td>307</td>
<td>0.05</td>
<td>-0.49</td>
<td>20.6</td>
<td>316</td>
<td>0.32</td>
<td>0.04</td>
<td>37.7</td>
<td>391</td>
<td>0.26</td>
<td>-0.05</td>
<td>12.5</td>
<td>28</td>
</tr>
<tr>
<td>α'-N-martensite (three sextets)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1NN</td>
<td>314</td>
<td>-0.01</td>
<td>-0.12</td>
<td>356</td>
<td>0.01</td>
<td>0.01</td>
<td>348</td>
<td>0.08</td>
<td>0.02</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2NN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3NN and 4NN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Fe₄N (three sextets)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fel (1a)</td>
<td>345</td>
<td>0.30</td>
<td></td>
<td>340.6</td>
<td>0.00</td>
<td>0.24</td>
<td>215.5</td>
<td>-0.22</td>
<td>0.52</td>
<td>219.2</td>
<td>0.43</td>
<td>-0.15</td>
</tr>
<tr>
<td>Fell or Felll (3c-A)</td>
<td>366</td>
<td>235</td>
<td>235</td>
<td>235</td>
<td>235</td>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

131
From the Mössbauer hyperfine fields, the magnetic moments have been estimated at the sites Fel, Fell, and Felll as either 1.3 ± 0.2, 2.5 and 3.8 μB, or as 2.33, 2.45 and 3.05 μB, respectively. For the epitaxial thin films of α"-Fe₁₆N₂ on GaAs, one single Mössbauer line was reported, stirring debate over the possibility of low resolution or a different species altogether. For α'/α" films deposited on lattice-mismatched Ag/Fe/MgO(001), room-temperature conversion electron Mössbauer spectra (CEMS) parameters (Table IX) indicate three sites with an occupation ratio 1:2:1 for Fel:Fell:Felll. A fourth site corresponding to α-Fe is not shown since it was assumed to arise from the Fe seed layer underneath the Ag layer.

CEMS measurements were also obtained for our α'/α" sample on Si(001) at 16 K and 300 K [Figures 13(a) and 13(b), respectively]. The Lorentzian probability analysis carried out for the annealed sample (α'/α") and shown in Figure 11(b) has a much sharper distribution than did the probability analysis for the unannealed sample (α') and also confirms the presence of three iron components. Similar results were obtained for α'/α" at low temperature. Lorentzian fitting of the three components gives site occupations as indicated in Table X (Intensity column). It is interesting to note that the relative site occupation of the sample changes with temperature. Only the α'/α" sample at 300 K has peak intensities with a ratio of 1:2:1 (Fel:Fell:Felll) for the three iron sites, which correspond to the expected occupancy in the Fe₁₆N₂ structure. This result is consistent with other researchers. In addition there are changes in the occupation at 16 K, indicating three-site occupancy of about 3:13:4. This ratio may be due to a change in spin orientation of Fel (first NN) upon cooling, or may indicate a change in N ordering, or both. Although Sugita and coworkers claim only one site for giant-moment, single-
Figure 13. CEMS spectra for an $\alpha'$-Fe$_8$N/$\alpha''$-Fe$_{16}$N$_2$ film at (a) 16 K and (b) 300 K.
phase Fe\(_{16}\)N\(_2\) films, their mixed \(\alpha'/\alpha''\) films also have three Fe sites with a 1:2:1 occupancy. It appears the Mössbauer spectra for \(\alpha''\) samples with giant moment (2.9 \(\mu_B\)) are different from spectra for those samples exhibiting the predicted values for the moment (2.4-2.5 \(\mu_B\)).

Table X. Mössbauer spectral parameters [isomer shift (IS) and quadrupole splitting (QS) against pure \(\alpha\)-Fe, width of the Lorentzian line, and hyperfine magnetic field] for the \(\alpha'/\alpha''\) film. Intensity (Fe atom %) gives the relative occupation of each distinct site.

<table>
<thead>
<tr>
<th>Fe Site</th>
<th>T (K)</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>Width (mm/s)</th>
<th>Field (kOe)</th>
<th>I (Fe%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fel</td>
<td>0.11</td>
<td>-0.15</td>
<td>0.48</td>
<td>296.9</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>Fell</td>
<td>15</td>
<td>0.28</td>
<td>0.09</td>
<td>0.54</td>
<td>328.4</td>
<td>63.3</td>
</tr>
<tr>
<td>Felll</td>
<td>0.26</td>
<td>-0.12</td>
<td>0.55</td>
<td>415.5</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>Fell</td>
<td>300</td>
<td>-0.08</td>
<td>-0.07</td>
<td>0.36</td>
<td>286.0</td>
<td>24.0</td>
</tr>
<tr>
<td>Felll</td>
<td>0.16</td>
<td>0.08</td>
<td>0.45</td>
<td>314.0</td>
<td>50.8</td>
<td></td>
</tr>
<tr>
<td>Felll</td>
<td>0.15</td>
<td>-0.11</td>
<td>0.52</td>
<td>392.0</td>
<td>25.2</td>
<td></td>
</tr>
</tbody>
</table>

Considering both samples at 300 K, the angle of magnetization with respect to the surface normal, \(\theta\), varies from 33.5° to 41.4°. The magnetization direction, therefore, is neither in-plane nor out-of-plane. Since the magnetization direction depends in part on the crystal anisotropy, this observation supports the change in crystal anisotropy with annealing that was proposed in Chapter IV, which in turn causes changes in the coercivity and saturation field observed by VSM. The magnetization angle for the first component (Fel) in the annealed sample changes from 34.4° at 300 K to 18.0° at 16 K, that is, the spin orientation turns toward the surface normal at low temperature. The angle of the other components in both samples stays the same within statistical fluctuation. Without knowledge of the FeN phase stability at low temperatures, it is difficult to describe a physical mechanism for the changes in occupancy and magnetization angle observed in this work.

While we have confirmed the expected structure for \(\alpha''\), it is not a straightforward matter to infer the site moments from the hyperfine fields. There are several different contributions to \(H_{hf}\) which have different
dependencies on $\mu_{Fe}^{21}$

\[ H_{hf} = H_{cp} + H_{val} + H_{orb} + H_{dip}. \]  \hspace{1cm} (5.10)

$H_{cp}$ is due to spin polarization of the 1s, 2s, and 3s core orbitals and is strictly proportional to the 3d spin moment. $H_{val}$ which depends on the chemical bonding varies most with the compound or the sites considered. $H_{orb}$ (orbital contribution) and $H_{dip}$ (classical dipolar field at the nucleus) are usually small and are neglected, although we discuss the possibility of a non-negligible orbital contribution for $\alpha''$ in Chapter VI. Electronic structure calculations give the first two terms in equation 5.10, known as the Fermi contact interaction, which depend on the unpaired spin density at the nucleus. By writing $H_{hf} = A\mu_{Fe}$, the factor $A$ can be evaluated empirically for the three sites in $\alpha''$-Fe$_{16}$N$_2$. $A$ can be deduced for the $\alpha''$-Fe (1a) and Fell (3c) sites in $\gamma'$-Fe$_4$N, from the site moments (measured by neutron diffraction) and the hyperfine fields. The values for $\alpha''$ are then deduced by interpolation between $\alpha$-Fe and $\gamma'$-Fe$_4$N.$^{21}$ Mössbauer spectroscopy was not performed for $\alpha$ and $\gamma$ films in the present study; therefore, no site moments were determined for $\alpha'/\alpha''$ films. Also, contributions to the field gradient term $V_{zz}$ (in the quadrupole splitting) from non-s conduction electrons and the orbital angular momentum could not be separated. Thus, an independent measure of the orbital contribution would be useful, and is described in Chapter VI.

Table XI. Mössbauer spectral parameters for determining magnetization direction in the $\alpha'$ and $\alpha'/\alpha''$ films. $H_2/H_3$ is the intensity ratio between the second and third lines of a sextet and gives the direction of the hyperfine field, $\theta$, with respect to the surface normal.

<table>
<thead>
<tr>
<th>Fe Site</th>
<th>T (K)</th>
<th>$\alpha'$ Film</th>
<th>$\alpha'/\alpha''$ Film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2/H_3$</td>
<td>$\theta'$</td>
<td>$H_2/H_3$</td>
</tr>
<tr>
<td>Fell</td>
<td>0.91</td>
<td>37.5</td>
<td>0.20</td>
</tr>
<tr>
<td>Fell*</td>
<td>0.84</td>
<td>36.1</td>
<td>0.80</td>
</tr>
<tr>
<td>Fell**</td>
<td>1.17</td>
<td>42.3</td>
<td>0.64</td>
</tr>
<tr>
<td>Fell</td>
<td>0.91</td>
<td>37.5</td>
<td>0.76</td>
</tr>
<tr>
<td>Fell*</td>
<td>0.93</td>
<td>37.9</td>
<td>0.72</td>
</tr>
<tr>
<td>Fell**</td>
<td>1.12</td>
<td>41.4</td>
<td>0.83</td>
</tr>
</tbody>
</table>

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Having characterized our $\alpha'/\alpha''$ films using CEMS, we have demonstrated that the $\alpha'/\alpha''$ films exhibit the expected structure for $\alpha''$. This is an important result since magnetic characterization of the phases depends on a reliable structural analysis. The magnetization direction and the temperature dependence of the Fe atom occupancies are interesting observations that may be explained in the future as a better model for the $\alpha''$ electronic structure is developed.

References
CHAPTER VI:
SPIN AND ORBITAL MAGNETIC MOMENTS IN THE IRON NITRIDES —
X-RAY MAGNETIC CIRCULAR DICHOISM

Introduction

Certainly the most important single issue in the study of Fe$_{16}$N$_2$ is whether or not it possesses a giant magnetic moment. Besides greatly improving inductive recording heads for writing media with densities up to 10 Gbit/in$^2$, a giant moment ($M_s > 2000$ emu/cc) would completely unseat the current thinking on the band theory of metals and the Slater-Pauling curve in terms of what is the maximum achievable moment in a ferromagnetic material. Attempts to modify current calculations for Fe$_{16}$N$_2$ are underway, with mixed results. One possible source of the discrepancy between experiment and theory is whether the orbital contribution to the moment is negligible. In most itinerant transition-metal systems, the orbital angular momentum is quenched ($L = 0$) so that its contribution to the moment may be neglected in calculations.

A relatively new experimental technique which measures the magnitude of the orbital magnetic moment, absolutely or relative to the spin magnetic moment, applied to Fe$_{16}$N$_2$ could elucidate this issue for the first time. X-ray magnetic circular dichroism (XMCD) has the ability to separate the spin and orbital contributions to the moment in a way that is element specific and uses X-ray absorption spectroscopy (XAS) with the incident light modified to possess circular polarization. When an external magnetic field is applied to the sample there are measurable differences in the XAS spectra depending on the relative orientations of the polarization and magnetic field vectors. This difference leads to a measure of the spin and orbital contributions to the moment and could shed some light on the significance of orbital magnetic moment in Fe$_{16}$N$_2$ and on the possibility of a giant magnetic moment.

Investigations of magnetic properties of matter using electromagnetic radiation began with Michael Faraday’s discovery in 1846 that the polarization of visible light may be changed upon transmission through a magnetic material. Today laser methods are used to observe changes in polarization of
transmitted light (Faraday effect) or reflected light (magneto-optical Kerr effect). Since typical laser light has energies in the 1-4 eV range, the Faraday and Kerr effects involve *interband* electronic transitions from filled to unfilled electronic valence states.

The change in polarization of the light observed in the Faraday and Kerr effects can be explained in terms of the electronic transition between two magnetic band states defined by quantum numbers $n$, $l$, $m_l$, and $m_s$. The incident laser light is linearly polarized; it is a coherent sum of left and right circularly polarized light. There is a difference in the dipole selection rule for right ($\Delta m_l = m_l - m'_l = +1$) and left ($\Delta m_l = -1$) circularly polarized light, thus, the components may be absorbed differently depending on the nature of the two band states within the material. This imbalance is reflected in the emitted radiation, which will be elliptically polarized with the major polarization axis rotated relative to that of the incident light.3

A similar change in polarization can also be measured for excitations between a *core* state and a *valence* state, the effect of which was calculated by Erskine and Stem4 in 1975 for the $M_{2,3}$ edges in Ni metal ($M_2$ and $M_3$ edges corresponding, respectively, to transitions from the spin-orbit split $3p_{3/2}$ and $3p_{1/2}$ core levels to the $3d$-valence band in Ni). This constitutes the birth of X-ray magnetic circular dichroism spectroscopy, although the first experimental demonstration of the effect did not occur until 1987, when Schütz and coworkers measured the XMCD signal at the K edge of Fe metal.5 At the same time a similar X-ray absorption effect was reported by Thole and coworkers6 in which rare-earth materials revealed a strong dependence of the near-edge X-ray absorption fine structure (NEXAFS) on the orientation of the magnetization direction relative to the electric field vector $E$ for *linearly* polarized X-rays. This became known as X-ray magnetic linear dichroism (XMLD) spectroscopy. For XMLD the spectrum is different for $E \parallel M$ and for $E \perp M$, regardless of the absolute orientation of both vectors with respect to a fixed coordinate frame, for example, the sample surface. With circularly polarized light, the spectrum depends on the relative orientation of the light helicity $\sigma$ and the sample magnetization $M$ in a geometry where these two vectors are nearly collinear (parallel or antiparallel), while the absolute
orientation of \( \sigma \) or \( \mathbf{M} \) has negligible influence.\(^7\)

The XMCD and XMLD as well as the Kerr and Faraday effects originate from electric dipole transitions caused by the electric field of the ferromagnetic radiation. The electric field \( \mathbf{E} \) does not act on the electron spin directly but only indirectly through the orbital momentum and the spin-orbit coupling. This is in contrast to resonant magnetic X-ray scattering, which arises from the direct interaction of the magnetic field vector \( \mathbf{B} \) with both the spin and the orbital moments. Magnetic X-ray scattering is much weaker than conventional charge scattering, and therefore requires more photon flux. On the other hand, magnetic X-ray dichroism is a relatively strong effect, similar in magnitude to conventional X-ray absorption and therefore requiring the same photon flux.\(^3\)

XMCD and XMLD spectroscopies are more than just extensions of their laser-based counterparts. Conventional techniques for studying magnetic materials (including Faraday and Kerr) measure the total magnetic response, which may contain contributions from various magnetic elements in the more complex systems. Using tunable X-rays, however, one can select specific elements in the sample through one of their characteristic absorption edges. One can study the magnetic properties of a complex material element by element using XMCD and XMLD, since these effects are associated with the fine structure near such edges. Furthermore, different edges of the same element provide information on the magnetic contributions of different kinds of valence electrons through the dipole selection rules (discussed below). Another significant advantage of the magnetic X-ray dichroism technique is that it can be used for element-specific magnetic imaging.\(^8\) In addition, element-specific hysteresis curves can be obtained by monitoring the intensity of an XMCD edge feature as a function of applied magnetic field.

