Lawrence Berkeley National Laboratory
Recent Work

Title
THE EFFECT OF VERY HIGH PRESSURES ON THE MOSSBAUER SPECTRUM OF Fe57 IN IRON METAL

Permalink
https://escholarship.org/uc/item/73k7z6xv

Author
Nicol, Malcolm Foertner.

Publication Date
1963-08-01
University of California
Ernest O. Lawrence Radiation Laboratory

THE EFFECT OF VERY HIGH PRESSURES ON THE MOSSBAUER SPECTRUM OF Fe$^{57}$ IN IRON METAL

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
THE EFFECT OF VERY HIGH PRESSURES ON THE MOSSBAUER SPECTRUM OF \( \text{Fe}^{57} \) IN IRON METAL

Malcolm Foertner Nicol
(Ph.D. Thesis)
August 1963

Reproduced by the Technical Information Division directly from author's copy.
# Table of Contents

Abstract .................................................. iii

I. Introduction .............................................. 1

II. Some Thoughts Behind the Experiment .................. 4

  A. Pressure and Recoilless Radiation .................... 7
  B. Fe\(^{57}\), the Mössbauer Nucleus ................... 10
  C. Magnetic Field at the Nucleus in a Ferromagnet .... 18
      1. Magnetic Field at the Nucleus Due to Atomic Electrons ....... 19
      2. Magnetic Field at the Nucleus of an Atom in a Solid ........ 21
      3. Origin of Ferromagnetism in Iron .................... 23
      4. Ferromagnetism and the Magnetic Field at the Nucleus ....... 28
      5. Magnetic Field at the Nucleus in Iron and the Effect of Pressure ...... 29
  D. Phases of Iron ........................................... 33

III. Details of the Experiment ............................. 35

  A. High-Pressure Techniques ............................. 35
  B. Sample ................................................ 36
  C. Pressure Scale ......................................... 41
  D. Spectrometer .......................................... 38
      1. Mechanical Assembly .................................. 38
      2. Electronics ......................................... 42
      3. Calibration ......................................... 47

IV. Results Obtained from the Experiment ................. 51

V. Conclusions .............................................. 67

Acknowledgements ........................................... 69

References .................................................. 70
THE EFFECT OF VERY HIGH Pressures ON THE
MOSSBAUER SPECTRUM OF Fe\(^{57}\) IN IRON METAL

Malcolm Foertner Nicol

Inorganic Materials Research Division,
Lawrence Radiation Laboratory and Chemistry Department
University of California, Berkeley, California

August 1963

ABSTRACT

A velocity-sweep type high-pressure Mössbauer spectrometer has been
developed for use at pressures to 150-kbar and greater. This spectrometer
was used to study the effect of pressure on the Mössbauer spectrum of Fe\(^{57}\)
in metallic iron to a pressure presumably higher than 140 kbar. At pressures
up to 120 kbar, a six-line spectrum characteristic of \(\alpha\)-iron was observed.
A seventh line appeared in the spectrum obtained at 140 kbar. This line
was attributed to the appearance of the high-pressure phase of iron. The
variation of the magnetic splitting of the Mössbauer spectrum in the \(\alpha\)-iron
phase compared favorably with results obtained at lower pressures by nuclear
magnetic resonance. The experiment indicates that Mössbauer spectroscopy
can be usefully applied to the study of magnetic materials at high pressures,
and some additional experiments are suggested.
Recoilless emission and absorption of gamma radiation in solids has been employed for a great variety of precise scientific experiments since its discovery in 1958 by Rudolf Mössbauer. These experiments range from tests of the theory of relativity to studies of rate processes in crystallizing solids. The effect, called the Mössbauer effect, has been observed in many isotopes among the heavy elements. However, the greatest fraction of recoilless radiation is found in the 14-keV radiation from the isotope Fe$^{57}$ because of a combination of favorable conditions; and the Mössbauer effect in Fe$^{57}$ has been the subject of a broad and thorough investigation. The Mössbauer spectrum of Fe$^{57}$ in metallic iron has been studied at temperatures from the liquid-helium range to above 1300°F. The Fe$^{57}$ spectrum also has been studied for iron as an impurity in many elements and alloys as well as for iron containing compounds ranging from simple oxides and fluorides to molecules as complex as ferrocene. The many uses to which the effect with this one isotope have been applied arise from the extremely sensitive involvement of the nucleus with the atomic environment in solids. The Mössbauer spectrum of Fe$^{57}$ provides direct information about the magnetic field and electric field gradients at the nucleus. The Mössbauer spectrum also can be used to aid in identifying the lattice symmetry, to estimate the electronic density at the nucleus, and to infer the electronic state of the iron atom. For high-pressure research, the Mössbauer effect appears to promise a wealth of information about changes on the atomic scale resulting from compression of solids; this information cannot be extracted from studies of macroscopic properties to which high-pressure research so often is limited.
The experiment that is reported here has two purposes: to establish experimental conditions for observing the Mössbauer effect in materials at high pressures, and to investigate the atomic origin of ferromagnetism in transition metals. Although this is not the first Mössbauer experiment in the high-pressure range, major improvements were made in experimental techniques. With these improvements, detailed spectra were readily observed at pressures up to three times as high as in the previous experiment. With respect to the study of ferromagnetism, this experiment also extended the pressure range available for study to many times that available when this investigation was conceived. Results obtained are in excellent agreement with lower-pressure Mössbauer experiments and other magnetic studies, which only recently have been extended to the pressure range of this experiment. This experiment also provides the first evidence concerning the magnetic properties of the high-pressure phase of iron metal.

As an investigation of magnetic behavior at high pressures, this experiment is only a stepping stone. Ferromagnetism can be explained in terms of a coupling of magnetic moments associated with electronic spin. The Mössbauer effect measures the magnetic field at the nucleus due to the electronic environment of the nucleus, and the temperature dependence of the magnetic field at constant pressure appears to measure the strength of the coupling. Unlike the temperature dependence, however, the pressure dependence of the magnetic field at the nucleus does not follow the pressure dependence of the magnetic coupling directly. The present experiment and other experiments on iron indicate that the relation of the pressure dependence of the magnetic field at the nucleus to the variation of the ferromagnetic coupling with pressure is straightforward. However, this relation must be checked in further experiments by determining the temperature dependence of the magnetic field at the nucleus.
in iron at a number of pressures. Also, the applicability of this correction to other ferromagnets, as well as to impurity nuclei in iron, should be investigated.

The present experiment, outlined briefly above, is discussed in much greater detail in the following sections. Section II reviews the background on which the experiment was designed, while Secs. III and IV describe the equipment, operations, and results of the experiment. Throughout this discussion attention is centered on relationships that could be important in investigating the effect of high pressure on ferromagnetism, besides the direct application of high-pressure experimental to Mössbauer-effect studies. Unfortunately, the conclusions most frequently reached are that the problem is too complex for the available theoretical treatments to be useful and that sufficient experimental data are not yet available for empirical evaluation of the necessary relationships. However, the effort expended on this experiment serves as a foundation on which further and, hopefully, quite profitable investigations can be based.
II. SOME THOUGHTS BEHIND THE EXPERIMENT

The Mössbauer effect involves observation of gamma radiation emitted during a transition between nuclear states, either or both of which may be degenerate. Under the conditions that Mössbauer demonstrated, part of the radiation emitted in the decay of an excited state into the stable ground state of a nucleus in a solid can be obtained as energetically well-defined lines. The number of lines obtained depends on the possible removal of the degeneracies and on the selection rules for the nuclear transition. However, the width of these lines is limited only by the lifetime of the excited state by the Heisenberg uncertainty principle and by the uniformity of the chemical environment. Sufficiently narrow lines can be obtained in many cases to permit resolution of transitions that differ in energy only because the energy of the nuclear states is affected by their interaction with the Coulomb and magnetic fields produced by the electrons that surround the nucleus. The utility of the Mössbauer effect in studying chemical environments arises because of the influence of these electrons on the spectrum of the γ radiation emitted from the transiting nucleus.

The influence of these electrons can be illustrated in terms of the Coulomb interaction. This interaction can be expressed in terms of moments of the nuclear charge distribution interacting with spatial derivative of the electron Coulomb potential. The interaction of the zero-order moment, the nuclear charge, with the electric potential at the nucleus cannot reduce the degeneracy of the nuclear states but only can shift the energy of these states. The magnitude of the shift depends on the electronic charge contained within the nuclear volume. If the nuclear states involved in the transition have different volumes, this zero-moment interaction
differs between states; and the γ-ray energy varies with the electronic charge density at the nucleus. This shift commonly is referred to as the chemical or isotope shift.

The interaction of higher-order electric moments can reduce the degeneracy of the nuclear states. However, many of these higher moments are prohibited by the symmetry of the nucleus and its environment. Thus, non-zero odd-order nuclear electric moments are prohibited by the inversion symmetry of the nucleus. The axial symmetry of the nucleus around the direction of the nuclear spin limits the highest-order moment that may be observed for a nuclear state of a given spin, and electric quadrupole moments are prohibited for nuclear states with \( I < 1 \) by this restriction. The symmetry of the electronic charge distribution also may prohibit higher-order interactions. In a perfect cubic lattice, the electric field gradient at the nucleus along the three principal axes must be zero; and the degeneracy of nuclear states cannot be lifted by nuclear electric-quadrupole-moment interactions in this lattice system. Because of restrictions such as these, the details of the Mössbauer spectrum can be used to characterize the nuclear states involved in the transition, as well as to study the symmetry of the lattice in which the nucleus is located.

The energy shifts produced by these electron–nucleus interactions are small with respect to the energy differences between nuclear states, and mixing of these states does not have to be considered. These interactions often also do not mix the electronic states of the solid. In this latter case these interactions can be treated semi-classically, e.g., as the interaction of a quantized nuclear magnetic moment with a
stationary magnetic field due to the electrons. Exact quantum mechanical knowledge of either the nuclear or the electronic states involved is not necessary for this treatment; the emission spectrum can be used to identify and to describe these states. If the properties of the nuclear states are known, the nucleus can be used in this respect as a probe into the electronic structure of solids, as evidenced by a long history of nuclear-magnetic-resonance and Mössbauer experiments.

In order to make use of the Mössbauer effect, a means of detecting the recoilless radiation and of measuring the differences in transition energies between the nondegenerate lines is needed. The conditions required for sharp absorption lines are identical to those for emission of sharp γ-ray lines, and the absorptions of the ground state of a Mössbauer nucleus provide well defined energies. These absorptions can be used to detect recoilless radiation by observing the intensity of the radiation transmitted through an absorber containing the Mössbauer nucleus in its ground state as the relative energies of the emitting and absorbing nuclei are shifted. The transmitted intensity decreases when the energies of an emission and an absorption coincide.

All the information about the electron - nucleus interaction appears as shifts in the energy of the nuclear states, and only energy differences need to be measured to describe these interactions. The absorption technique also can be used to determine the energy differences between the components of the emission spectra if the energy shift between the emitting and absorbing nuclei can be measured. The absolute energy of either nuclear transition does not have to be known, but all measurements can be referred to a particular absorption. In Fe⁵⁷ work, stainless steel often is used for the reference because Fe⁵⁷ nuclear states are unsplit in this
This produces a single absorption line. The energy shift is accomplished by Doppler shifting the absorber with respect to the source and is measured in terms of the velocity of the absorber relative to the source. This velocity $v$ can be converted to an energy if the $\gamma$-ray energy $E_\gamma$ is known by

$$\Delta E = \frac{v}{c} E_\gamma,$$  \hspace{1cm} (2.1)

where $c$ is the velocity of light. A shift of 1 mm/sec corresponds to $4.79 \times 10^{-8}$ eV for the 14-keV radiation of Fe$^{57}$. This technique measures the energy differences due to the electron - nucleus interaction directly and alleviates the problems associated with measuring very small differences in a very large energy to obtain accurate information about the electronic environment of the nucleus.

The theory of the Mössbauer effect and the important nucleus - electron interactions have been worked out quite thoroughly; many techniques by which these measurements can be made are available in the literature. It would serve little purpose to review this literature in depth here as many excellent compendia can be found. In this section, only the most basic developments essential to the understanding and interpretation of those effects produced in the Mössbauer spectrum of Fe$^{57}$ in iron by application of very high pressures are discussed. The conditions for the emission of recoilless radiation are described in the following subsection, with emphasis placed upon those parameters that are influenced strongly by pressure. Those properties of the nuclear states of Fe$^{57}$ pertinent to the spectroscopy and those interactions that are expected to be important in iron metal will be discussed with respect to the existing experimental and theoretical understanding of metallic iron. This section concludes
with a discussion of the phase diagram of metallic iron in the pressure region of interest.

A. Pressure and Recoilless Radiation

Until Mössbauer's discovery of recoilless \( \gamma \) radiation, application of nuclear \( \gamma \)-ray absorption spectroscopy was limited severely by Doppler broadening of spectral lines due to nuclear motion, and by shifting of emission and absorption spectra due to nuclear recoil. Line broadening was thought to be the simpler problem to solve since nuclear motion can be reduced by imbedding the nucleus in a relatively rigid environment, such as solid lattice. Nuclear recoil, however, produces energy shifts between absorption and emission spectra that are orders of magnitude greater than both the natural line width of the gamma radiation and energy differences between nuclear substates.

The effect of recoil on the \( \gamma \)-radiation spectrum of a nucleus arises from the requirement of the law of conservation of momentum that, when a nucleus undergoes a transition of energy \( E \), emitting a photon, the nucleus must recoil with momentum equal in magnitude to that given the photon. Recoil requires energy \( R \), which must come from the nuclear transition. This recoil energy is not available to the photon, and the photon energy differs from \( E \) by \( R \). In terms of the mass of the recoiling object \( m \) and the speed of light \( c \), the recoil energy is given by

\[
R = \frac{E^2}{2mc^2}, \tag{2.2}
\]

to zero order in \( R \).

In the absorption of a photon, a similar argument applies, except in this case the momentum of the photon must be transferred to the nucleus.
Recoil energy comes from the photon energy, which must exceed E by the energy of (2.2) for absorption. The centers of the absorption and emission spectra, therefore, are separated by 2R. Typically, 2R may be a few orders of magnitude greater than the width of the nuclear levels.

Mössbauer demonstrated that the recoil barrier to nuclear absorption spectroscopy also could be reduced by imbedding the nucleus in a solid lattice. The solid in effect increases the mass of the recoiling object from that of one nucleus by a factor of the order of $10^{23}$. Although on the average the energy going into recoil remains unchanged from that for the free nucleus, there is a finite probability that in a given $\gamma$ emission the population of phonon modes of the solid will not change. If no phonons are excited (or destroyed), no energy is taken from the $\gamma$ radiation for recoil. Only then, the photon and transition energies are equal. This argument applies equally to photon absorption. Thus, for recoilless events, the separation of absorption and emission spectra by 2R is reduced to zero.