XMCD is a desirable technique for the investigation of ferromagnets, ferrimagnets and paramagnets; however, it fails for certain antiferromagnets (specifically, systems in which for a given atom in a specific sublattice, the magnetic coupling is antiferromagnetic) since it depends on the existence of a net magnetic moment along a preferred magnetic direction (magnetic handedness) for each element. In this case, the complementary XMLD technique may be used because it only requires the existence of a magnetic
anisotropy axis and the effect depends on the angle between the X-ray E vector and the anisotropy axis. While XMCD is the difference in absorption cross-section for right- and left-circular polarization (proportional to the expectation value of the local magnetic moment \( \langle M \rangle \)), XMLD is the difference in cross-section for light polarized perpendicular or parallel to the magnetic moment, and it depends on \( \langle M^2 \rangle \) of the ions. Antiferromagnetic hematite (\( \alpha-Fe_2O_3 \)) has been the model system for XMLD and supports the assertion that XMLD can be strong in any system with collinear magnetic ordering, whether it be antiferromagnetic or ferromagnetic.

The element specificity of XMCD has been employed by several workers, such as Chen, et al., to perform magnetometry of magnetic heterostructures. Hysteresis curves for samples containing more than one magnetic element can be obtained by observing the intensity of the L\(_3\) XMCD feature for each element as a function of applied magnetic field. A complicated hysteresis loop obtained using conventional methods can be unambiguously decomposed to reveal subtle features not otherwise apparent. XMCD hysteresis curves are not necessary for FeN films since only one magnetic element is present.

**X-ray absorption spectroscopy**

In the X-ray absorption process a core electron is excited to an unoccupied level. For 3\(d\) transition metals such as Fe, strong absorption edges are observed for transitions, following dipole selection rules \( \Delta m_\ell = \pm 1 \) and \( \Delta m_\sigma = 0 \), from spin-orbit split 2\(p_{1/2}\) (L\(_2\) edge) and 2\(p_{3/2}\) (L\(_3\) edge) core levels to unoccupied 3\(d\) valence levels (as shown in Figure 1\(^{11}\)). For example, excitation near the L\(_3\) and L\(_2\) edges will yield information on the empty \( d \)-like density-of-states because of the \( p \rightarrow d \) (\( \Delta m_\ell = \pm 1 \)) dipole selection rule. Similarly, K-edge studies (for elements such as N) are sensitive to the \( p \)-like component of the empty density-of-states, since transitions allowed by the dipole selection rule are from 1\(s\) core levels to \( p \)-like empty levels.

Measurement of an X-ray-absorption spectrum (XAS) requires a monochromatized X-ray source in the soft X-ray region. A reflection grating is used in conjunction with relay mirror optics so that a small spot of monochro-
matted photons of selectable energy and variable bandpass is delivered to the sample. A typical monochromator will extend from 200 to 1500 eV of photon energy, which covers all the absorption edges of interest in magnetic materials. Typical XAS spectra are shown in Figure 2 for Fe, Co, Ni, and Cu. Note that the $L_{2,3}$ white lines for Cu are absent due to its filled $3d$ band.

The absorption edges can be measured using a variety of techniques including transmission, partial electron yield, total electron yield, partial fluorescence yield, sample current, and reflection. Each method has advantages and disadvantages, depending on desired probing depth and control of experimental artifacts. The most straightforward, but most difficult, method for measuring XAS is transmission. The probing depth is the entire sample thickness (~100 Å for a free-standing film), and therefore gives information representative of the bulk material. A second method (for XMCD) uses the reflected incident flux of circularly-polarized radiation to extract magnetic information. A variable incidence angle is used, which offers variable probing depth and, hence, depth-dependent magnetic information. Data interpretation is more difficult than for transmission.
Figure 2. X-ray absorption spectra recorded by total-electron-yield detection near the L$_3$ and L$_2$ edges for Fe, Co, Ni, and Cu atoms in a NiFe/Co/Cu multilayer, showing the existence of white lines for Fe, Co, and Ni and their absence for Cu, due to its filled 3$d$ band.\textsuperscript{3} since the probing depth is different for each element.

Alternatively, instead of directly measuring the amount of X-ray absorption, one can indirectly measure the absorption cross-section by measuring the core-hole creation rate via the core-hole decay products.\textsuperscript{12} This can be done by measuring the fluorescence yield of the sample associated with the radiative decay of the core-hole, or by measuring the electron yield (total yield or partial yield) of the sample from the nonradiative decay. Fluorescence requires an X-ray detector and has a probing depth of around 100 Å. Due to fluorescence-photon reabsorption in thicker samples (the saturation effect), this method is more often used in dilute samples.\textsuperscript{13} Also, resolution is coarse if elemental peaks overlap in complex samples. The simplest method is to collect the total electron yield (TEY) emitted from the sample as the photon energy is swept through the core-level binding energies. For TEY one can use a biased channeltron, with a probing depth of 100 Å, or simply measure the sample current, which is sensitive to the entire irradiated...
region. The most surface-sensitive technique is partial electron yield (PEY), which collects the electron yield in a narrow range of energies, but is not widely used because it often gives the same results as TEY. Applied magnetic fields can create artifacts in the collected spectra of the PEY and channeltron TEY methods. All the spectra collection methods differ in applicability to samples grown ex situ, depending on capping layer thicknesses and substrate materials.

**Synchrotron radiation at the ALS**

Synchrotron radiation is produced by the acceleration of a relativistic electron while it is constrained to stay in a circular orbit by a magnetic-dipole field. The resulting photon spectrum is a continuum extending from the far infrared to the X-ray region. The distribution of light within this range depends on the electron energy and the magnetic-dipole field. For the Advanced Light Source (ALS), these parameters are 1.5 GeV and 1.07 T, respectively, and the peak of the distribution is around 500 eV. Synchrotron radiation from a bending magnet is linearly polarized in the orbit plane. Equivalently, radiation from an insertion device with a vertical magnetic field is linearly polarized. Synchrotron radiation emitted off (above or below) the orbit plane of a bending magnet, or from specific insertion devices with asymmetric vertical fields or with a horizontal component in the magnetic field, can acquire a large degree of circular polarization.

The \( L_{2,3} \) absorption edges of the 3d transition metals lie in the soft X-ray energy region at photon energies of approximately 500-900 eV. The ALS is an ultrahigh brightness ("third generation") source that has been optimized for the photon-energy range of 100-1500 eV, which encompasses these \( L_{2,3} \) edges and also the \( M_{4,5} \) edges (3d\( _{3/2} \) and 3d\( _{5/2} \) core levels to 4f-valence band) of the magnetic rare-earth elements. Circularly polarized soft X-rays from a high brightness synchrotron radiation source open up the possibility to use XMCD *microscopy* to measure local magnetic properties of materials, complementary to XMLD and XMCD spectrosopies. The optical configuration used at the ALS (Beamline 9.3.2) for our XMCD experiments will be discussed in the final section.
X-ray magnetic circular dichroism

XMCD is a modified form of X-ray absorption spectroscopy in which circularly polarized X-rays are used. If circularly polarized incident X-ray photons are used, an additional selection rule ($\Delta m_s = \pm 1$) is superimposed on the allowed transitions. Referring again to Figure 1, the density-of-states for the “spin-up” electrons (i.e., those electrons whose magnetic moment is aligned antiparallel to the applied magnetic field $H$, or those in the majority band) is shifted down in energy, relative to that for the “spin-down” electrons (those in the minority band with moment aligned parallel to the applied field). The inherent spin asymmetry of this system leads to a difference in absorption for photon helicity aligned parallel or antiparallel to the magnetization. These transitions can therefore indicate differences in spin-up and spin-down density-of-states quantitatively. The difference in the X-ray absorption spectra, recorded with circularly polarized X-rays of right and left helicity, termed MCD, then gives a direct measure of the local component of the vector magnetization of the sample along the beam direction. Since we are interested in probing the magnetic characteristics of the $d$ valence shell, we excite $p$ core electrons. It is therefore important to consider the interactions affecting the $p$ core shell. For the $3d$ magnetic elements, Fe, Co, and Ni, it is advantageous to excite the $2p$ shell for XMCD experiments because $L_{2,3}$ edges exhibit much larger edge jumps or signal-to-background ratios than the shallower $3p$ or $M_{2,3}$ edges. Also, the $M_3$ and $M_2$ edges overlap energetically. The largest splitting of the $p$ shell is caused by the spin-orbit interaction, which leads to the well-known separation of the $L_3$ ($2p_{3/2}$) and $L_2$ ($2p_{1/2}$) edges. The measured bonding energies for the edges are: 707 eV ($L_3$) and 720 eV ($L_2$) for Fe, 778 eV ($L_3$) and 793 eV ($L_2$) for Co, and 853 eV ($L_3$) and 870 eV ($L_2$) for Ni. Hence the spin-orbit splitting ranges from 13 to 17 eV. Also important are the $p$-$d$ Coulomb and exchange interactions, which are about 3-6 eV and for transition-metal compounds give rise to detailed multiplet splitting in the spectra.

A typical beamline optical arrangement is illustrated in Figure 3(a). The decoupled horizontal and vertical focusing mirrors (HFM, VFM) of the beamline allow the user to select any center for the vertical angular
acceptance within a range $\psi = 4$ mrad without affecting the horizontal focusing of the monochromator. ($\psi$ is the beam divergence.) By translating the VFM vertically, one can position the center of radiation at a specific offset angle, $\psi_{\text{off}}$, with respect to the orbit plane. To restore full illumination of the grating, the entrance slit must then be translated vertically in proportion to the translation of the VFM. For any given $\psi_{\text{off}}$, the grating scanning angle and exit-slit distance are recalculated to take into account the change in the grating-incidence angle. For example, the data presented by Chen, et al.,$^{15}$ (see

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**Figure 3.** (a) Dragon beamline optical arrangement for obtaining circularly polarized soft X-rays. (b) Experimental setup for measuring the magnetic circular dichroism in nickel.$^{15}$
below) were taken with 12 mrad horizontal angular acceptance and 0.44 mrad vertical angular acceptance ($\Delta\psi$).

It is instructive to describe the XMCD technique in the context of a few key demonstration experiments. Chen, et al.,\textsuperscript{15} presented the Ni $L_{2,3}$ photoabsorption spectra taken at normal incidence on a Ni(111) single crystal by monitoring the sample photocurrent. As shown in Figure 3(b), the sample was rigidly attached to a viewport at the back of a small vacuum chamber. In this way, the sample was electrically isolated and its surface was only a short distance (~4 mm) from an external permanent magnet. The magnetic field at the surface of the sample was measured to be ~2000 G, a value sufficient to fully align the bulk magnetic domains at room temperature. The parallel or antiparallel orientation between the spin direction of the photons and that of the majority $3d$ electrons was selected by simply reversing the orientation of the external permanent magnet. Two metal rings, positioned in front of the sample, were biased to prevent the sample from recapturing the photoemitted electrons as well as from collecting electrons generated at the aluminum window. During the absorption measurements, the $I_0$ beam intensity was continuously monitored by detecting the total electron yield of a 90% transmission gold mesh, mounted in a $\mu$-metal-shielded $I_0$ chamber. (Mumetal has the composition 77 at% Ni, 16 % Fe, 5 % Cu and 2 % Cr, and has a relative permeability around $2 \times 10^4$.\textsuperscript{16}) With this setup, no influence of the permanent magnet was observed in either the sample or the $I_0$ signals.

The $L_{2,3}$ photoabsorption spectra of a nickel crystal taken for the two different magnetization orientations are shown in Figure 4(a).\textsuperscript{15} The solid curve is the spectrum taken with the spin direction of the photons parallel to that of the majority $3d$ electrons, while the dashed curve is taken with these two spins being antiparallel to each other. The intensities of the $L_3$ and $L_2$ white lines are different for opposite magnetic-field orientations, and the enhancement or decrease observed at the $L_3$ line is reversed at the $L_2$ line. This effect is more visible in the difference spectrum shown in Figure 4(b), which is the MCD spectrum. By collecting radiation below the orbit plane the effect observed at the two white lines is reversed in sign and, at any $\psi_{\text{off}}$, spectra taken with no magnetic field are equal to the average of those taken
with opposite magnetic field.\textsuperscript{15} Note that one can measure the MCD spectra either by reversing the orientation of the external permanent magnet while maintaining a single polarization direction or by changing the beam polarization (from above- to below-plane) while maintaining the same magnet orientation. Usually the former is carried out to avoid changes in background intensity.

The essence of the Erskine and Stern model\textsuperscript{4} is the observation that the unoccupied \(3d\) states of ferromagnetic Ni occupy a very narrow energy range just above the Fermi level and are exclusively of minority spin character \((3d\downarrow)\). Notably, they neglected spin-orbit splitting in the valence band. The relative absorption cross-sections are defined by \(\mu(\omega) = -\ln[l(\omega)/l_0(\omega)]\), in which \(l_+ (l_-)\) is the absorption intensity measured with the projection of the spin of incident photons parallel (antiparallel) to the spin of the Fe \(3d\) majority electrons, and \(l_0\) is the incident intensity. Following the treatment by Chen, et al.,\textsuperscript{15} a straightforward application of the dipole-selection rules yields the following expressions for the total absorption cross-sections \((\mu_+ + \mu_-)\) and the MCD cross-sections \((\mu_+ - \mu_-)\):

![Image]

Figure 4. (a) \(L_{2,3}\) absorption spectra of nickel taken at two different orientations between the spin direction of the incident photons and that of the majority \(3d\) electrons. (b) Magnetic circular dichroism of nickel obtained from the intensity difference of the two spectra shown in (a).\textsuperscript{15}
The quantities $A$, $B$, and $C$ are proportional, respectively, to the squared dipole matrix elements

$$\left| \langle Y_2^\pm | x \pm iy | Y_1^\pm \rangle \right|^2,$$

$$\left| \langle Y_2^\pm | x \pm iy | Y_1^0 \rangle \right|^2,$$

and

$$\left| \langle Y_2^\pm | x \pm iy | Y_1^\pm \rangle \right|^2,$$

where $Y_{l}^{m}$ are spherical harmonics and the $x \pm iy$ is the dipole operator of circularly polarized photons. No matter how the $A$, $B$, and $C$ terms are weighted, this model predicts that the ratio of total cross-sections for $L_3$ and $L_2$ white lines will be 2:1 (identical to the degeneracies of the $2p_{3/2}$ and $2p_{1/2}$ core levels), and the corresponding ratio for the MCD cross-sections be -1:1. The MCD ratio -1:1 implies that the sum (integral) over the dichroism spectrum should be zero.

The XMCD results at the $L_{2,3}$ edges of Ni (Figure 4) are qualitatively consistent with a simple exchange-split valence-band model. Quantitatively, however, the intensity ratios of the $L_2$ and $L_3$ white lines and their MCD counterparts do not agree with this simple model, as the measured peak area ratios for Ni are about 2.6:1 for the total cross-sections and about -1.6:1 for the MCD cross-sections. The appreciable difference in both ratios could be related to the change of spin dependent unoccupied density-of-states near the Fermi level caused by the $L$-$S$ coupling (spin-orbit interaction) and the Zeeman effect (electron-energy-level splitting due to a magnetic field). It has been noted previously in the related case of Pt that spin-orbit interaction within the valence $d$ band can enhance the proportion of $j = 5/2$ ($5d_{5/2}$) character at the top of the $d$ band and therefore favor the $L_3$ over the $L_2$ edge (since $|\Delta m| = 1$), whereas according to Hund's rules we expect $j = 3/2$ to be favored near the top of the $d$ band. More sophisticated calculations which include these effects are now appearing in the literature, and will be discussed in the next section. Thus, one may conclude that the MCD measurements are sensitive to details of the electronic and magnetic structure beyond elementary atomic-dipole selection rules.
In support of this conclusion, Chen, et al., noted the existence of weaker features in the spectra at about 4 and 6 eV above their respective white line. The 6 eV feature [labeled as A, A’ in Figure 4(a)] appears only in the total spectrum and is attributed to an edge in the density-of-states. Exchange splittings are negligible this high in the unoccupied band structure, and so it is not surprising that these features have no counterpart in the MCD spectrum. By way of contrast, the 4 eV feature [labeled as B, B’ in Figure 4(b)] is imperceptive in the total spectrum but manifests a distinct shoulder in the MCD spectrum. Chen, et al., tentatively attribute this feature to exchange-split d states weakly hybridizing with the unoccupied s and p states above the nominal top of the d band. Shifts on the order of 2-6 eV can also occur due to crystal field effects, but this occurs in ionic crystals and not elemental metals. It is assumed from band-theory calculations that FeN is similarly metallic and will not show crystal field splitting.

**XMCD spin and orbital contribution to magnetic moment**

The results presented above demonstrate that spin-orbit splitting within the d band must be taken into account at the outset. The spin-orbit interaction mixes the spin and orbital magnetic moments. Thus, a nonzero sum over the dichroism spectrum implies a nonzero orbital magnetic moment. Indeed, Thole, et al., and Carra, et al., have developed two powerful magnetooptical sum rules which can be used quantitatively to extract the orbital and spin magnetic moments from the integral over the dichroism spectrum. No consensus has been reached regarding the sum rules’ validity for itinerant systems, although Idzerda points out that indirect X-ray absorption techniques, for example, the total electron and fluorescence yield methods, are known to suffer from saturation and self-absorption effects that are very difficult to correct in the analysis. For this reason transmission measurements may be more reliable.

Based on this conclusion, experimental confirmation of the sum rules was carried out by Idzerda, et al., and Chen, et al., using the transmission method to measure L$_{2,3}$ edges of Fe and Co, using 30-50 Å films that were grown in situ on 1-μm parylene (C$_8$H$_{8}$)$_n$ substrates. The film thickness was
chosen to keep the absorption at the L₃ peak in the range 20-30%, optimizing signal to background ratio while preventing any uncorrectable saturation effect.₁² XAS spectra were obtained by measuring the photon flux transmitted through the films using a soft X-ray sensitive photodiode mounted 0.5 m behind the sample. The photon incident angle, energy resolution, and circular polarization degree were set at 45°, 0.5 eV, and 76%, respectively. Figure 5 shows the incident-flux-normalized transmission XAS spectra of Fe/parylene thin films taken with the projection of the spin of incident photons parallel (I₊, solid curve) and antiparallel (I₋, dashed curve) to the spin of the Fe 3d majority electrons. Magnetization-independent spectra of parylene substrates were also measured (Iₛ, dotted curve) in order to calculate the absorption cross-sections using the transmission

Figure 5. L₂,₃-edge XAS and MCD spectra of iron: (a) transmission spectra of Fe/parylene thin films, and of the parylene substrates alone, taken at two opposite saturation magnetizations; (b) the XAS absorption spectra calculated from the transmission data shown in (a); (c) and (d) are the MCD and summed XAS spectra and their integrations calculated from the spectra shown in (b). The dotted line shown in (d) is the two-step-like function for edge-jump removal before integration. The p and q shown in (c) and the r shown in (d) are the three integrals needed in the sum-rule analysis.₂³
absorption equation,

\[ \mu_\pm(\omega) = -\ln \left[ \frac{I_\pm(\omega)/I_\pm(\omega)}{n_d} \right], \]  

in which \( n \) and \( d \) are the atomic density and effective thickness of the film, respectively. After taking into account the photon incident angle and the circular polarization degree, i.e., multiplying \([\mu_+(\omega) - \mu_-(\omega)]\) by \([1/\cos(45^\circ)]/0.76\), while keeping \([\mu_+(\omega) + \mu_-(\omega)]\) the same, Figures 5(b, c, and d) show, respectively, the resulting \( \mu_\pm(\omega) \), \([\mu_+(\omega) - \mu_-(\omega)]\) (the MCD spectra), and \([\mu_+(\omega) + \mu_-(\omega)]\) (the XAS spectra). Unlike all previous works taken with indirect X-ray methods, no additional data manipulations are needed for these transmission spectra by Chen, et al.

According to the XMCD sum rules, the orbital\(^{18}\) and spin\(^{19}\) magnetic moments can be determined from the XAS and MCD spectra by the following equations:\(^{23}\)

\[
m_{\text{orb}} = \frac{4 \int_{L_3+L_2} (\mu_+ - \mu_-) d\omega}{3 \int_{L_3+L_2} (\mu_+ + \mu_-) d\omega} (10 - n_{3d}),
\]

\[
m_{\text{spin}} = -\frac{6 \int_{L_3} (\mu_+ - \mu_-) d\omega - 4 \int_{L_3+L_2} (\mu_+ - \mu_-) d\omega}{\int_{L_3+L_2} (\mu_+ + \mu_-) d\omega} (10 - n_{3d}) \left( 1 + \frac{7\langle T_z \rangle}{2\langle S_z \rangle} \right)^{-1},
\]

in which \( m_{\text{orb}} \) and \( m_{\text{spin}} \) are the orbital and spin magnetic moments in units of \( \mu_B/\text{atom} \), respectively, and \( n_{3d} \) is the \( 3d \) electron occupation number of the specific transition metal atom. The \( L_3 \) and \( L_2 \) denote the integration range. \( \langle T_z \rangle \) is the expectation value of the magnetic dipole operator and \( \langle S_z \rangle \) is equal to half of \( m_{\text{spin}} \) in Hartree atomic units. In these equations, they replaced the linearly polarized spectra, \( \mu_0(\omega) \), by \([\mu_+(\omega) + \mu_-(\omega)]/2\). In order to verify the individual orbit and spin sum rules, a \( 3d \) electron occupation number and a function for removing the \( L_{2,3} \) absorption edge jumps are needed. However, for testing the orbital-to-spin relative sum rule, or \( m_{\text{orb}}/m_{\text{spin}} \), this additional information is not needed and only the MCD spectra alone are required. The simplified expression for this ratio is:\(^{22}\)
where $\langle L_z \rangle$ is the expectation value of the orbital angular momentum. To help evaluate the required MCD integrals, Figures 5(c) and 5(d) also show the integrations of the MCD spectra, starting from 20 eV below the L₃ white line to 40 eV above the L₂ white line. The saturation behavior near the end of the integrated spectra clearly illustrates that there is no significant MCD signal at photon energies 40 eV above the L₂ white line. The integral for the whole range, L₃ + L₂, can be precisely determined from the integrated spectrum, i.e., the $q$ value shown in the figures. There is a minor uncertainty, however, for integrating the L₃ edge alone, because some of its signal may overlap with that of the L₂ edge. By choosing a cutoff at the onset of the L₂ white line, one can determine the integral for the L₃ edge, i.e., the $p$ value shown in the figures. Since $p$ is much larger than $q$, a slight uncertainty in $p$ will not change significantly the $m_{\text{orb}}$-to-$m_{\text{spin}}$ ratios. First-principle band structure calculations give $\langle T_z \rangle/\langle S_z \rangle$ a value of -0.38% for BCC Fe. Therefore, by neglecting the $\langle T_z \rangle/\langle S_z \rangle$ term in the spin sum rule, the $m_{\text{orb}}/m_{\text{spin}}$ ratio can then be calculated simply as:

$$m_{\text{orb}} = \frac{2q}{m_{\text{spin}}} \left( \frac{9p - 6q}{9p - 6q} \right).$$

(6.9)

The $m_{\text{orb}}/m_{\text{spin}}$ ratios determined from the MCD data compare well with

<table>
<thead>
<tr>
<th>Method</th>
<th>Fe (BCC)</th>
<th>Co (HCP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD + sum rules</td>
<td>0.043</td>
<td>0.095</td>
</tr>
<tr>
<td>Gyromagnetic ratio</td>
<td>0.044</td>
<td>0.097</td>
</tr>
<tr>
<td>Neutron scattering</td>
<td>0.062</td>
<td>0.070</td>
</tr>
<tr>
<td>OP-LSDA</td>
<td>0.042</td>
<td>0.089</td>
</tr>
<tr>
<td>OP-LSDA (OP off)</td>
<td>0.027</td>
<td>0.057</td>
</tr>
<tr>
<td>SPR-LMTO</td>
<td>0.020</td>
<td>0.054</td>
</tr>
<tr>
<td>FLAPW</td>
<td>0.023</td>
<td>0.045</td>
</tr>
</tbody>
</table>
gyromagnetic ratio measurements and with theoretical calculations which include orbital-orbital interaction (Table 122). Idzerda, et al., attempted to verify the applicability of the individual orbital and spin sum rules by using a technique for edge jump removal and estimating $n_{3d}$ for Fe and Co. The MCD experimental error bars for $m_{orb}/m_{spin}$ were estimated at 2%, while $m_{orb}$ and $m_{spin}$ errors were estimated at 4%. They also added values for $\langle T_z \rangle/\langle S_z \rangle$, with no improvement in results. They conclude that while the ratios are in good agreement with other data, high precision XAS and MCD spectra as well as reliable $\langle T_z \rangle$ and $n_{3d}$ values are necessary for testing and utilizing the absolute sum rules with confidence.

**XMCD of Fe$_{16}$N$_2$ films**

To understand the origin of magnetic properties in $\alpha$-Fe$_{16}$N$_2$, we attempted to resolve the Fe spin and orbital contributions to the magnetic moment using XMCD measurements. These can be resolved using the sum

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Figure 6. XMCD sample rod for manipulating FeN/Ag/Si(001) samples. One-cm samples (Si wafers) were mounted on a grounded Cu plate using conductive Ag paint. The Cu plate was electrically isolated from the sample rod by an insulating Delron™ plastic rod. Photoemitted electrons were collected by the unbiased grid, which consisted of a wire frame covered with Au mesh. Fluorescing paint was used to locate samples in the beam.
rules outlined above. Measurements were made using externally-generated magnetic fields to switch the magnetization in situ. The vacuum chamber consisted of a sample rod built in-house with rotation, x-axis translation, y-axis tilt, and z-axis translation to position the sample in the beam path (Figure 6), and a 6-Tesla superconducting electromagnet to apply a field either parallel or antiparallel to the beam propagation direction. The magnet required a liquid helium reservoir to cool the superconducting solenoid, which consequently cooled the samples to approximately 150 K. The samples were attached to a grounded copper plate using conductive silver paint. The sample surfaces were rotated with respect to the beam by approximately 45° so that a component of the film would be saturated in the film plane but still be penetrated by the beam. In this way sample position could also be fixed visually from a side viewport. The total-electron-yield (TEY) method was used to measure X-ray absorption; photocurrent was collected off an unbiased grid positioned above the samples. The grid consisted of a wire frame covered by a gold mesh screen which transmitted 90% of the incoming beam. The measured current, which was in the nanoampere range, was amplified by $10^9$ and converted to a voltage signal before being sent to a frequency-voltage converter which produced the “counts” stored in the computer data file.

The main obstacles encountered with this method of data collection were signal strength and signal-to-noise ratio. Noise was reduced in several ways: all probes of temperature, pressure, etc., were turned off during spectrum collection; all physical motion and vibration near the apparatus was kept to a minimum; direct grounding wires were used liberally to avoid eddy currents (and so noise) in the electrical path to ground and; all electronic instruments were kept as far away as possible from the magnetic field, which easily penetrated the chamber walls to the outside experimental area. Also, electrical connections near the samples and grid were kept short to reduce resistance and increase signal intensity. A positive grid bias that was used initially to pull photoemitted electrons away from the sample was turned off when it was discovered that this was a significant source of noise as well.