The probability of recoilless radiation, or the recoil-free fraction $f$, can be expressed approximately by using the Debye model of a solid as the Debye-Waller factor of x-ray diffraction. The fraction $f$ is an indication of the coupling between an individual nucleus and the lattice as a whole. It is related to the Debye temperature $\Theta$ of the solid at temperature $T$ by (2.3), in which $k$ is the Boltzmann constant:

$$f = \exp \left\{ -\frac{6R}{kT} \left[ \frac{1}{4} + \left( \frac{T}{\Theta} \right)^2 \int_0^{\Theta/T} \frac{t}{e^t - 1} \, dt \right] \right\}. \quad (2.3)$$

From (2.3), it is apparent that recoilless radiation is enhanced by low $\gamma$-ray energies, low temperatures, high masses, and high Debye temperatures. These conditions for Mössbauer spectroscopy are fulfilled quite well by Fe$^{57}$. The 14-keV radiation is one of the lowest known $\gamma$ energies and is quite well
separated from other energies involved in the production of the excited state of Fe$^{57}$. The Debye temperature of iron metal, 467°K, is quite high.\textsuperscript{1} The Mössbauer spectrum of Fe$^{57}$ has been observed in iron metal at 1 atm to temperatures\textsuperscript{9} above 1300°K, in contrast with the inability to detect a measurable fraction of recoilless radiation at room temperature for most Mössbauer nuclei. The recoil-free fraction observed at room temperature for Fe$^{57}$ in metallic iron characteristically is of the order of 0.4.

The Debye approximation is an adequate qualitative description of the recoil-free fraction. However, the insensitivity of this approximation to the details of the high-frequency modes of the phonon spectrum, which Lipkin demonstrated to be very important in conservation of the average recoil momentum,\textsuperscript{10} makes quantitative agreement quite poor. Debye temperatures measured by the recoil-free fraction typically differ by a factor of two from those obtained by thermal measurements.\textsuperscript{12} Thus the Mössbauer effect is not a good tool for studying the thermodynamic properties of materials.

The most important information contained in the Debye-Waller factor to the high pressure experimenter is the dependence of the intensity of recoilless radiation on the Debye temperature of the lattice. In this approximation, the Debye temperature measures the highest vibrational frequency of the lattice and varies with pressure in the same manner as the vibrational frequencies. This variation is expressed approximately by the Grüneisen relation:\textsuperscript{13}

\[ \gamma = -\frac{d \ln \theta}{d \ln V} \quad (2.4) \]

For iron,\textsuperscript{14} the Grüneisen constant $\gamma$ is approximately 1.6. It is apparent from (2.4) that the Debye temperature is increased by compression of the lattice, or by increased pressure. This effect has been discussed in detail by Hanks\textsuperscript{15} for the region $T \ll \theta$, which is close to the conditions of this
experiment. An increase of a factor of 2.3 in the recoil-free fraction to 130 kbar is estimated on the basis of Hanks' theory for Fe$^{57}$ in iron metal. The qualitative behavior of the recoil-free fraction with pressure was verified in an earlier Mössbauer experiment at high pressures with the nucleus Dy$^{161}$ in gadolinium metal, by Stone et al.$^3$

Other factors, however, also make important contributions to the apparent fraction of recoilless radiation observed in this experiment. The attenuation of the 14-keV radiation by the walls of the pressure chamber is severe because of the low energy of the Fe$^{57}$ radiation. Furthermore, as the pyrophyllite gasket containing the sample is compressed this attenuation increases. The 123-keV radiation, however, is only weakly scattered by the gasket. Some of this higher-energy radiation appears as 14-keV radiation electronically, because it is incompletely absorbed by the detector. As the increase of the attenuation of the 14-keV radiation with respect to this other radiation can be greater than the increase of the recoil-free fraction, the observed recoil-free fraction can decrease with pressure.

B. Fe$^{57}$, the Mössbauer Nucleus

In this experiment, the excited states of Fe$^{57}$ were produced from the electron-capture decay of Co$^{57}$. The decay scheme for this process is shown in Fig. 2.1. The Co$^{57}$ captures an orbital electron to form the 137-keV state of Fe$^{57}$ with a half-life of 270 days. This half-life is longer by many orders of magnitude than the half-lives of the other decays involved and controls the intensity of the 14-keV radiation. For counting periods of the order of a day, the decay rate is nearly constant.

The 137-keV state of Fe$^{57}$ may decay directly to the ground state. However, the decay of this state proceeds through a state 14.37-keV above the ground state in 91% of the disintegrations, with the emission of a
Fig. 2.1 Energy-level diagram of $^{57}$Co and daughter nuclei. (Source: reference 47.)
123-keV γ ray. The 14-keV state decays directly to the ground state by γ radiation, which is the radiation used for Mössbauer spectroscopy. The polarization of this radiation is that of a magnetic dipole, the contribution of electric quadrupole radiation being at least four orders of magnitude lower.\(^{17}\)

The properties of the ground state and the 14-keV state which influence the Mössbauer spectrum are well known. The most important of these properties are tabulated in Table II. Both states have nonzero spins. The resulting magnetic moments, interacting with a magnetic field \(H(0)\), split the degeneracies of these states according to

\[
E_m - E_0 = -\frac{\mu m}{I} H(0),
\]

where \(\mu\) is the magnetic moment of the state with spin \(I\) and \(m\) is the component of the spin along \(H(0)\) for the particular nuclear sublevel. In \(\text{Fe}^{57}\), a magnetic field at the nucleus splits the ground state into a doublet, and the 14-keV state into a quartet.

The 14-keV state has an electric quadrupole moment\(^{16}\) that splits the state into a doublet in the presence of an electric field gradient. No quadrupole moment is allowed the ground state because of the \(\frac{1}{2}\) spin. The interaction of a nuclear electric quadrupole moment \(eQ\) with a cylindrically symmetric electric field gradient \(eQ\) along the \(z\) axis is given by (2.6a);

\[
V = \frac{d^2 V}{dz^2} = V_{zz}
\]

\[
E_m - E_0 = \frac{e^2 Q}{4I(2I-1)} [3m^2 - I(I+1)].
\]

When the symmetry is not cylindrical, \(m\) may not be a good quantum number. Mixing of sublevels of different \(m\) depends upon the parameter
Table II.1. Properties of the Fe$^{57}$ Nuclear States

<table>
<thead>
<tr>
<th>State</th>
<th>Ground</th>
<th>14-keV</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>0</td>
<td>14.37</td>
<td>16</td>
</tr>
<tr>
<td>$I$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{3}{2}$</td>
<td>16</td>
</tr>
<tr>
<td>$\mu$(n.m.)</td>
<td>$\pm 0.0903$</td>
<td>$\pm 0.155^a$</td>
<td>9</td>
</tr>
<tr>
<td>Q (barns)</td>
<td>0</td>
<td>0.1</td>
<td>16</td>
</tr>
<tr>
<td>Lifetime</td>
<td>stable</td>
<td>1.0 x 10$^{-7}$</td>
<td>16</td>
</tr>
<tr>
<td>Decay</td>
<td>--</td>
<td>mL</td>
<td>17</td>
</tr>
<tr>
<td>Radius of nucleus (arb units)</td>
<td>1.000</td>
<td>0.998</td>
<td>18</td>
</tr>
</tbody>
</table>

$^a$ The absolute sign is uncertain in the literature, but the change of sign between states is well established.
\[ \eta = \frac{|V_{xx}| - |V_{yy}|}{|V_{zz}|}, \]

where \( V_{xx} \) is defined by (2.6a) by replacing \( z \) with \( x \). By convention, \( |V_{zz}| \geq |V_{xx}| \geq |V_{yy}| \). When both a magnetic field and an electric field gradient are present, the splittings of (2.5) and (2.6b) are additive only if the axial electric field gradient parallels the magnetic field.