Figure 7 is a schematic of Beamline 9.3.2 at the ALS29,30 and gives an idea of the size and complexity of the beam optics; BL 9.3.2 is over 50 m (160
ft) long and one to two meters high along the beam axis. Figure 8 is a schematic of the beamline optical arrangement at BL 9.3.2, and is very similar to that used by Chen, et al. [see again Figure 3(a)]. The vertical focusing mirror (VFM) can be translated vertically to a specific offset angle, $\psi_{\text{off}}$, with respect to the orbit plane. Full illumination of the grating must then be restored by translating the entrance slit vertically in proportion to the translation of the VFM. For any given $\psi_{\text{off}}$, the grating scanning angle and exit-slit distance were recalculated to account for the change in the grating-incidence angle. For this experiment the horizontal angular acceptance was 7 mrad for linear polarization (or 0.8 mrad for circular polarization) and the vertical angular acceptance (the polarization selection direction) was 1.2 mrad. With these acceptance angles, the degree of circular polarization was measured as ~80%. In this position the beam intensity is reduced by approximately one-third compared to linearly polarized (on-axis) light. “Linearly” polarized light is actually 90% linearly polarized with the balance being left and right circular components.

The slit width was varied from 10 μm to 100 μm, but was usually 20 μm. Small slit widths increase resolution but decrease overall intensity. The angular acceptances do not depend on the slit width because the slits are at the image plane of the VFM (entrance slit) and the grating (exit slit).

The MCD spectra could be generated either by measuring the XAS with a constant magnetic field and opposite polarizations or with constant
polarization and opposite magnetic fields. In practice, switching the polarization caused a shift in the Fe L_{2,3} onset (a problem which has since been eliminated by ALS staff), making it difficult to form the difference spectrum, hence, the latter approach had better results. A typical set of raw data is shown in Figure 9 for an uncapped $\alpha$-Fe film grown on Ag/Si(001). The light was left-circularly polarized (LC) and the field applied in situ was $+3 \, \text{T}$ using the superconducting magnet. This relatively large field was expected to be necessary to saturate the $\alpha'/\alpha''$ films, since the applied field was not parallel to the film plane (wherein lies the easy-axis). The incident X-ray intensity ($I_0$), measured upstream from the vacuum chamber, is shown in the Figure 9(a). One can see the exponential decay of the incident beam during the collection, which looks linear in scans only a few minutes long. The second graph [Figure 9(b)] is the amplified absorption signal, which is then normalized by $I_0$ and multiplied by 1000, and the result plotted in Figure 9(c).

The background intensity was removed for each spectrum by subtracting (from the whole spectrum) the average value of the spectrum before the L$_3$ edge onset. A similar averaging was performed after the L$_2$ edge to normalize the spectrum to a value of one on the right side. Once this procedure was performed, all XAS spectra were comparable and could be used to generate MCD spectra. Figure 10(a) shows the normalized XAS spectra generated using the data shown in Figure 9 for the $\alpha$-Fe film. The effect of the magnetic-field/polarization orientation is clearly shown by the
difference in peak intensities for parallel beam/magnetization direction (LC, +3 T, solid line) and antiparallel beam/magnetization direction (LC, -3 T, dashed line) XAS. By subtracting one spectrum from the other, the MCD spectra [Figure 10(b)] results. Its integral is shown with the dashed line. From this curve the values of $p = -2.79$ at 726.00 eV and $q = -0.35$ at 744.00 eV were determined, and $m_{\text{orb}}/m_{\text{spin}} = 0.03$ via equation 6.9. This agrees well with values shown in Table I.

Figure 11 shows XAS and MCD spectra of $\alpha'$-Fe$_8$N films grown on Ag/Si(001). In this case, the light was right-circularly (RC) polarized and the magnetic field was $\pm$3 T. From the MCD integration, $p = -5.89$ at 724.00 eV and $q = -4.66$ at 744.00 eV, resulting in $m_{\text{orb}}/m_{\text{spin}} = 0.37$. Considering that the moment of the $\alpha'$ film is higher than that of $\alpha$-Fe (i.e., the spin contribution is higher), the data imply a higher orbital contribution relative to the spin contribution to the Fe-atom moment. That is, orbital angular momentum may not be quenched ($L \neq 0$) as previously calculated. How the value of $p$ is chosen can induce a large error in the $m_{\text{orb}}/m_{\text{spin}}$ ratio when $q \approx$
$p$ (compared to when $q \ll p$ for $L = 0$). For this reason and others discussed below, this ratio is not considered accurate. Assuming that the error is less than an order of magnitude, however, one can say that $\alpha'$-Fe$_8$N has a higher

![Normalized XAS spectra](image)

Figure 10. (a) Normalized XAS spectra of an $\alpha$-Fe film on Ag/Si(001), measured with the 3-T magnetic field parallel (solid line) and antiparallel (dashed line) to the left-circularly-polarized beam propagation direction. (b) MCD spectrum (solid line) and corresponding integrated MCD spectrum (dashed line). Values for $q$ and $p$ are given in the text.
Figure 11. (a) Normalized XAS spectra of an α'-Fe₈N film on Ag/Si(001), measured with the 3-T magnetic field parallel (solid line) and antiparallel (dashed line) to the right-circularly-polarized beam propagation direction. (b) MCD spectrum (solid line) and corresponding integrated MCD spectrum (dashed line). Values for q and p are given in the text.

The orbital contribution to the moment than α-Fe. This is a significant finding since band theory calculations currently assume that the orbital contribution to the moment in FeN martensite is negligible (as it is in Fe).
Although this preliminary data is interesting, there are several discrepancies in the data which require discussion. In both sets of data, the peak shape, especially that of the L$_3$ peak, shows a clear second peak due to a shift in the edge onset for some of the Fe atoms in the film. This is most likely due to iron oxide formed on the surface of the uncapped films. Since the X-rays penetrate into the film only 100 Å or so, this can be a significant contribution to the spectra. If the oxide was nonmagnetic, the shifted peaks would disappear in the MCD spectrum, resulting in the same MCD information as an unoxidized sample. Alas, it appears to make a ferromagnetic contribution to the magnetization and, therefore, the data is difficult to interpret. Without the oxidation, it may have been possible to examine the fine structure of the Fe-L edge as well as the MCD, that is, for each of the three Fe sites in α**, the edge position would differ slightly. If the hybridization of the N-2p and Fe-3d orbitals was significant, particularly on the Fe$_1$ site (1 NN Fe to N), this would be detected by a shift in the Fe-L edge. This was not resolved due to the surface oxidation.

To get a reliable data set for pure iron, a control sample of polycrystalline Fe sputtered on Si was capped *in situ* with approximately 30 Å of SiC (produced by Jeff Kortright at the ALS). The XAS and MCD spectra for this sample, taken with RC polarization and ±2 T, are shown in Figure 12. Similar to the previous result for Fe, the value of the orbital/spin moment ratio is 0.04 ($p = -4.35$ at 711.20 eV and $q = -0.65$ at 755.00 eV), indicating that the data collection method is sound. It should be noted that the signal-to-noise ratio on the spectra is improved, which may be due to the cleaner and smoother surface of the capped film.

Several attempts to similarly cap the FeN films were unsuccessful. The challenge was to produce a capping layer *in situ* during the sputtering deposition which was continuous and yet thin enough to allow X-ray penetration. The simplest choice for a cap was silver, since it was used for the underlayer on silicon and the sputtering chamber had only two targets (Ag and Fe). Unfortunately, due to the perfect immiscibility of Fe and Ag below 911 °C, both Fe-on-Ag and Ag-on-Fe growth is by the VW island growth mode. (See again the discussion in Chapter III.) In fact, even when the silver was
Figure 12. (a) Normalized XAS spectra of a capped, polycrystalline α-Fe film on Si(001), measured with the 2-T magnetic field parallel (solid line) and antiparallel (dashed line) to the right-circularly-polarized beam propagation direction. (b) MCD spectrum (solid line) and corresponding integrated MCD spectrum (dashed line). Values of p and q are given in the text.

deposited at fast growth rates and appeared to have uniform coverage in a 20-Å layer, the Ag atoms would migrate at room temperature, forming tall hillocks in a matter of days and leaving the Fe film exposed. A 30-Å aluminum cap, deposited after opening the chamber and changing the RF target from Ag to
AI, was not thick enough to prevent iron oxidation due to its own passivation layer which allowed oxygen transfer to the Fe film. Removing the iron-oxide film with dilute nitric acid prior to loading the samples into the beamline station was also unsuccessful, and may have roughened the surface and decreased the jump ratio of the absorption. With hindsight, it may have been worth the effort to find the growth conditions for sputtering α'-Fe$_{16}$N$_{2}$ directly on lattice-matched MgAl$_2$O$_4$ (spinel) so that the second sputtering target could be used for a capping layer material (perhaps 50 Å of Al). In addition, spinel is a transparent substrate which might allow XMCD experiments on FeN to be performed in transmission; this is the most accurate method for determining orbital and spin contributions to the moment.\cite{12}

Given our difficulty in capping the FeN films in the current sputtering system, another alternative was to separate the peaks of the current XAS spectra using a deconvolution program. This program is contained in a “procedure” (written by Edward Moler at the ALS) within a sophisticated graphing application program called Igor Pro™ 3.0. The program consists of two pairs of peaks which are empirically fit to the data using a set of variable parameters. Initially, a peak shape was chosen to fit the L$_3$ edge of the control sample shown in Figure 12. This was a Lorentzian function plus a step-like function at the peak position, convoluted with an exponential function. This combination best fit the sharp edge onset and asymmetrical decay typical of transition-metal absorption spectra, and is similar to fitting curves used by others.\cite{9,23} Each peak had five parameters; intensity, position, exponential width, Lorentzian width, and step height. These four curves (one L$_3$ and one L$_2$ peak each for iron nitride and iron oxide), along with a line fitting the background before the edge onset, were then added together to form the fitted curve. Once the fit was satisfactory, the background and the two peaks due to the iron oxide were removed, the two FeN peaks added and normalized, and the MCD spectrum calculated in the usual way by taking the difference of the two deconvoluted XAS spectra. The details of this program are given in Appendix C, which contains the fitting procedure, a typical curve fitting and its corresponding table of fitting parameters.

Figure 13 shows fitted XAS and MCD spectra of the raw data shown
Figure 13. (a) Fitted XAS spectra of a capped, polycrystalline $\alpha$-Fe film on Si(001) (shown previously in Figure 12), measured with the 2-T magnetic field parallel (solid line) and antiparallel (dashed line) to the right-circularly-polarized beam propagation direction. (b) The resulting MCD spectrum (solid line) and corresponding integrated MCD spectrum (dashed line).

previously in Figure 12 for a capped Fe film. The fitting for two peaks was quite good, and the MCD results were nearly equivalent to the raw data ($m_{orb}/m_{spin} = 0.03$). Figure 14 shows XAS and MCD spectra using a fitting of the data.
shown previously in Figure 10 for an oxidized Fe film. The fitting for four peaks was not very good, which may have been due to the increased complexity of the fit as well as the lower quality of the raw data for the uncapped sample.

Figure 14. (a) Fitted XAS spectra of an uncapped α-Fe film on Ag/Si(001) (shown previously in Figure 10), measured with the 3-T magnetic field parallel (solid line) and antiparallel (dashed line) to the right-circularly-polarized beam propagation direction. (b) The resulting MCD spectrum (solid line) and corresponding integrated MCD spectrum (dashed line).
To compare two XAS spectra, the fitting must be performed with the same peak positions for nitride (or oxide), and this position was arrived at iteratively by alternately fitting each spectrum and averaging the values. This is also true for the Lorentzian widths which, once determined, should be the same for all samples for a given transition. The Lorentzian peak shape is often used for fitting absorption spectra\textsuperscript{9,23} and its width, based on instrumental broadening, is usually the same for each transition (L\textsubscript{3} or L\textsubscript{2}) for all samples in a given experiment with the same magnetic compound. For our data, the best fit used the same width for both L\textsubscript{3} and L\textsubscript{2} peaks (0.45), but this was coincidental. The step function is required to account for the secondary electron emission which occurs after the edge onset and raises the background level by a constant value for each peak. For a pure sample such as α-Fe, Chen, et al.,\textsuperscript{23} assumed that the L\textsubscript{3} (L\textsubscript{2}) step height was 2/3 (1/3) of the average intensity of the last 15 eV of the spectra, according to its quantum degeneracy, 2j + 1. For two L\textsubscript{2,3} peak pairs then, the step height parameters could be set as a ratio, L\textsubscript{3} step/L\textsubscript{2} step = 2 for each set. We attempted a fixed step ratio but it did not improve the fitting quality of our data, even for the two-peak capped Fe sample, and ultimately step heights were allowed to vary independently, and these parameters were included in the results shown in Figures 13 and 14.

So far there have been only empirical fits for magnetic XAS data. This seems to be a significant disadvantage of the XMCD technique for samples containing a specific element in more than one magnetic compound. The real difficulty, however, lies in the low quality of the film surface. Future XMCD work on FeN films must focus on effective, thin capping layers to produce the most accurate measurements of orbital and spin contribution to the moment. Growing FeN films on transparent or thin (≤ 500 Å) substrates would also be a distinct advantage. Clearly, if this information can be resolved for Fe in FeN films, one can expect XMCD to add significant new results to our understanding of the giant moment in Fe\textsubscript{16}N\textsubscript{2}.

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CONCLUSION
GROWTH AND PROPERTIES OF IRON NITRIDE —
A SUMMARY OF KEY RESULTS

Introduction

In the industry of magnetic recording there is continued interest in ferromagnetic materials with high saturation magnetization for use in magnetic recording heads for high density storage disks. It has been claimed that $\alpha''$-Fe$_{16}$N$_2$ has an unusually large magnetization or “giant” moment.\textsuperscript{1} After two decades this claim is still under considerable scrutiny, especially due to the widely-varying magnetization values observed by different workers, and by the lack of reproducible single-phase $\alpha''$. The recent resurgence of interest in Fe$_{16}$N$_2$ is largely due to the growth of single-phase $\alpha''$ films, by molecular beam epitaxy, on lattice-matched In$_{0.2}$Ga$_{0.8}$As(001) and Fe/GaAs(001) with volume magnetization $M_v = 2310$ emu/cc, reported by Komuro,\textsuperscript{2} Sugita\textsuperscript{3} and coworkers. Attempts at growth on simpler substrates have resulted in only a modest enhancement in moment and often in multiphase mixtures. While the giant moment has been claimed in bulk $\alpha''$ as well,\textsuperscript{4,5} the moment was extracted from mixed-phase samples ($\alpha$-Fe and $\gamma'$-Fe$_4$N present in addition to $\alpha'$-Fe$_8$N or $\alpha''$) in which volumetric analysis is problematic. Mixed phases are commonly observed in FeN growth, since stable $\gamma'$-Fe$_4$N and/or $\alpha$-Fe either accompany or are formed preferentially to the metastable $\alpha''$-Fe$_{16}$N$_2$ phase. Furthermore, conventional band theory is incompatible with a giant moment: theoretical calculations based on the band structure of Fe$_{16}$N$_2$ predict values for the magnetization around 1780 emu/cc,\textsuperscript{6-9} well below Sugita’s claims, but consistent with the values reported by several other workers.\textsuperscript{10-12} Clearly, the variety of experimental and theoretical results raises many important questions.

The behavior of nitrogen in iron has been studied for many years because of its importance in steel technology. Jack first discovered Fe$_{16}$N$_2$ in 1951,\textsuperscript{13} and determined its crystal structure to be body-centered tetragonal (BCT) with nitrogen atoms occupying every other octahedral site. It is formed by annealing the metastable nitrogen martensite, $\alpha'$-Fe$_8$N, in which the
nitrogen occupation is randomly distributed in the octahedral sites of a similar BCT structure.

The nitrogenation of Fe produces a broad range of magnetic properties in the different FeN phases. It is still not entirely clear why ordering of the nonmagnetic nitrogen atoms leads to strong ferromagnetic behavior. Theoretical understanding of the high value of saturation magnetization in \( \alpha' \) Fe is still lacking. Iron is normally strongly ferromagnetic since the exchange interactions lead to an almost completely-filled majority sub-band and a partially-filled minority sub-band. An expansion between iron atoms in one direction enhances positive exchange-splitting (parallel magnetic ordering of adjacent moments) and thereby increases the moment. The central role of the N atom, which gives rise to a net enhancement of magnetic moment in the iron nitrides, is to expand the Fe lattice. Recent linearized muffin tin orbital (LMTO) calculations \(^7\text{-}^14\) of the electronic structure of these majority/minority bands of Fe\(_{16}\)N\(_2\) yielded a spin-only contribution of 2.3 T (2.4 \( \mu_B/\text{Fe atom} \)). When spin-orbit interactions were also included, \(^6\) the orbital contribution was calculated to be very minor (0.06 - 0.08 \( \mu_B/\text{Fe atom} \)). Calculations for a hypothetical BCT Fe (expanded BCC Fe) without nitrogen reveal an enhancement of the moment due to the magnetovolume effect which, given the expansion along the c-axis, contributes to the anisotropy observed in Fe\(_{16}\)N\(_2\). \(^7\text{-}^9\) Upon insertion of the nitrogen, however, the calculated moment is reduced on certain Fe sites. The presence of nitrogen, in addition to expanding the lattice, divides the unit cell into three non-equivalent sites with different local density of states. There is a reduction in moment for the first [FeI or 4(e) site] and second [FeII or 8(h) site] nearest neighbor (NN) positions, with values of 2.27 \( \mu_B \) and 2.25 \( \mu_B \), respectively, while the third NN position [FeIII or 4(d) site] is enhanced significantly (2.85 \( \mu_B \)). Hybridization of Fe-3d and N-2p states is considered responsible for these different magnetic moments. \(^15\)

Qualitatively, then, a lower concentration (deficit) of N atoms in Fe\(_{16}\)N\(_2\) leads to a larger average magnetic moment per Fe atom if the expansion is ideally maintained. However, the critically important moment per unit volume is little changed. In general, the magnetic moment of Fe atoms in the \( \alpha' \) martensite phase increases monotonically with increasing concentration of N.
up to 11.1 at% (equivalent to Fe$_{16}N_2$).\textsuperscript{3,14}

In addition to the concentration of nitrogen, the magnetic moment in FeN is also affected by the degree of order of nitrogen in the Fe lattice. Experimentally, the disordered nitrogen martensite phase ($\alpha'$-Fe$_8$N) has a lower moment than the ordered phase ($\alpha''$-Fe$_{16}N_2$), for example, 2.6 $\mu_B$ compared to 2.9 $\mu_B$.\textsuperscript{4,5} The lattices of $\alpha'$ and $\alpha''$ are similarly expanded for the same nitrogen concentration (up to 12 at%), so the significant change in moment is unexpected. This enhancement with N order is not predicted by conventional band theory results and, to date, this effect has not been adequately explained.

**Summary of FeN dissertation research**\textsuperscript{16,17}

Magnetic property measurements of single-phase Fe$_{16}N_2$ are badly needed to confirm the giant moment in $\alpha''$. An understanding of the growth conditions and the N order-disorder phenomenon will help future workers produce single-phase Fe$_{16}N_2$, and a perception of the electronic structure may ultimately bring together theoretical and experimental results. Furthermore, it is wise to produce these films using commercially relevant substrates and processes. Therefore, we attempted deposition of $\alpha''$ using a silicon substrate with an uncomplicated template and process. We performed extensive structural and magnetic characterization of individual FeN phases on Si(001). If the giant moment of Fe$_{16}N_2$ can be confirmed and reproduced, its use in inductive recording heads would allow writing to disks with information storage approaching 10 gigabits per square inch, far greater than today's storage density.\textsuperscript{8}

A simple examination of the crystal structure of Ag (FCC, $a = 4.08$ Å) and $\alpha''$-Fe$_{16}N_2$ ($a = 5.72$ Å, $c = 6.29$ Å) shows that the lattice mismatch of the (001) planes is 1% when they are rotated in-plane by 45° with respect to each other. A similar epitaxy of Ag can be achieved with Si(001), but with a somewhat larger lattice mismatch of 6.4%. Thus, a template was generated for the epitaxial growth of the FeN phases on Si(001) substrates with Fe$_{16}N_2$(100)$\parallel$Ag[110]$\parallel$Si[100] and Fe$_{16}N_2$(001)$\parallel$Ag(001)$\parallel$Si(001). The substrates were cleaned in a standard sulfuric acid process ("piranha" etch),
followed by hf etching of the native oxide layer and hydrogen passivation of the surface. Silver was sputtered directly on Si(001) at 100 °C and 5 Å/s by RF magnetron sputtering in argon (3 mT), with a nominal thickness of 1000 Å. The growth of individual FeN phases (α-Fe, γ'-Fe₄N, and α'-Fe₈N) was accomplished by the optimization of substrate temperature, sputtering rates and gas flow rates. All FeN films were deposited by DC magnetron sputtering of pure iron at a growth rate of 0.5 Å/s within a thickness range of 600-1000 Å. It was found that a specific FeN phase could be reproducibly grown by optimizing the growth temperature and Ar/N₂ ratio; α-Fe was grown at 25 °C in Ar, γ'-Fe₄N at 100 °C in 46/5 sccm Ar/N₂, and α'-Fe₈N at 45 °C in 46/4 sccm Ar/N₂. The phases were very sensitive to both N₂ gas flow rate and substrate temperature. α' films were annealed at 150 °C for 2 hours in vacuum (at least 10⁻⁶ Torr) to produce an α'/α” mixture.

In the study of Fe₁₆N₂ there are several important properties that should be analyzed based on the relevant issues. Since Fe₁₆N₂ is a metastable phase, the competing phases γ', α, and sometimes ε may be present in the films. Usually X-ray diffraction (XRD) can identify the phases present and their epitaxial orientation, and can also be used to determine volume content of the phases if the integrated X-ray peak intensities (related to the various atomic structure factors) and XRD experimental setup are carefully considered. In order to characterize the magnetic properties of Fe₁₆N₂ in a potentially mixed-phase sample, the magnetic properties of each phase must be known in the pure form. Thus, the stable phases were grown individually to determine their contribution to the saturation magnetization of a mixed-phase film.

X-ray θ-2θ scans of α, γ', α', and α'/α” films were measured. The Ag underlayers were of good quality with strong (001) epitaxy. FeN films were also (001) epitaxial but had slightly broader peaks. This was quantified by X-ray rocking curves of the Ag(002) and α'(002)/α”(004) reflections in which the measured peak widths (FWHM) were 1.19° and 1.63°, respectively. The important Bragg peaks for Fe₁₆N₂ are at 2θ_B = 58.6° and 28.3°. The peak at 58.6° is shared by the N-disordered phase, α'(002), and the N-ordered phase, α”(004). The α”(002) superlattice peak indicative of nitrogen ordering (which doubles the unit cell of α') is at 28.3°. Using values we calculated for the
structure factors and making simple approximations for the Lorentz, polarization and multiplicity factors, we calculated the intensity ratio of the relevant peaks as

\[
\frac{I_{2\theta=58.6^\circ}}{I_{2\theta=28.3^\circ}} = \frac{I_{\alpha'(002)} + I_{\alpha''(004)}}{I_{\alpha''(002)}},
\]

to quantify our measured ratios. We estimated that the \( \alpha'/\alpha'' \) mixtures contained 48 vol% \( \alpha'' \). Although this analysis represents a one-dimensional slice of the crystal structure, the rocking-curve widths indicate that variations in film structure with crystallographic direction are not significant.

The nature of annealed \( \alpha' \) films is affected by the silver morphology as well as the annealing temperature and duration. An \( \alpha' \) film grown on Ag deposited at 5.2 Å/s showed similar X-ray characteristics to an \( \alpha' \) film grown under the same conditions except for the Ag deposition rate (1.9 Å/s). Upon annealing at 150 °C for 2 hours, however, the resulting \( \alpha'/\alpha'' \) mixtures varied in quality and purity. Compared to the FeN film deposited on Ag grown at 5.2 Å/s, the FeN film deposited on Ag grown at 1.9 Å/s contained a similar \( \alpha'/\alpha'' \) ratio mixed with a small amount of \( \alpha'-\text{Fe} \). Ag morphology may affect metastable \( \alpha' \) epitaxial growth in such a way that it causes the \( \alpha' \) film to phase-separate upon annealing. The slower growth rate for Ag resulted in a narrower rocking-curve width for the Ag(002) reflection (FWHM = 1.02°), but this was disadvantageous for stabilizing the \( \alpha' \)-to-\( \alpha'' \) transformation during annealing. For all \( \alpha' \) films, annealing temperatures above 150 °C resulted in phase separation of \( \alpha' \) into \( \gamma'-\text{Fe}_4\text{N} \) and \( \alpha'-\text{Fe} \), in general agreement with the phase diagram. Annealing times longer than 2 hours did not show additional improvement in the degree of N order.

Transmission electron microscopy (TEM) was used to characterize the orientation relationship between film layers and the substrate. The growth configurations of all the FeN films were confirmed by selected-area electron diffraction of plan-view samples. We deduced the orientation relationships for \( \alpha'-\text{Fe}_8\text{N} \), and \( \alpha'\text{-Fe}_8\text{N}/\alpha''\text{-Fe}_{16}\text{N}_2 \) films to be FeN[100]||Ag[110]||Si[100] and for \( \gamma'-\text{Fe}_4\text{N} \) films to be \( \gamma'-\text{Fe}_4\text{N}[110]||\text{Ag}[110]||\text{Si}[100] \). It was clear from SAD patterns of the \( \alpha' \) film that some N-ordered \( \alpha'' \) phase was present in the as-deposited \( \alpha' \) film, which was not detected in the XRD analysis. Grain size...
was small (~100 Å) but indeterminable due to film oxidation. Centered dark-field TEM images confirmed the presence of distinct 10-20-Å regions of α" which were uniformly dispersed among α' regions. While the α'/α" film annealed for 2 hours appeared to have a minor increase in average grain size compared to the as-deposited α' film, bright-field TEM images of the α'/α" film annealed for 16 hours indicated some grain growth. This confirmed the presence of a small growth rate despite no increase in the volume fraction of α" in α' between 2 hours and 16 hours of annealing. High-resolution electron microscopy indicated that the FeN films were nearly single-crystal, despite some c-axis misalignment of grains.

Phase purity and distribution were measured using micro-diffraction in the TEM, which has a probe size around 200 Å. This technique showed that there was no γ'-Fe₄N present in the α'-Fe₈N film, although the presence of a small amount of α-Fe could not be ruled out since the α reflections overlap with the α' reflections in the [001] zone-axis condition. Also, there were regions of at least 200 Å with no N order in the annealed α'/α" film, indicating that α" nucleation sites may be more than 200 Å apart.

To draw conclusions from the magnetic property data measured for FeN phases, the stoichiometry (chemical concentration ratio of Fe and N) must be confirmed as well. The amount and uniformity of nitrogen incorporation during growth can affect film density, phase uniformity, strain, lattice parameter and, subsequently, magnetic properties. Especially important are changes in stoichiometry, such as nitrogen loss, which may occur during annealing of α' films in vacuum to produce α'/α" mixtures. Electron energy-loss spectroscopy (EELS) is a technique which can determine the local elemental concentration of each atomic species present. The stoichiometry of Fe and N for each phase was measured using EELS. Within experimental error (±1.2 at%), α'-Fe₈N and γ'-Fe₄N were stoichiometrically correct, and there was no significant change in the stoichiometry upon annealing α' to form the α'/α" mixture. This implies that magnetic data for α' and α" (extracted from pure α' and mixed α'/α" films) may be directly compared to the expected values for their structures and to each other. Oxygen was present in all the films, but appeared to be confined to the film surface.
Saturation magnetization, coercivity and overall hysteresis behavior were measured using vibrating-sample magnetometry (VSM). VSM data were acquired at room temperature and normalized with sample volume. Assuming a magnetization of 1708 emu/cc for α-Fe, the film volume was estimated. The film thickness was then calculated from the estimated area, and was used as a calibration for γ'-Fe₄N (including volume expansion), since the α and γ films were grown under similar sputtering conditions. The γ' magnetization was then estimated to be 1478 emu/cc. The magnetic properties of these two phases are well established, however, for the controversial α' and α'/α'' phases an accurate volume determination was made. Since the film areal width is much greater than its thickness (approximately 1 cm versus 10⁻⁵ cm), an accurate measure of the film thickness is paramount. The thickness of α'-Fe₈N was measured with a cross-sectional TEM specimen. After calculating the film volume α' was estimated to have a magnetization of 1780 emu/cc. The film thickness after annealing was assumed to be approximately the same as the single-phase α'. Normalized SQUID magnetometry data were taken at 15K for the α'/α'' film; we estimated that the magnetization of the α'/α'' film was also around 1780 emu/cc. Therefore, we did not see improvement in magnetization with increased N order, even though the crystalline quality improved and the Fe:N stoichiometry remained nearly the same after annealing. These magnetic moments varied widely (±8 %) depending on the volume estimates used for each film.