The corrections due to misalignment of \( V_{zz} \) and \( H(0) \) in \( \alpha \)-iron, however, should be negligible as \( H(0) \) is very large and \( V_{zz} \) must be zero for the undistorted lattice.

The energy of the nuclear states also is affected by the Coulomb interaction with the electric charge density contained within the nuclear volume. The magnitude of this energy is a function of the charge density at the nucleus and the nuclear volume. In general, the interaction energy differs between nuclear states due to differences in nucleon distributions resulting in different volumes. The 14-keV state of \( \text{Fe}^{57} \) apparently has a smaller volume than the ground state. Therefore, the \( \gamma \)-ray energy decreases as the electronic density at the nucleus increases. For this experiment the interaction is independent of nuclear orientation since an orientation dependence would appear as a quadrupole interaction. This interaction produces a uniform shift of the emission spectrum relative to the absorption spectrum if the emitting and absorbing nuclei are in different environments. This uniform shift of the spectra is designated the chemical shift because of the sensitivity of the electronic density to the chemical environment of the atom, as well as to pressure and temperature.

The chemical shift is not a unique contribution to the shift of the emission and absorption spectra. A similar shift arises from a relativistic effect due to the vibration of nuclei; this effect also depends on chemical
environment. However, this second contribution may be small as Pound et al. observed for the shift in the Fe\(^{57}\) spectrum to 3kbar. The calculated relativistic correction accounted for less than 5% of the observed shift.

Walker et al. have interpreted the chemical shifts in the Fe\(^{57}\) spectrum relative to stainless steel for a number of configurations of the 3d and 4s electrons. They constructed the diagram shown in Fig. 2.2 which relates the chemical shift to the 4s electron density at the Fe\(^{57}\) nucleus from observed shifts in a number of chemical environments and estimates of the electronic configurations involved. These estimates can be used both to predict the electronic structure involved and to obtain a crude estimate of the compressibility of a given electronic configuration.

The difference between the energy of a given transition in the Fe\(^{57}\) emission spectrum \(E(m,m')\) and the absorption energy of Fe\(^{57}\) in stainless steel \(E'\) is given by

\[
E(m,m') - E' = \mu_0 H(0) \cdot \left(\frac{2\mu_e}{3\mu_0} \cdot m' - 2m\right) + \frac{e^2 Q}{12} \left(3m'^2 - \frac{15}{4}\right) + V_c \tag{2.7}
\]

where \(m\) and \(m'\) are the components along \(H(0)\) of the spins of the ground and excited states of Fe\(^{57}\), respectively; \(\mu_e/\mu_0\) is the ratio of the magnetic moments of the 14-keV and ground states; and \(V_c\) is the energy of the chemical shift. This equation may be simplified in terms of the parameters \(A\) and \(B\) defined by (2.8) and (2.9) which can easily be determined from the spectra [see (3.1) and (3.2)]:

\[
A = \mu_0 H(0) \tag{2.8}
\]

\[
B = \frac{1}{4} \frac{e^2 Q}{\mu_0} \tag{2.9}
\]

Thus,

\[
E(m,m') - E' = A \left(\frac{2m'}{3} - 2m\right) + B \left(m'^2 - \frac{5}{4}\right) + V_c. \tag{2.7a}
\]
Fig. 2.2 The dependence of the chemical shift on the electronic configuration of iron. (After Wertheim; source: ref. 18.)
The Fe$^{57}$ nuclear states are split by a magnetic field of 330.5 kG in ferromagnetic α-iron. This field produces splittings of the order of $10^{-7}$ eV between the otherwise degenerate nuclear sublevels. Upon application of an external magnetic field, the splittings decrease, which indicates that the field is directed oppositely, or is negative, with respect to the magnetization vector. The magnetic field at the nucleus varies similarly to the saturation magnetization as a function of temperature at 1 atm and goes to zero at the Curie temperature. Zero magnetic field also is observed in the high-temperature γ phase of iron.

The same field is observed in nuclear-magnetic-resonance experiments in iron. Recently Litster and Benedek observed that this magnetic field decreases linearly with pressure according to

$$\frac{d \ln H(0)}{d P} = -1.67 \times 10^{-4} \text{ kbar}^{-1}$$

in a nuclear-magnetic-resonance experiment to 65 kbar. The origin of this magnetic field is discussed in Section II. C.

No quadrupole contribution to the splitting is observed in α-iron because of the restrictions placed on the electric potential by the symmetry of the lattice. In a lattice with an axis of higher than twofold rotational symmetry, this axis must be the z axis of the electric field gradient and η will be zero. Obviously, a nonzero electric field gradient at the nucleus is allowed in a lattice with more than one such axis only if lower symmetry distortions exist. The body-centered cubic lattice of α-iron is such a lattice.

The electric field gradient is not restricted to zero in the hexagonal close-packed lattice. Thus, observation of a significant quadrupole contribution to the splitting could be used to identify such a structure for
the high-pressure iron phase (see sec. II.D). However, the pressure is applied uniaxially in this experiment to a nonhydrostatic-pressure medium (the iron). This permits large pressure gradients to form. Such pressure gradients can distort the cubic lattice sufficiently for the observation of quadrupole contributions to the splitting in the cubic phase. Therefore, observation of a quadrupole contribution to the splitting of the nuclear states is not a sufficient condition to establish a phase change to a non-cubic symmetry in this experiment.

C. Magnetic Field at the Nucleus in a Ferromagnet

A magnetic field of the order of 330 kG at an Fe$^{57}$ nucleus in α-iron due to the electrons is not explained on a simple basis. The symmetry of the body-centered cubic lattice prohibits direct interaction of the nucleus with d electrons, which commonly are thought to be responsible for both a local magnetic moment and the ferromagnetism. Higher-order connections to the direct interaction permitted by lower symmetry distortions also are inappropriate in both sign and magnitude to explain this field. Much of the difficulty arises from use of the familiar free-hydrogen-atom description of electronic states in metals without consideration of those interactions in many-electron condensed systems that mix one-electron hydrogen-atom states. Freeman and Watson$^{21}$ have studied this problem and have demonstrated the significance of many corrections to the one-electron-state model that are needed to describe the magnetic field observed at nuclei in ferromagnets. These corrections are intimately connected to the description of the origin of ferromagnetism, which is yet poorly understood on an atomic scale. The corrections also give some insight into possible applications of the Mössbauer effect to the study of magnetism.
It is beyond the scope of this work to present an authoritative interpretation of ferromagnetism and the relation of ferromagnetism to the magnetic field at the nucleus. However, it is appropriate to detail some of the current interpretation of these effects. In this discussion attention is focused on those parts of the explanation of these phenomena that appear to be similar. Unfortunately, the available theoretical interpretations are either too qualitative or too complex to be useful in interpreting the existing data. Therefore, this discussion centers on some aspects of ferromagnetism to which further experimentation with the Mössbauer effect might usefully be applied.