The coercive fields of all the films were relatively high (165-500 Oe), at least for recording-head applications which require $H_c \sim 1$ Oe. While single-crystalline films produce higher magnetization, polycrystalline films produce better soft magnetic properties (low values of $H_c$, $H_s$, and magnetostriction); usually a trade-off is required for applications. The field required to saturate the films ($H_s$) increased in α'/α'' films relative to α' films, indicating a change in the magnetization process. It was proposed that after annealing both domain wall motion and domain rotation were more hindered by an increase in the crystal anisotropy (combined with preferred orientation in the films), rather than by an increase in magnetostriction or dislocation density with annealing.

In order to compare our magnetic data to experimental and theoretical
results for Fe$_{16}$N$_2$, it is important to confirm that the chemical environment of Fe within our $\alpha''$ films agrees with the expected crystal structure. The Mössbauer effect, which is the recoilless emission and resonant absorption of a $\gamma$-ray by a nucleus, has been applied with success to the study of many magnetic materials.\textsuperscript{18} In particular, information on the valence (isomer shift) and the local site symmetry and environment (quadrupole and magnetic hyperfine structures) can be readily obtained. For $\alpha''$-Fe$_{16}$N$_2$, with three non-equivalent iron sites (4e, 8h and 4d), three distinct hyperfine fields are expected in the Mössbauer spectrum. On the other hand, $\alpha$-Fe has a single iron site with cubic symmetry and one corresponding hyperfine field ($\sim$34 T at 0 K). Part of the recent controversy with the results of Sugita and co-workers\textsuperscript{19} is that their Mössbauer data for $\alpha''$-Fe$_{16}$N$_2$ exhibits only a single hyperfine field, which is inconsistent with its accepted crystal structure. Through a collaboration with Kyoto University we performed Mössbauer measurements of our FeN films. For $\alpha'/\alpha''$ films on Ag/Si(001), Mössbauer data at room temperature confirm that there are three distinct iron sites (with hyperfine fields of 28.6 T, 31.4 T, and 39.2 T) with the expected occupation ratio of 1:2:1. In addition, there are changes in the occupation at 16K, indicating three-site occupancy of about 3:13:4. This ratio may be due to a change in spin orientation of FeI (first NN) upon cooling, or may indicate a change in N ordering, or both. The $\alpha'$ films were also composed of three distinct Fe sites, with a ratio different from that of the $\alpha'/\alpha''$ film but also varying with temperature. The easy-axis of the $\alpha'/\alpha''$ magnetization was neither in-plane nor out-of-plane, but uncommonly canted at 35° to the film normal. This value differs from that of the $\alpha'$ film prior to annealing, which might explain the change in hysteresis behavior observed above.

Regarding the issue of whether Fe$_{16}$N$_2$ possesses a giant moment, one possible source of the discrepancy between experiment and theory is whether or not the orbital contribution to the moment is negligible. A relatively new technique, X-ray magnetic circular dichroism (XMCD), uses X-ray absorption spectroscopy (XAS) with the incident light modified to have circular polarization, and has the ability to separate the spin and orbital contributions to the moment in a way that is element specific.\textsuperscript{20} MCD is the difference
spectrum between two XAS spectra measured with either the magnetic field parallel or antiparallel to the beam propagation direction. A sum-rule analysis of the MCD spectrum leads to the spin and orbital contributions to the magnetic moment of Fe in \( \alpha''-\text{Fe}_{16}\text{N}_2 \). XMCD measurements were carried out at the Advanced Light Source using externally-generated magnetic fields to switch the magnetization \textit{in situ}. For a pure iron film, the ratio of orbital-to-spin contribution to the moment was measured as \( m_{\text{orb}}/m_{\text{spin}} = 0.03 \), which was calculated using relative sum rules developed by Idzerda, et al. This agreed well with both the calculated and experimental values for Fe. For the \( \alpha'-\text{Fe}_8\text{N} \) film, \( m_{\text{orb}}/m_{\text{spin}} \) was 0.37, which was considered too large to be physical but indicated that martensite may have a significant orbital contribution to the moment. The data was difficult to interpret because of surface oxidation which caused a shift in the onset of the Fe-L peaks for oxidized iron atoms; there were two resolvable peaks for each of the \( L_3 \) and \( L_2 \) edges, and both apparently were ferromagnetic. Several attempts at producing capped FeN films and at removing the contribution of iron oxide to the absorption spectra using modelling techniques were unsuccessful. If one could resolve the Fe spin and orbital contributions to the moment using well-preserved samples, XMCD would add significant new results to our understanding of the giant moment in \( \text{Fe}_{16}\text{N}_2 \).

In this work it was established that several phases of FeN (\( \alpha-\text{Fe}, \gamma'-\text{Fe}_4\text{N} \) and \( \alpha'-\text{Fe}_8\text{N} \)) could be grown single-phase on silicon using reactive sputtering. \( \alpha''-\text{Fe}_{16}\text{N}_2 \) was also deposited on silicon, but only as a mixture with \( \alpha'-\text{Fe}_8\text{N} \). All the films were well-characterized for crystal structure, epitaxial orientation, morphology, stoichiometry, chemical structure, and magnetic properties. \( \text{Fe}_{16}\text{N}_2 \) was not found to have a giant moment when deposited on silicon by sputtering. Researchers claiming a giant moment for \( \text{Fe}_{16}\text{N}_2 \) films have usually deposited the films on lattice-matched substrates using MBE. The strain and defects associated with growth on mismatched substrates may have an affect on the magnetic properties of FeN in our films, however, no relationship between strain or defect density and magnetic properties was developed in this work. Recently Clark, et al., grew \( \alpha'/\alpha'' \) films by sputtering on Ag/Si(001) and, using high-resolution TEM, reported that at areas where Ag
twins intersect the \( \alpha'/\text{Ag} \) interface, \( \alpha' \) growth was suppressed. The growth orientation of their films, however, was \( \alpha'[110]||\text{Ag}[100]||\text{Si}[100] \), that is, silver grew on (001) silicon without the 45° in-plane rotation that we measured for our Ag films. In any case, there is no reason to believe that our films do not contain Ag twins. No comprehensive defect analysis has been performed by us or others on \( \alpha' \) or \( \alpha'' \) films, which may be due in part to the difficulty in preparing single-phase films and their tendency to oxidize. Recently single-crystal \( \text{Fe}_{16}\text{N}_2 \) has been grown directly on transparent NaCl substrates, and this may be a good approach [along with lattice-matched \( \text{MgAl}_2\text{O}_4 \) (spinel)] to producing films especially for XMCD and TEM studies. Since our sputtering chamber has only two targets, direct growth of FeN without buffer layers would allow the remaining target to be used for a capping layer (such as Al), thus preventing the oxidation problems we encountered with XMCD measurements and TEM specimen preparation.

Besides lattice mismatch, another significant contribution to defect density is subsurface damage caused by the sputtering deposition process itself. While MBE is a gentle, low-energy process, sputtering is a high-energy process which can create atomic defects such as substitutional and interstitial impurities, self-interstitials and vacancies. This may have a dramatic effect on the quality of N ordering in the \( \alpha'' \) phase, and may explain the limitation to achieving 100% \( \alpha'' \) from the annealed \( \alpha' \) that we observed for our sputtered films. This lack of perfect N order might ultimately inhibit the giant moment from developing. Another issue that arises when considering the N-ordering phenomenon is whether \( \alpha' \) and \( \alpha'' \) are distinct phases, with distinct grains, or whether \( \alpha' \) and \( \alpha'' \) are simply the endpoints of a N order-disorder continuum. In sputtered films this may be a mute point since significant N defects in the films would preclude a perfect \( \alpha'' \) phase from forming, thereby reducing the phase transition during annealing to simply an increase in the degree of N order in one phase, beginning with pseudo-\( \alpha' \) (as-deposited \( \alpha' \) films already contained some N order) and ending with pseudo-\( \alpha'' \) (48 vol% \( \alpha'' \) in \( \alpha' \)). On the other hand, we observed regions 10-20 Å in size of pure \( \alpha'' \). Unfortunately, there is no unique way of determining the quality of those \( \alpha'' \) regions (especially that of the N ordering). The author proposes that \( \alpha' \) is not a distinct
phase but, rather, is equivalent to BCT nitrogen martensite (with the stoichiometry Fe₈N) and a variable degree of N order, while α"-Fe₁₆N₂ is a distinct phase in which the N is perfectly ordered and the magnetic behavior takes an unusual turn. Regions of perfect α" may not have been achieved in the sputtered films, but may have been achieved in single-phase α" films grown by MBE in which a giant moment was observed.

In a recent TEM study of α" films grown on NaCl(001) substrates,²⁶ it was proposed that there may be two kinds of structures of Fe₁₆N₂ which are BCC-related and FCC-related, although the lattice parameters of the BCT unit cell remain the same. The structural parameters x and z measured by Jack¹³ (see again Table III in Chapter III) each have two possible values in this scheme; values of x = 0.250 and z = 0.3125 correspond to a BCC-related structure in which Fe(4e) is the first NN of the N atom, while values of x = 0.222 and z = 0.3060 correspond to an FCC-related structure in which Fe(8h) is the first NN of N. In both structures the farthest Fe atom from N is Fe(4d). A discussion about the discrepancies regarding magnetization (giant or not) and Mössbauer spectra (one Fe site versus three) of Fe₁₆N₂ is put forward based upon the observed structural properties. These discrepancies have also been approached with new theoretical treatments in the literature, with some groups reporting calculated magnetizations closer to giant-moment claims,²⁷ while others continue to deny the possibility.²⁸,²⁹ Only a handful of researchers have reported a giant moment for α"²,²⁵,³⁰,³¹ so the controversy continues as other groups try to verify and explain this unusual phenomenon. It is the opinion of the author that the giant moment may exist in iron nitride, however, the accepted structure of Fe₁₆N₂ cannot be reconciled with the high magnetization reported. Therefore, a search for another FeN phase or an alternative α" structure is required, and a reliable procedure for producing this structure must be developed.

References
³Y. Sugita, K. Mitsuoka, M. Komuro, H. Hoshiya, Y. Kozono and M.
### APPENDIX A:
**UNITS FOR MAGNETIC PROPERTIES**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Gaussian &amp; cgs[^a]</th>
<th>Conversion Factor, C[^b]</th>
<th>SI &amp; rationalized[^c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic flux density, magnetic induction</td>
<td>B</td>
<td>gauss (G)[^d]</td>
<td>(10^{-4})</td>
<td>tesla (T), Wb/m(^2)</td>
</tr>
<tr>
<td>Magnetic flux</td>
<td>(\Phi)</td>
<td>maxwell (Mx), G cm(^2)</td>
<td>(10^{-8})</td>
<td>weber (Wb), volt second (V·s)</td>
</tr>
<tr>
<td>Magnetic potential difference, magnetomotive force</td>
<td>U, F</td>
<td>gilbert (Gb)</td>
<td>(10/4\pi)</td>
<td>ampere (A)</td>
</tr>
<tr>
<td>Magnetic field strength, magnetizing force</td>
<td>(H)</td>
<td>oersted (Oe), Gb/cm</td>
<td>(10^{3}/4\pi)</td>
<td>A/m [^f]</td>
</tr>
<tr>
<td>(Volume) magnetization [^g]</td>
<td>M</td>
<td>emu/cm(^3)</td>
<td>(10^{3})</td>
<td>A/m</td>
</tr>
<tr>
<td>(Volume) magnetization [^g]</td>
<td>(4\pi M)</td>
<td>G</td>
<td>(10^{3}/4\pi)</td>
<td>A/m</td>
</tr>
<tr>
<td>Magnetic polarization, intensity of magnetization</td>
<td>(J, I)</td>
<td>emu/cm(^3)</td>
<td>(4\pi \times 10^{-4})</td>
<td>T, Wb/m(^2) [^i]</td>
</tr>
<tr>
<td>(Mass) magnetization</td>
<td>(\sigma, M)</td>
<td>emu/g</td>
<td>(1)</td>
<td>A·m(^2)/kg</td>
</tr>
<tr>
<td>Magnetic moment</td>
<td>(m)</td>
<td>emu, erg/G</td>
<td>(10^{-3})</td>
<td>A·m(^2), joule per tesla (J/T)</td>
</tr>
<tr>
<td>Magnetic dipole moment</td>
<td>(j)</td>
<td>emu, erg/G</td>
<td>(4\pi \times 10^{-10})</td>
<td>Wb·m [^j]</td>
</tr>
<tr>
<td>(Volume) susceptibility</td>
<td>(\chi, \kappa)</td>
<td>dimensionless, emu/cm(^3)</td>
<td>(4\pi ) ((4\pi)^{2} \times 10^{-7})</td>
<td>dimensionless</td>
</tr>
<tr>
<td>(Mass) susceptibility</td>
<td>(\chi_{p}, \kappa_{p})</td>
<td>cm(^3)/g, emu/g</td>
<td>(4\pi \times 10^{-3}) ((4\pi)^{2} \times 10^{-10})</td>
<td>henry per meter (H/m), Wb/(A·m)</td>
</tr>
<tr>
<td>(Molar) susceptibility</td>
<td>(\chi_{mol}, \kappa_{mol})</td>
<td>cm(^3)/mol, emu/mol</td>
<td>(4\pi \times 10^{-6}) ((4\pi)^{2} \times 10^{-13})</td>
<td>m(^3)/kg</td>
</tr>
<tr>
<td>Permeability</td>
<td>(\mu)</td>
<td>dimensionless</td>
<td>(4\pi \times 10^{-7})</td>
<td>H/m, Wb/(A·m)</td>
</tr>
<tr>
<td>Relative permeability</td>
<td>(\mu_{r})</td>
<td>not defined</td>
<td></td>
<td>dimensionless</td>
</tr>
<tr>
<td>(Volume) energy density, energy product [^k]</td>
<td>(W)</td>
<td>erg/cm(^3)</td>
<td>(10^{-1})</td>
<td>J/m(^3)</td>
</tr>
<tr>
<td>Demagnetization factor</td>
<td>D, N</td>
<td>dimensionless</td>
<td>(1/4\pi)</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>

\[^a\] Gaussian & cgs: G, cm, T, Wb, Oe, Gb, \(\Omega\).

\[^b\] Conversion Factor: \(C\).

\[^c\] SI & rationalized: T, Wb/m\(^2\), A/m, A·m\(^2\)/kg, Wb·m/kg, A·m\(^2\), joule per tesla (J/T).

\[^d\] G: Gauss.

\[^e\] Oe: Oersted.

\[^f\] A/m: Ampere per meter.

\[^g\] Volume magnetization: \(M\).

\[^h\] Emu/cm\(^3\) for volume magnetization.

\[^i\] T, Wb/m\(^2\): Tesla, Weber per square meter.

\[^j\] Wb·m: Webermeter.

\[^k\] Energy density, energy product: \(W\).