1. The Magnetic Field at the Nucleus Due to Atomic Electrons

The magnetic field with which the magnetic moment of the nucleus interacts can be attributed to a combination of three effects. (This experiment was performed in zero external magnetic field, and the contribution of external fields will not be discussed.) These are most conveniently divided into two fields due to the motion of electrons outside the nucleus and a field due to penetration of electrons into the nucleus. The interaction of the nuclear magnetic moment with electrons outside the nucleus consists of a contribution from the current loop produced by the orbital motion of the electronic charge around the nucleus and a contribution from the dipole-dipole interaction with the magnetic dipole associated with the electronic spin. Smaller higher-order terms can be neglected. The fields produced by these contributions in an atom are given by the diagonal matrix elements of

\begin{align}
H_L &= -2\beta \sum_i \frac{j_i}{r_i^3}, \quad (2.11) \\
H_S &= 2\beta \sum_i \frac{1}{r_i^3} (s_i - \frac{(r \cdot s_i)r_i}{r_i^2}), \quad (2.12)
\end{align}
where $\ell_i$ and $s_i$ are the one-electron operators for orbital and spin angular momenta, respectively; $r_i$ is the position operator of the $i$th electron; and $\beta$ is the Bohr magneton. As the expectation value of $\ell_i$ is zero for an $s$ electron, $H_\ell$ is zero for an $s$ electron.

The magnetic field resulting from the penetration of the electronic charge into the nucleus was discussed by Fermi. Electronic wave functions for atoms go as $r^2$ near the nucleus; the penetration is nonzero only for $s$ states ($\lambda = 0$) in a point-nucleus approximation. The field due to $s$ electrons at the nucleus can be expressed approximately by

$$H_F^i = \frac{16\gamma}{3} \sum_i <s_i> \left| \psi_i(0) \right|^2,$$

where $\psi_i(0)$ is the electronic wave function at the nucleus, and the summation extends over all $s$ electrons; $<s_i>$ is the time average of the electronic spin over an interval at least of the order of $\hbar/\omega H$. Corrections for a finite nucleus and the contribution of states without $s$ character can be calculated in principle. However, detailed information about nuclear and electronic wave functions is needed for this calculation. It is not unreasonable to assume that the interaction depends on electronic variables in a manner similar to (2.13) and that $H_F$ is linear in the spins of all the electrons in an atom.

These three fields are not oriented in a laboratory axis system for a free atom if no external magnetic field is present. Furthermore, $\sum_i <s_i>$ are zero when these summations are carried over a completely filled shell. Therefore, completely filled shells do not contribute a magnetic field at the nucleus if the radial wave functions do not depend on the signs of the orbital and spin angular moments. Spin-dependent electron-electron interactions in many electron systems can destroy the symmetry of the electronic
terms in the Hamiltonian with respect to spin direction. This can remove
the independence of the radial one-electron wave functions on spin in
with unfilled electronic shells; filled shells on such atoms can contribute
to the magnetic field at the nucleus.

2. Magnetic Field at the Nucleus of an Atom in a Solid

The presence of adjacent atoms in solids adds terms to the Hamiltonian
that have lower symmetry than the spherical symmetry of the free-atom
Hamiltonian. These lower-symmetry terms dominate the influence of the free-
atom terms for some electronic states and mix states from different atomic
sites into electronic states characteristic of the solid, rather than a
particular atom. The extent to which atomic states are mixed is usually
small for all but the most energetic states such as the 4s states of iron.
Thus electronic states in metals may be conveniently divided into two broad
classes: the localized core states, for which the free-atom description is
useful; and the highly nonlocal nearly-free-electron states, for which the
presence of the atomic cores appears as a perturbation on a background of
a uniformly attractive potential. The division of electronic states into
the two types is not sharp, and the 3d states in iron may represent an inter-
mediate case. Furthermore, the degeneracy of the free-atom 3d states can be
reduced by the symmetry of the solid, giving rise to both core-like and
nonlocal-like 3d states.

Nonlocal states in solids are important in understanding the coupling
of electronic states localized around different lattice sites. They produce
the bonding of atoms into the solid and can be used to explain the ferro-
magnetic coupling of the local magnetic moments. They also are the most
sensitive electrons with respect to the lattice. Inasmuch as these states
are not associated with particular atoms, however, free-atom phenomena such
as the orbital angular momenta lose their meaning for electrons in these states. Thus nonlocal electrons do not contribute to $H_2$ or $H_S$ of (2.11) or (2.12). Electron spin, however, is not a free-atom phenomenon and nonlocal states are not prohibited from contributing to the magnetic field at the nucleus through a Fermi contact interaction.

The lattice symmetry also restricts the properties of the core electronic states. Thus the electric potential must be the same along each of the three (100) directions of high symmetry in the perfect cubic lattice, and the spatial distribution of the electrons must be equivalent along each of these axes. The expectation value of $m_2$ along one of these axes can be used as a constant of motion to describe the electronic distribution, but it can be nonzero along only one direction. Therefore, the time average of the three components of the electronic orbital angular momentum of the core states must be zero in a cubic lattice; time average quantities such as $H_S$ that depend on the direction of the electronic orbital angular momentum are quenched by this symmetry.

The dipole-dipole interaction giving $H_S$ depends on the symmetry of the electronic distribution in a similar manner, and this also is quenched in perfect cubic symmetry. Nonzero values of $H_2$ and $H_S$ in cubic phases, although not necessarily small, arise only because of distortions of lower symmetry. Marshall\textsuperscript{23} studied these higher-order corrections for transition metals and estimated the magnitude of these higher-order corrections to the magnetic field at the nucleus. These corrections (of the order of 50 to 100 kG) are directed parallel to the magnetization. The observation that the magnetic field at an Fe\textsuperscript{57} nucleus in metallic iron is directed oppositely to the magnetization indicates that these higher-order corrections alone are insufficient to explain the magnetic field.
The only remaining interaction to which the large field can be attributed is the Fermi contact interaction. However, besides involving non-\( s \) states, the sign of the field is inappropriate for a direct Fermi contact interaction with the moment-carrying \( 3d \) states. The field can be explained in terms of an indirect Fermi contact interaction through an exchange polarization within the core states. This interaction is closely associated with the problem of ferromagnetic coupling and will be discussed after a brief development of some theories of the atomic origin of ferromagnetism.

3. Origin of Ferromagnetism in Iron

Unlike the electronic orbital angular momentum, the spin angular momentum of the core electrons is not quenched by the symmetry of the cubic lattice of \( \alpha \)-iron. In fact, a combination of spin-dependent interactions that stabilize nonzero spin configurations appear among the electronic terms of the Hamiltonian. One such interaction is that between electrons of the same core shell, which gives rise to Hund's rule for free atoms. This rule states that the ground electronic state of an atom is that combination of one-electron states in which the spin is a maximum. This rule can be derived on a purely electrostatic basis and usually carries over directly to the solid for core electrons. Predominance of this interaction over other spin-dependent interactions in iron for those electrons in the unfilled set of \( 3d \) core states can account for a local magnetic moment.

Spin-dependent or exchange interactions are not restricted to electrons within the same atomic shell. In the Heitler-London treatment of the hydrogen molecule, an exchange term removes the degeneracy of singlet and triplet states. Heisenberg suggested \(^{24}\) that the stability of a parallel-spin ferromagnetic state in iron also can be explained by exchange. However, a direct connection between exchange in metallic iron and in molecular hydrogen is
complicated by the large difference in the number of electrons involved. The exchange interaction in hydrogen involves only two electrons and, therefore, only matrix elements between those states directly coupled by the interaction. This often is called direct exchange. In iron, however, processes in which two states are coupled through interactions with a possibly virtual intermediate state can be of primary importance. This coupling is called indirect exchange although the division is conceptual and, therefore, somewhat arbitrary. Both direct and indirect exchange have been used to describe ferromagnets. Some of these descriptions are developed in this section to illustrate the possible behavior of the electronic system in iron.

Dirac demonstrated\(^\text{25}\) that the exchange coupling suggested for transition metal ferromagnets by Heisenberg could be obtained by the inclusion of a term in the Hamiltonian

\[
\hat{H}_e = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{2.14}
\]

where \(\mathbf{S}_i\) and \(\mathbf{S}_j\) are the spins of the \(i\)th and \(j\)th core electrons on neighboring atoms. In the general form, \(J_{ij}\) is an operator on the electronic and spin coordinates of these electrons. A positive \(J_{ij}\) makes the mixing of those states with spin parallel, stable with respect to the combination with the spins antiparallel. The problem of the origin of ferromagnetism is then reduced to determining the appropriate \(J_{ij}\)'s.

This model was extended in terms of the direct exchange interaction by Bethe.\(^\text{26}\) He assumed that only the direct \(d\)-\(d\) exchange between nearest neighbors was important and that \(J\) was isotropic. By using these assumptions, the energy of magnetization can be calculated (2.14a) by summing the diagonal matrix elements of (2.14) over the electrons on adjacent atoms:
where \( S_i \) is now the total spin of the d electrons on the \( i \)th atom, and the summation extends over all neighbors \( j \) of every atom \( i \). (This equation can be used to describe the thermodynamics of ferromagnets at temperatures well below the Curie temperature if \( J \) is not defined but is evaluated empirically.) In Bethe's model the magnitude of \( J \) is determined by the overlap of atomic d orbitals on adjacent atoms. For lack of better wave functions, Bethe used hydrogen-atom-like orbitals to demonstrate that the overlap can be generalized in terms of the ratio of the nearest-neighbor distance \( R \) to the d orbital radius \( r \). From this model he obtained the dependence of \( J \) on \( R/r \) suggested in Fig. 2.3, the so-called Bethe curve.

The most striking suggestion of the Bethe model is the critical value of \( R/r \) (\( =1.5 \)) below which ferromagnetism is unstable. However, although many properties of transition metals and alloys can be discussed in terms of this model, the quite abrupt disappearance of ferromagnetism by compression of a ferromagnet predicted by this model has never been observed. Bozorth\(^27\) has suggested the coordinates appropriate to some transition elements shown in Fig. 2.3. His value of \( R/r \) for iron (1.63) is close to the critical value of 1.5, which suggests that large changes in the magnetic behavior of iron would be detected at high pressures if this model is correct. As explained later, the slow variation of the magnetic field at the nucleus with pressure observed in this experiment does not support this prediction for iron.

Much of the difficulty with the Bethe model arises from the arbitrary exclusion of all but direct d-d exchange. Any model that assumes the form of (2.14a) can account for ferromagnetism by finding a positive \( J \), but such a model is not necessarily sensitive to details that are significant on an
Fig. 2.3 The Bethe curve, showing the dependence of the exchange interaction on $R/r$. (After Bozorth; source: ref. 27.)
atomic scale. Furthermore, recent calculations of the direct exchange energy between 6 electrons in ferromagnets with better wave functions have been unable to produce either the sign or the magnitude of $J$ required for this model. $^{28,29}$ This model also cannot account for the magnetic field at the nucleus without introducing other electron-electron interactions of comparable importance.

A model which describes both the ferromagnetism and the magnetic field at the nucleus can be developed by not restricting the exchange interactions that are considered. One such model combines Zener's $^{30}$ semiempirical description of the coupling of 6 electrons in transition metals and the interpretation of the origin of the magnetic field at the nucleus by Freeman and Watson. $^{21}$ Although they treat different aspects of the electronic behavior in iron, these two theories are quite similar and compatible. Both treatments start from the approximation of a free iron atom placed in a solid lattice with the consequent delocalization of some electrons into conduction bands. However, some electrons are considered to remain in tightly-bound narrow bands which can be treated as localized partially-occupied 3d atomic shells. Hund's rule is assumed to apply to these local states, as well as the rest of the interactions between these states and the rest of the core states found in the free atom. These core interactions are treated by Freeman and Watson (see subsec. II.C.4).

Zener continues by suggesting, contrary to Bethe's assumption of a positive $J$ for direct exchange, that direct exchange between 6 electrons on different transition-metal atoms gives, if any, antiferromagnetic coupling. Ferromagnetic alignment of 3d electrons arises, according to Zener, due to a strong ferromagnetic exchange between the 3d electrons and the conduction electrons. As described by Zener, this exchange with
the conduction electrons changes the relative population of the two spin states in the conduction band. Coupling of d electrons on different atoms is achieved because of the nonlocal character of the conduction states. The criterion for ferromagnetism then is that the energy-lowering achieved by coupling to the conduction electrons exceed the energy required to change the polarization of the conduction electrons and the energy of direct exchange.

Although this model appears to be quite crude, it can be developed to predict the behavior of a wide range of transition-metal systems quite accurately. Furthermore, this indirect exchange interaction has been demonstrated to be important for the magnetic behavior of 4f-electron rare-earth elements. This model also can be derived from the more exact second-order perturbation treatments of ferromagnetism by Kasuya and others, which are not so directly connected to experimentally observable quantities.

As stated by Zener, this model suggests that the exchange interaction produces changes in the population of the conduction-electron states of different spin, producing a net spin for the conduction electrons. However, such a real polarization is not necessary for the indirect ferromagnetic coupling. The indirect coupling can be accounted for equally well if the exchange resulted in different spatial wave functions in the region of the core d states for conduction electrons with different spin. Because exchange counteracts the electrostatic repulsion of the core for conduction electrons with spin parallel to the occupied 3d states, the charge density of these conduction electrons can increase within the core with respect to that of conduction electrons with antiparallel spin. This phenomenon has been called exchange polarization. The spin coupling produced by exchange polarization depends only on the lattice periodicity of the excess parallel-spin
density at the cores. A ferromagnetic stabilization is obtained if electrons of the same spin predominate at every core.

An exact theoretical treatment of this spatial exchange polarization would be exceedingly complex and could not be readily evaluated. Furthermore, a real spin polarization and exchange polarization are not mutually exclusive for the conduction electrons; and probably both polarizations can be found in a real ferromagnet. The importance of this suggestion, however, lies in the fact that the difference in the conduction-electron wave function for electronic states of different spin also produces a Fermi contact field at the nucleus.

4. Ferromagnetism and the Magnetic Field at the Nucleus

Dependence of the spatial wave functions on spin for an unpolarized state is exactly what Freeman and Watson needed to explain the observed magnetic field at the nucleus. Because the s states of the iron core are completely filled, there is no opportunity for a real spin polarization of these states. However, a Fermi contact field can be obtained if the radial distribution differs between core s states of different spin. Freeman and Watson demonstrated that, by mixing 3d character into core states such as the 2s states with spin parallel to that of the unpaired 3d electrons, exchange expands the spatial distribution of these electrons with respect to the 2s electrons of the opposite spin. Such an expansion lowers the parallel-spin density at the nucleus with respect to the antiparallel-spin density, producing a net antiparallel magnetic field. In general, exchange expands (contracts) the parallel-spin density of states whose average radius is smaller (greater) than the 3d average radius. This lowers (raises) the parallel-spin density at the nucleus with respect to the antiparallel-spin density, resulting in a net negative (positive) Fermi contact magnetic
field. According to some rough estimates by Freeman and Watson, 1s and 2s electrons in an iron core produce a field of the order of -300 kG at the iron nucleus. The sign and magnitude of the field due to 3s electrons are subject to question, while polarization of the conduction electrons may result in a positive field of the order of 60 kG. Predominance of the large core polarization field over other contributions explains the large negative field observed at the nucleus.