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a. Gaussian units and cgs emu are the same for magnetic properties. The defining relation is $B = H + 4\pi M$.

b. Multiply a number in Gaussian units by C to convert it to SI (e.g. $1 \text{ G} \times 10^{-4} \text{ T/G} = 10^{-4} \text{ T}$).

c. SI (Système International d'Unités) has been adopted by the National Bureau of Standards. Where two conversion factors are given, the upper one is recognized under, or consistent with, SI and is based on the definition $B = \mu_0 (H + M)$, where $\mu_0 = 4\pi \times 10^{-7} \text{ H/m}$. The lower one is not recognized under SI and is based on the definition $B = \mu_0 H + J$, where the symbol $I$ is often used in place of $J$.

d. $1 \text{ gauss} = 10^5 \text{ gamma (}\gamma\text{)}$.

e. Both oersted and gauss are expressed as $\text{cm}^{-1/2} \cdot \text{g}^{1/2} \cdot \text{s}^{-1}$ in terms of base units.

f. A/m was often expressed as "ampere-turn per meter" when used for magnetic field strength.

g. Magnetic moment per unit volume.

h. The designation "emu" is not a unit.

i. Recognized under SI, even though based on the definition $B = \mu_0 H + J$. See footnote c.

j. $\mu_r = \frac{\mu}{\mu_0} = 1 + \chi$, all in SI. $\mu_r$ is equal to Gaussian $\mu$.

k. B-H and $\mu_0 M \cdot H$ have SI units $\text{J/m}^3$; M-H and B-H/4$\pi$ have Gaussian units $\text{erg/cm}^3$.

APPENDIX B: TEMPERATURE DEPENDENCE OF THE MAGNETIC SUSCEPTIBILITY AND MAGNETIZATION OF PARAMAGNETIC AND FERROMAGNETIC MATERIALS

Categories of magnetic materials

Magnetic materials are classified according to their bulk susceptibility. Diamagnets are materials for which \(4\pi\chi\) is small and negative, \(4\pi\chi = -10^{-5}\), and the induced magnetic moment opposes the applied magnetic field. Examples include copper and silver, as well as superconductors for which \(4\pi\chi = -1\). When the aligned magnetic moments strengthen the magnetic field, this is paramagnetism, and the susceptibility is small, positive and typically in the range \(4\pi\chi = 10^{-3}\) to \(10^{-5}\). Examples of paramagnetism are aluminum and platinum. Both effects occur only while the material is under an external magnetic field. In a ferromagnet, the material can be magnetized in the absence of an external field. The susceptibility is positive, much greater than 1, and typically can have values \(4\pi\chi = 50\) to 10,000. Examples of ferromagnets are iron, cobalt and nickel as well as several rare earth metals and their alloys.

Temperature dependence of the magnetic susceptibility and magnetization

For a paramagnet, Curie\(^2\) found that the mass susceptibility (\(\chi = \kappa/\rho\), \(\rho\) is density, in emu/g-Oe) varied inversely with temperature, \(\chi = CT/\rho\), in which \(C\) is a constant. In the Langevin theory of paramagnetism,\(^3\) which supposes that the atomic moments are non-interacting, the magnetization is given by\(^1\)

\[
M = \frac{nm^2H}{3k_BT},
\]

in which \(n\), the number of atoms per unit volume, is equal to \(N_A/V\). This leads directly to the Curie law since \(\chi = M/\rho H\), and defines the Curie constant as

\[
C = \frac{N_Am^2}{3Ak_B}, \text{ per gram.}
\]

In the case of ferromagnetism the local magnetic field is the sum of the applied
magnetic field and the internal magnetic field, which is proportional to the magnetization, so that we replace $H$ with $H + \gamma M$ in the susceptibility equation, where $\gamma$ is called the Weiss constant. Weiss\(^4\) supposed that the individual atomic moments in a ferromagnet interact with each other, and $\gamma M$ is the interaction field. Ferromagnets lose their magnetization above a certain temperature, called the Curie point, when thermal energy overcomes magnetic ordering and they become paramagnetic. Above the Curie point, the $M$-$H$ relationship is linear and the magnetic susceptibility is given by the Curie-Weiss law,

$$\chi = \frac{C}{(T - \theta)},$$  \hspace{1cm} (B.3)

in which $\theta$ is the Curie point. For iron, it has been experimentally determined that $\theta = 1043$ K. Thus, one can define the Weiss constant and the magnetic moment, respectively, as

$$\gamma = \frac{\theta}{\rho C},$$ \hspace{1cm} (B.4)

and

$$m = \left( \frac{3AK_B C}{N_{Av}} \right)^{1/2}.$$ \hspace{1cm} (B.5)

The interaction field $\gamma M$ is a perturbation in the Langevin theory\(^1\) so that

$$M = M_s \left\{ \coth \left[ \frac{m(H + \gamma M)}{k_B T} \right] - \frac{k_B T}{m(H + \gamma M)} \right\},$$ \hspace{1cm} (B.6)

in which $M_s = N_m m$. This results in very different behavior for a ferromagnet than a paramagnet below $T_c$ (i.e., $\theta$). For zero applied field, one can look at the spontaneous magnetization, $M_s = M_s(T)$, normalized by the spontaneous magnetization at absolute zero, $M_s = M_s(0)$, when all the spins are perfectly aligned (saturation). This normalized behavior is the same for all ferromagnets and is known as the law of corresponding states. It is shown schematically in Figure 1, combined with the (paramagnetic) behavior of $1/\chi$ above $T_c$.

The quantum theory of magnetism modifies the above equations for both paramagnetism and ferromagnetism somewhat, in which the quantum Brillouin function is substituted for the classical Langevin function. This
includes a quantized term for the total angular momentum in a multielectron atom, $J$. As $J \to \infty$, and there are no quantum mechanical restrictions on the allowed directions and values of magnetic moment in the atom, we arrive at the classical Langevin expression.

In transition metals the electrons responsible for magnetic behavior are the outer electrons which are relatively free to move through the solid. Therefore the localized model described above is not realistic. In this case the itinerant electron model is appropriate, which is discussed in Chapter II.

References
4 P. Weiss, *Compt. Rend.* 143, 1136 (1906).
APPENDIX C:
CURVE FITTING OF XMCD DATA USING A PROCEDURE WITHIN THE IGOR PRO™ APPLICATION PROGRAM

This appendix contains the fitting procedure used for modelling of XMCD data in Chapter VI. It also contains an example of a fitting result for FeN, displayed graphically and the varied parameters listed in a table. The fitting procedure is discussed at length in Chapter VI.

User procedure

```plaintext
#pragma rtGlobals=1           // Use modern global access method.
#include "user procedures:user-fit procedure"
#include "user procedures:Eds_FunctsB"
// 3 peaks - by EJM for fitting photo-emission spectra, originally.
// each peak is a voigt with step_function background + assumes an empiricle
// background wave
// look at make_waves_from_params to see the definition of each coefficient.

This section contains Macros and functions that are Specific to Specific
fit/theory functions
Menu "Macros"
  "waves from params", make_waves_from_params()
end Menu

Macro init_theoryGlobals()
    string G emp_background | contains name of background wave
    string g peak1_wave="peak_1"
    string g peak2_wave="peak_2"
    string g peak3_wave="peak_3"
    string g peak4_wave="peak_4"
    string g this_bkgd_wave="bkgd"
    variable g guess_point | to initialize some parameters for
automated fits...
EndMacro

macro init_theory_waves()
    silent 1; pause update
    make_theory_waves()
end macro

macro make_theory_waves()
    silent 1; pause update
    if (exists(fit_wave)==1)
        Duplicate/O
$fit_wave,$peak1_wave,$this_bkgd_wave,$peak2_wave,$peak3_wave,$peak4_wave
```

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else
    make/o/n=2/d
$peak1_wave,$this_bkgd_wave,$peak2_wave,$peak3_wave, $peak4_wave
endif
end macro

Macro save_theory_specific_guess()  l this routine is called from
save_fit_params, to make any changes before saving, if needed
    variable/g hold_fitliml,hold_fitlimr
    silent 1;pauseupdate
    I guess that the peak 1 position is about in the same place for each spectrum
    $fitlimitwave[0]=hold_fitliml;$fitlimitwave[1]=hold_fitlimr
    Save/T/O/P=fit_folder
$coeffwave,$lowlim,$hilim,$varywave,$fitlimitwave,w_sigma as fit_wave+".fit"
End

Macro Load_fit(thefile)  l Loads wave from thefile, used in auto-fit extensively. The user should set this routine up so that if thefile is given, then the wave is loaded without user interaction. Then, it should finally pass the loaded wave name to autofit_loadfit_finish(wavename) function
    string thefile
    prompt thefile,"Which file to load?",popup,indexedfile(in_folder,-1,"TEXT")
    silent 1;pauseupdate
    LoadWave/T/O/P=in_folder/Q thefile  l get loaded with waves
    set_fit_wave(S_waveNames)  l ALWAYS call this.
end macro

Macro recall_theory_specific_guess(thewave,coeff)  l this routine is called from Load_Fit is invoked, setting up the params for automated fitting
    String thewave,coeff
      prompt thewave,"Which wave is target?",popup,wavelist("**","","")
prompt coeff,"Which wave is the coefficient wave?",popup,wavelist("**","","")
    variable/g guess_point,hold_fitliml,hold_fitlimr
    silent 1;pauseupdate
    Loadwave/T/O/p=fit_folder/Q thewave+".fit"
    $fitlimitwave[0]=leftx($fit_wave); $fitlimitwave[1]=rightx($fit_wave)-
deltax($fit_wave)
    $varywave=1;$varywave[0,3]=0;$varywave[11]=0;$varywave[6]=0
End
Macro do_theory_specific_stuff()  l first, fill all result-waves with their respective values
    silent 1;pauseupdate
    fill_with_THEORY(coeffs,destiny)
EndMacro
function fill_with_THEORY(w, dest)
    wave w, dest
    variable g V_FilterStart = 1
    variable npts = numpnts(dest)
    variable ncfs = numpnts(w)
    variable thispnt = 0
    do
        V_FilterStart = (ncfs + 1) * thispnt + 1
        dest[thispnt] = THEORY(w, pnt2x(dest, thispnt))
        thispnt += 1
    while (thispnt < npts) // as long as condition is true
end

old stuff from THEORY
$peak1_wave = w[3] * norm_voigt(w[5], (x - w[6]), w[4])
$peak2_wave = w[7] * norm_voigt(w[9], (x - w[10] - w[6]), w[8])
$peak3_wave = w[11] * norm_voigt(w[13], (x - w[14]), w[12])
$peak4_wave = w[15] * norm_voigt(w[17], (x - w[18] - w[14]), w[16])
$peak2_wave = w[7] * exp_step((x - w[10] - w[6]), w[8])
$peak3_wave = w[11] * exp_step((x - w[14]), w[12])
$peak4_wave = w[15] * exp_step((x - w[18] - w[14]), w[16])

$peak1_wave = w[3] * doniacsunjic(w[6], w[5], w[4], x)
$peak2_wave = w[7] * doniacsunjic(w[10] + w[6], w[9], w[8], x)
$peak3_wave = w[11] * doniacsunjic(w[14], w[13], w[12], x)
$peak4_wave = w[15] * doniacsunjic(w[18] + w[14], w[17], w[16], x)

w[21], w[20]))
w[21], w[20]))
w[21], w[20]))
w[21], w[20]))

w[21], w[20]))
w[21], w[20]))
I various functions and misc routines assoc. w/ fitting

Function THEORY(w,xx)

  wave w
  variable xx
  variable ncoeffs=numpnts(w) I number of coefficients in coeff wave
  variable npts=numpnts(destiny) I number of points in destination wave
  variable/g V_FitterStart I global used in fit routines
  variable pntnum=trunc((V_FitterStart-l)/(ncoeffs+l)) I which point is
  being requested, starts at zero
  variable cvard=V_FitterStart -1-pntnum*(ncoeffs+1)-1 I which
  coefficient is being varied. Value of -1 means no coeff is varied
  variable result=0; I return value
  wave peak_1=peak_1,
  peak_2=peak_2,peak_3=peak_3,peak_4=peak_4,bkgd=bkgd I definitions
  of sub-waves used
  variable p1res,p2res,p3res,p4res I temp value of subwave result for
  return value when cvard is -1 recalc the subwave