5. Magnetic Field at the Nucleus in Iron and the Effect of Pressure

Those interactions which are thought to be most important for understanding the magnetic field at the nucleus in a ferromagnet have been developed in the preceding sections. In this section, the effect of pressure on the magnetic field at the nucleus is discussed with respect to the utility of using \( H(0) \) to study the pressure dependence of bulk properties of ferromagnets. Attention will be focused on relationships between \( H(0) \) and the exchange coupling, \( J \) of (2.14a).

The total magnetic field at the Fe\(^{57} \) nucleus in iron metal can be represented as a combination of three important terms:

\[
H(0) = H_{\text{core}} \langle S_\uparrow \rangle + H_d \langle S_\uparrow \rangle + H_{\text{cond}} \langle S_\uparrow \rangle, V, \tag{2.15}
\]

where \( \langle S_\uparrow \rangle \) is the average component of the spin per atom \( S_\uparrow \) along the direction of magnetization, and \( V \) is the volume of the solid. The dependence of \( H(0) \) on these variables is discussed in this section. The term \( H_{\text{core}} \) is the large negative Fermi contact contribution of the core electrons. This field arises primarily from exchange polarization of core s states. The magnitude of the exchange polarization of the core electrons depends on the spin of the 3d electrons and the overlap of these 3d states with other core states. Because of the small spatial extent of these core states with respect to nearest-neighbor distances, these states should be
nearly independent of volume over the range of this experiment. Those d states responsible for the local magnetic moment also can be considered core states with respect to compression; and \( H_{\text{core}} \) does not depend strongly on volume. The 3d electrons also make a positive contribution to the magnetic field at the nucleus due to the unquenched orbital angular momentum and dipole-dipole interactions. To the extent that these d electron states are core like, this contribution \( H_d \) also is only weakly dependent on volume.

The term \( H_{\text{cond}} \) is the Fermi contact contribution due to polarization of the conduction electrons. This is the same polarization as that used by Zener to describe the ferromagnetic coupling of the local spins; but this interaction is with the nuclear charge distribution instead of the electronic charge density. Unlike the first two terms, \( H_{\text{cond}} \) probably has a strong volume dependence because conduction-electron states extend throughout the solid. Because of this extension, the bulk compressibility of the conduction-electron density probably is of the order of the compressibility of the lattice. However, it may not be uniform on an atomic scale throughout a unit cell. The variation of the conduction electron density at the nucleus may be small for an appreciable change in the volume of the lattice. In the absence of other effects, an increased conduction-electron density at the nucleus due to compression of the lattice results in an increased \( H_{\text{cond}} \). However, compression of the conduction-electron density with respect to an approximately unchanged core-electron density can reduce the effectiveness of the core exchange polarization of conduction-electron states. Such a change in the strength of the conduction-electron polarization easily can dominate the effect of the increased conduction-electron density at the nucleus. This results in a
net decrease in the magnitude of the conduction-electron contribution to
the magnetic field at the nucleus. Such a decrease is observed upon
compression of iron.

Variation of $H_{\text{cond}}$ at constant temperature is related to the volume
dependence of that part of the ferromagnetic coupling due to exchange
polarization of the conduction electrons in Zener's model. Of the energy
terms Zener considers, this may be the most sensitive to the volume of
the lattice; evaluation of this relationship would be a useful test of
the Zener model. Unfortunately, this cannot be evaluated without know-
ledge of both the magnitude of $H_{\text{cond}}$ and the compressibility of the
conduction-electron density at the nucleus with respect to the compressi-
bility of this density throughout the volume of the core states. Knowledge
of the electronic wave functions throughout the core is needed to evaluate
this relationship, but these functions are not known. Only the approximate
comparison of the pressure dependence of the chemical shift with respect
to the bulk compressibility of the lattice is available to test this rela-
tionship. Furthermore, the magnitude of $H_{\text{cond}}$ is not available at the
present time, and theoretical evaluation of this relation is too difficult
to be of use.

There is another experiment that might be performed to test this
interpretation. The magnetic field at a nonmagnetic nontransition-element
impurity in iron would arise solely from the exchange polarization inter-
action, as direct exchange would be prohibited. If this is the correct
interpretation of the coupling to the impurity and if $H_{\text{cond}}$ is proportional
to the polarization of the conduction electrons, the pressure dependence
of the two fields should be the same. Such an experiment has not yet
been performed, to the author's knowledge.
All three contributions (2.15) to the magnetic field at the nucleus are linear with respect to the spin localized at a lattice site at a given temperature and pressure in the theoretical limit that all local magnetic moments are aligned in parallel in a ferromagnet. However, thermal processes reduce the degree of parallel alignment of spins at finite temperatures. On a bulk scale this reduction is observed in the reduction of the saturation magnetization $\sigma$, which is proportional to $<S_1>$, with increasing temperature. This phenomenon can be treated quantum mechanically at temperatures low with respect to the Curie temperature in terms of excitations of spin waves, collective modes of oscillation of the component of the localized moment along the direction of magnetization. The reduction of the saturation magnetization in the low temperature region is linear in $(T/S_1J)^{3/2}$, where $T$ is the absolute temperature. The variation of $\sigma$ with pressure at constant $S_1$ and $T$ measures the variation of $J$ directly.

Frequencies characteristic of spin waves are high with respect to $\omega h/\hbar$, and the magnetic field seen by the nucleus also will be reduced by spin wave excitation. The correspondence between the temperature dependence of $H(0)$ and $\sigma$ has been observed in an experiment on Fe$^{57}$ in iron by Nagle et al.\textsuperscript{8} Therefore, it appears that $J$ can be determined from the temperature dependence of $H(0)$. However, the coupling of the saturation magnetization to the nucleus depends on both the volume and the temperature.\textsuperscript{35,7} The changes in the magnetic properties with temperature and pressure observed near room temperature are the same order of magnitude as the compressibility and thermal expansivity of the iron lattice. Thus the magnetic properties must be studied over a wide range of experimental conditions in order that less obvious contributions to $H(0)$ are not masked. As Benedek and Armstrong demonstrated,\textsuperscript{35} the pressure and temperature derivatives of $H(0)$ must be corrected for the dependence of
the coupling of the conduction electrons to the nucleus on the volume and on the energy of the Fermi surface to obtain the pressure dependence of the saturation magnetization. The present experiment suggests that the volume dependence extends to very high pressures. Therefore, additional experiments are needed to determine the pressure dependence of \( J \) accurately.

D. Phases of Iron

Kaufman et al.\(^{36}\) recently reviewed the phase diagram of iron metal at temperatures up to 1200°K and pressures as high as 150 kbar. Below 100 kbar only two structural phases are found in this temperature region: the body-centered cubic \( \alpha \) phase and, at high temperatures, the face-centered cubic \( \gamma \) phase. The \( \alpha-\gamma \) phase boundary has been determined to 100 kbar by static high-pressure techniques; however, no reliable static data are available for this boundary above 100 kbar.