I convLSwExp arguments are destw,pos,lwid,larea,expwid,stepht

  I peak_1 part
  if ( (cvard==-1 )%& (pntnum==0)) I true means recalc the wave
    lprint "recalc peak_1"
    convLSwExp(peak_1,w[5],w[5],w[5],w[4],w[1])
  endif
  p1res=peak_1[pntnum] I default return value

  if (cvard==6) I parameter 6 has been varied, used temp saved calc for result
    if (pntnum==0) I recalc the wave if first time through
      lprint "recalc peak_1b"
      duplicate/o peak_1,peak_1b
      convLSwExp(peak_1b,w[6],w[5],w[5],w[4],w[1])
    endif
    p1res=peak_1b[pntnum]
  endif

  if (cvard==5) I parameter 5 has been varied
    if (pntnum==0) I recalc the wave if first time through
      lprint "recalc peak_1c"
      duplicate/o peak_1,peak_1c
      convLSwExp(peak_1c,w[6],w[5],w[5],w[4],w[1])
    endif
    p1res=peak_1c[pntnum]
  endif

  if (cvard==3) I parameter 3 has been varied
    if (pntnum==0) I recalc the wave if first time through
      lprint "recalc peak_1d"
      duplicate/o peak_1,peak_1d
      convLSwExp(peak_1d,w[6],w[5],w[5],w[4],w[1])
endif
p1res=peak_1d[pntnum]
endif

if (cvard==4) I parameter 4 has been varied
    if (pntnum==0) I recalc the wave if first time through
    lprint "recalc peak_1e"
        duplicate/o peak_1,peak_1e
        convLSwExp(peak_1e,w[6],w[5],w[3],w[4],w[19])
    endif
    p1res=peak_1e[pntnum]
endif

if (cvard==19) I parameter 4 has been varied
    if (pntnum==0) I recalc the wave if first time through
    lprint "recalc peak_1f"
        duplicate/o peak_1,peak_1f
        convLSwExp(peak_1f,w[6],w[5],w[3],w[4],w[19])
    endif
    p1res=peak_1f[pntnum]
endif

result+=p1res

I peak_2 part
if ( (cvard==-1) & (pntnum==0) ) I true means recalc the wave
    convLSwExp(peak_2,w[6]+w[10],w[9],w[7],w[8],w[20])
endif

p2res=peak_2[pntnum] I default return value

if (cvard==10) I parameter 6 has been varied, used temp
    if (pntnum==0) I recalc the wave if first time through
    duplicate/o peak_2,peak_2b
    convLSwExp(peak_2b,w[6]+w[10],w[9],w[7],w[8],w[20])
    endif
    p2res=peak_2b[pntnum]
endif

if (cvard==9) I parameter 5 has been varied
    if (pntnum==0) I recalc the wave if first time through
    duplicate/o peak_2,peak_2c
    convLSwExp(peak_2c,w[6]+w[10],w[9],w[7],w[8],w[20])
    endif
    p2res=peak_2c[pntnum]
endif

if (cvard==7) I parameter 3 has been varied
    if (pntnum==0) I recalc the wave if first time through
    duplicate/o peak_2,peak_2d

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convLSwExp(peak_2d, w[6]+w[10], w[9], w[7], w[8], w[20])
endif
p2res=peak_2d[pntnum]
endif
if (cvard==8) I parameter 4 has been varied
if (pntnum==0) I recalc the wave if first time through
duplicate/o peak_2, peak_2e
convLSwExp(peak_2e, w[6]+w[10], w[9], w[7], w[8], w[20])
endif
p2res=peak_2e[pntnum]
endif
if (cvard==20) I parameter 4 has been varied
if (pntnum==0) I recalc the wave if first time through
duplicate/o peak_2, peak_2f
convLSwExp(peak_2f, w[6]+w[10], w[9], w[7], w[8], w[20])
endif
p2res=peak_2f[pntnum]
endif
p3res=p2res
result+=p2res
I peak_3 part
if ( (cvard==-1) && (pntnum==0)) ltrue means recalc the wave
convLSwExp(peak_3, w[14], w[13], w[11], w[12], w[21])
endif
p3res=peak_3[pntnum]
I default return value
if (cvard==14) I parameter 6 has been varied, used temp
saved calc for result
if (pntnum==0) I recalc the wave if first time through
duplicate/o peak_3, peak_3b
convLSwExp(peak_3b, w[14], w[13], w[11], w[12], w[21])
endif
p3res=peak_3b[pntnum]
endif
if (cvard==13) I parameter 5 has been varied
if (pntnum==0) I recalc the wave if first time through
duplicate/o peak_3, peak_3c
convLSwExp(peak_3c, w[14], w[13], w[11], w[12], w[21])
endif
p3res=peak_3c[pntnum]
endif
if (cvard==11) I parameter 3 has been varied
if (pntnum==0) I recalc the wave if first time through
duplicate/o peak_3, peak_3d
convLSwExp(peak_3d, w[14], w[13], w[11], w[12], w[21])
endif
p3res=peak_3d[pntnum]
196
endif
if (cvard==12)  
  I parameter 4 has been varied
  if (pntnum==0) I recalc the wave if first time through
  duplicate/o peak_3,peak_3e
  convLSwExp(peak_3e,w[14],w[13],w[11],w[12],w[21])
endif
p3res=peak_3[e][pntnum]
endif
if (cvard==21)  
  I parameter 4 has been varied
  if (pntnum==0) I recalc the wave if first time through
  duplicate/o peak_3,peak_3f
  convLSwExp(peak_3f,w[14],w[13],w[11],w[12],w[21])
endif
p3res=peak_3[f][pntnum]
endif
result+=p3res

I peak_4 part
if ( (cvard=-1 )%& (pntnum==0)) I true means recalc the wave
  convLSwExp(peak_4,w[18]+w[14],w[17],w[15],w[16],w[22])
  w[22]=w[21]/2
endif
p4res=peak_4[pntnum]  
  I default return value
if (cvard==18)  
  I parameter 6 has been varied, used temp
  saved calc for result
  if (pntnum==0) I recalc the wave if first time through
  duplicate/o peak_4,peak_4b
  convLSwExp(peak_4b,w[18]+w[14],w[17],w[15],w[16],w[22])
endif
p4res=peak_4[b][pntnum]
endif
if (cvard==17)  
  I parameter 5 has been varied
  if (pntnum==0) I recalc the wave if first time through
  duplicate/o peak_4,peak_4c
  convLSwExp(peak_4c,w[18]+w[14],w[17],w[15],w[16],w[22])
endif
p4res=peak_4[c][pntnum]
endif
if (cvard==15)  
  I parameter 3 has been varied
  if (pntnum==0) I recalc the wave if first time through
  duplicate/o peak_4,peak_4d
  convLSwExp(peak_4d,w[18]+w[14],w[17],w[15],w[16],w[22])
endif
p4res=peak_4[d][pntnum]
endif
if (cvard==16)  I parameter 4 has been varied
    if (pntnum==0)  I recalc the wave if first time through
duplicate/o peak_4,peak_4e
    endif
endif
convLSwExp(peak_4e,w[18]+w[14],w[17],w[15],w[16],w[22])
endif
p4res=peak_4e[pntnum]
endif
if (cvard==22)  I parameter 4 has been varied
    if (pntnum==0)  I recalc the wave if first time through
duplicate/o peak_4,peak_4f
    endif
endif
convLSwExp(peak_4f,w[18]+w[14],w[17],w[15],w[16],w[22])
endif
p4res=peak_4f[pntnum]
endif
result+=p4res

I background part
if ( ((cvard==-1)%I(cvard==0)%I(cvard==1))%& (pntnum==0)) ltrue
means recalc the wave
    bkgds =w[0] +xx*w[1] +x^2*w[2]
endif
result+=bkgds[pntnum]

V_FitlerStart+=l
return result

End

Macro make_waves_from_params()
      I assumes global coeffwave
is valid for these files
string thefile
variable count
silent 1;pauseupdate
make/n=2/O/d k_pk1,area_pk1,bkgd_scalar,area_pk1
make/n=2/O/d lwid_pk1,gwid_pk1,shirley_tail,nrg_pk1
count=0
thefile=TextFile(fit_folder,count)  I filename is returned
do
    Loadwave/T/O/Q/p=fit_folder thefile
    bkgd_scalar[count]=$coeffwave[0]
    area_pk1[count]=$coeffwave[2]
    area_pk2[count]=$coeffwave[8]

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\[ l\text{wid}_p k1[count]=\text{coeffwave}[4] \]
\[ g\text{wid}_p k1[count]=\text{coeffwave}[5] \]
\[ n\text{rg}_p k1[count]=\text{coeffwave}[3] \]
\[ s\text{hirley-tail}[count]=\text{coeffwave}[6] \]
\[ k\_pk1[count]=\text{coeffwave}[7] \]
\[ \text{count}+=1 \]
\[ \text{thefile}=\text{TextFile(fit\_folder,count)} \quad \text{I filename is returned} \]
\[ \text{if (count>1)} \]
\[ \text{if (CmpStr(thefile,\"\")!=0)} \]
\[ \text{insertpoints} \]
\[ \text{count},1,k\_pk1,area\_pk1,area\_pk2,bkgd\_scalar \]
\[ \text{insertpoints} \]
\[ \text{count},1,l\text{wid}_p k1,g\text{wid}_p k1,s\text{hirley-tail},n\text{rg}_p k1 \]
\[ \text{endif} \]
\[ \text{while (CmpStr(thefile,\"\")!=0)} \]
\[ \text{EndMacro} \]

<table>
<thead>
<tr>
<th>Miscellaneous Display Macros</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro \text{append_theory_specific_waves()} \</td>
</tr>
<tr>
<td>expects window for appending is</td>
</tr>
<tr>
<td>front one</td>
</tr>
<tr>
<td>silent 1;pauseupdate \</td>
</tr>
<tr>
<td>append \</td>
</tr>
<tr>
<td>$\text{peak1_wave},$this_bkgd_wave,$\text{peak2_wave},$\text{peak3_wave},$\text{peak4_wave}</td>
</tr>
<tr>
<td>lput the various other waves there.</td>
</tr>
<tr>
<td>\text{Sub_theory_plot_mode(peak1_wave)} \</td>
</tr>
<tr>
<td>\text{Sub_theory_plot_mode(this_bkgd_wave)} \</td>
</tr>
<tr>
<td>\text{Sub_theory_plot_mode(peak2_wave)} \</td>
</tr>
<tr>
<td>\text{Sub_theory_plot_mode(peak3_wave)} \</td>
</tr>
<tr>
<td>\text{Sub_theory_plot_mode(peak4_wave)} \</td>
</tr>
<tr>
<td>EndMacro</td>
</tr>
</tbody>
</table>

| Macro \text{fitwave\_plot\_mode()} \ |
| sets graphing characteristics of data |
| pauseupdate;silent 1 \ |
| dowindow/f $\text{fit\_winname}$ \ |
| if (exists(\text{fit\_wave})==1) \ |
| \text{Modifygraph} \ |
| \text{mode($\text{fit\_wave}$)=0,marker($\text{fit\_wave}$)=8,rgb($\text{fit\_wave}$)=(13233,5898,65535)} \ |
| end \ |
| End Macro |

| Macro \text{destwave\_plot\_mode()} \ |
| sets graphing characteristics of calculations |
| pauseupdate;silent 1 \ |
| dowindow/f $\text{fit\_winname}$ \ |
| \text{Modifygraph} \ |
| \text{mode($\text{dest\_wave}$)=0,rgb($\text{dest\_wave}$)=(65535,7,1)} \ |
| End Macro |

199
Macro Sub_theory_plot_mode(thewave) I sets look of user sub-theory plots
string thewave
prompt thewave,"Which wave to plot in sub_theory style?",popup,WaveList("\"","","")
pauseupdate;silent 1
dowindow/f fit_window
Modifygraph rgb($thewave)=(1048,50943,2769)
EndMacro

macro customize_fitwindow() I user hook to set fitwindow graph characteristics
pauseupdate;silent 1
dowindow/f $fitwinname
Modify tick=2
Modify mirror=1
Modify font="Times"
Modify minor=1
Modify fSize=12
Modify lblMargin(left)=11,lblMargin(bottom)=12
Label left "F'\"Times\"Z14Counts" 
Label bottom "F'\"Times\"Z14eV"
Textbox/N=fitwavetext/F=0/A=RT/X=5.23/Y=5.19 "\\%s",fit_wave)
end macro

Window fn196_9_FeN_plot() : Graph
PauseUpdate; Silent 1 I building window...
Display /W=(5,42,400,250) fn196_9_FeN
Cursor A fn196_9_FeN 1060;Cursor B fn196_9_FeN 1571
ShowInfo
EndMacro

Window fn196_13_FeN_plot() : Graph
PauseUpdate; Silent 1 I building window...
Display /W=(353,276,748,484) fn196_13_FeN
Cursor A fn196_13_FeN 731.832;Cursor B fn196_13_FeN 758.099
ShowInfo
EndMacro

Window fn196_9_FeNnorm_plot() : Graph
PauseUpdate; Silent 1 I building window...
Display /W=(55,52,450,260) fn196_9_FeNnorm
EndMacro

Window fn196_13_FeNnorm_plot() : Graph
PauseUpdate; Silent 1 I building window...
Display /W=(49,281,444,489) fn196_13_FeNnorm
EndMacro
Figure 1. Typical curve fitting of XMCD data (left polarized light, -3 T applied field) for $\alpha'/\alpha''$ FeN film with four-peak deconvolution.
Table I. Parameters from Igor Pro fitting program for FeN film corresponding to fitting curves in Figure 1. Constant parameters with a value of 1 are fixed.

<table>
<thead>
<tr>
<th>Point</th>
<th>Coefficients</th>
<th>Constant parameters</th>
<th>Fitting range (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bkgd (quadratic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 Constant c</td>
<td>9.44213</td>
<td>1</td>
<td>680</td>
</tr>
<tr>
<td>1 Constant b (x)</td>
<td>-0.012276</td>
<td>1</td>
<td>760</td>
</tr>
<tr>
<td>2 Constant a (x^2)</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Peak 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity</td>
<td>1.22111</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Lorentz. width</td>
<td>1.09158</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Exp. width</td>
<td>0.4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Position</td>
<td>709.1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Peak 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity</td>
<td>0.364945</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Lorentz. width</td>
<td>0.928108</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Exp. width</td>
<td>0.4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Position</td>
<td>12.9</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Peak 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity</td>
<td>0.977831</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Lorentz. width</td>
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</tr>
<tr>
<td>Exp. width</td>
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</tr>
<tr>
<td>Position</td>
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<tr>
<td>Peak 4</td>
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<tr>
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<td>0</td>
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</tr>
<tr>
<td>Lorentz. width</td>
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</tr>
<tr>
<td>Exp. width</td>
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</tr>
<tr>
<td>Position</td>
<td>12.9</td>
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</tr>
<tr>
<td>Step height</td>
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<tr>
<td>Peak 1</td>
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<tr>
<td>Peak 2</td>
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<tr>
<td>Peak 3</td>
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<tr>
<td>Peak 4</td>
<td>0.00026618</td>
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</table>