At 1 atm, the Curie temperature of iron is approximately 1070°K in the \( \alpha \) phase. Patrick\(^{37}\) could not observe any change within \( \pm 1°K \) in the Curie temperature with pressure to 1 kbar. If this transition is purely second-order and is nearly temperature-independent, the joining of the Curie transition and the \( \alpha-\gamma \) phase transition might account for an apparent change in the slope of the \( \alpha-\gamma \) phase boundary near 1050°K and 20 kbar.\(^{21}\)

At room temperature, a phase transition has been observed by both static and dynamic high-pressure techniques at a pressure in excess of 100 kbar.\(^{38,39}\) Observation of this phase boundary by dynamic high-pressure techniques indicates that the connection to the \( \alpha-\gamma \) phase boundary is not smooth. Johnson et al.\(^{40}\) have suggested that this is a new phase, which they called the \( x \) phase. Although a sharp \( \alpha-x \) phase transition is observed at 131 kbar in dynamic high-pressure work, typically 50 kbar of superpressuring is necessary to complete the transition in static work. Recent
dynamic high-pressure resistance studies indicate that the high-pressure phase is the same as that obtained by static methods. In some x-ray diffraction experiments on iron in this pressure range, Lawson and Jamieson obtained, in addition to the α-iron lines, one line suggesting that the structure of the new phase was hexagonal close packed.

The sensitivity of the Mössbauer spectrum to the structural environment of the nucleus has been demonstrated many times. Because the spectrum is an atomic-scale phenomenon, the presence of two phases in the sample results in two distinct, although possibly overlapping, spectra. In a high-temperature experiment with Fe in iron, Preston et al. detected the α-γ phase transition by a discontinuity in the chemical shift as a function of pressure. Although this type of Mössbauer spectroscopy may require highly precise energy measurement, the Mössbauer spectrum of iron at high pressures can be used to search for the existence and characterization of the x phase.
III. DETAILS OF THE EXPERIMENT

A. High-Pressure Techniques

In designing an experimental apparatus for a high-pressure Fe\textsuperscript{57} Mössbauer experiment, the low energy of the Mössbauer radiation and the correspondingly high attenuation of this radiation by the walls of the pressure chamber are problems of major importance. The proximity of an intense x ray at 8 keV and the high intensity of the 123-keV gamma radiation set a lower limit on the intensity of the 14-keV Mössbauer γ ray that can be discriminated by the detection equipment. A rough experiment demonstrated that 14-keV radiation is attenuated about 50% in passing through 0.030 in. of compacted pyrophyllite at 1 atm. As this attenuation should increase with pressure, it is impractical to attempt to pass the radiation through the wall of the pressure chamber more than once. The emitting nucleus must be contained at high pressures.

To obtain the maximum intensity of radiation from the pressurized sample, it also is necessary to maximize the area of the pressure chamber through which radiation can be emitted, while minimizing the thickness of material through which the γ radiation passes between the emitting nucleus and the detection equipment. A set of Bridgman anvils, as modified by Jura et al.\textsuperscript{43} was used in this experiment for this reason. The anvils were made with Kennametal K11-grade tungsten carbides having a 0.250-in. face diameter in order to obtain pressures as high as possible.

A ring of pyrophyllite was used to contain the sample at high pressures. A pyrophyllite ring, 0.010 in. in height with an internal diameter of 0.188 in. can contain a disk of iron, 0.175 in. in diameter and 0.007 in. high. The γ radiation must pass through only 0.031 in. of pyrophyllite in this geometry. To increase the friction between ring and anvils, the ring
was coated with Fe₂O₃. The Fe⁵⁷ contained in this oxide is an additional source of possible strong attenuation of the 14-keV radiation which could distort the spectrum by resonant scattering of the recoilless radiation. Thus, iron oxide enriched to 99.7% in Fe⁵⁶ (obtained from the Oak Ridge National Laboratory) was used to coat the ring. The stated content of Fe⁵⁷ was 0.1 ± 0.05%.

B. Sample

For simplicity, the sample was a disk of iron 0.175 in. in diameter and 0.007 in. thick onto which Co⁵⁷ was electroplated as the source of the 14-keV radiation. To minimize self-absorption of the radiation within the disk, iron enriched to 99.7 ± 0.1% in Fe⁵⁶ from the batch of iron oxide used to coat the ring, was used. The stated chemical impurities were 0.02% manganese and a trace (less than 0.05%) of silicon.

On the first sample prepared, 10 millicuries of Co⁵⁷ was electroplated onto the iron disk by Nuclear Science and Engineering Corporation. The cobalt was plated near the edge of one of the circular faces of the disk. The sample was annealed at 1000°C in a hydrogen atmosphere for two hours to permit the cobalt to diffuse into the iron. When this sample was placed in the Bridgman anvils, it was impossible to detect the 14-keV radiation through the ring. Further annealing for four hours at 1000°C in hydrogen did not increase the intensity of the 14-keV radiation observed outside the anvils. Apparently this was due to severe attenuation of the 14-keV radiation by the iron metal. In fact, it was found that simply turning the plated face of the iron disk away from the detector would make the 14-keV radiation disappear.

A second sample was prepared in a similar manner except that the Co⁵⁷ was electroplated on the 0.007 in. face along one-half of the circumference of the disk. Only about six-tenths of the amount of Co⁵⁷ used in the first
sample was used in this case. The sample was annealed in a hydrogen atmosphere at 1000°C for two hours. This change of geometry resulted in a 14-keV peak which could be resolved clearly even after transmission through the pyrophyllite ring and absorbing foil.

Between the times at which the first and second samples were prepared, the amount of Co\textsuperscript{57} per "millicurie" supplied by the vendor was changed. On the newer scale, the second sample contained 4 millicuries. For a 270-day half-life, the amount of Co\textsuperscript{57} corresponding to 4 millicuries, distributed evenly throughout the iron within 0.005 in. from the edge of the disk onto which it was electroplated, gives a cobalt concentration of 0.05 atom percent.

**C. Pressure Scale**

The anvils were loaded by a 200-ton-capacity press. The load was transmitted to the anvils through a calibrated strain-gauge load cell of 200-ton capacity. The load cell was used both to set and to monitor the load on the anvils. During any run the average pressure on the 0.250-in. diameter flat could be held constant within less than 2 kbar.

No information is available about the distribution of pressure in an iron disk in this geometry, so pressures reported are average pressures on the anvil face. Experience in this geometry with silver chloride as a pressure medium\textsuperscript{4} indicates that only about 82% of the area of the anvil face is load-bearing, and the average pressure on the disk is about 20% higher than the average pressure on the anvil face. Neither iron nor silver chloride is a hydrostatic-pressure medium, and pressure is not uniformly distributed across the load-bearing area. In silver chloride, the actual pressure was found to be highest at the interface with the pyrophyllite ring. Because 14-keV radiation is attenuated severely by
iron metal, most of the radiation detected comes from the region of the iron-ring interface, so the actual pressure at the Fe<sup>57</sup> nucleus may be considerably higher than the average pressure on the anvil face. In future experiments the uncertainty in the pressure can be reduced by replacing the solid metal disk with a circular section from the circumference and filling most of the volume with a well-studied pressure medium.

D. Spectrometer

1. Mechanical Assembly

The γ-ray spectroscopy was performed at the absorber. Two modes of operation are commonly used in Mössbauer spectroscopy: constant-velocity-drive spectrometers and loudspeaker, or velocity-sweep, spectrometers. By using a constant-velocity-drive spectrometer, the intensity of radiation transmitted in a fixed time interval through an absorber moving at constant velocity is measured at a number of velocities in the range of the spectrum. After correcting for changes in the intensity of radiation incident on the absorber due to decay and geometrical shifts in the sample, a complete spectrum may be obtained. This method has the distinct advantage that velocities are easily measured accurately. The velocity range may be made as narrow as desired by appropriate collimation, giving quite high energy resolution.

A significant disadvantage of a constant-velocity spectrometer is the necessity of correction for changes in the intensity of emitted radiation reaching the absorber. This is particularly annoying when gradual changes occur in the geometry of the source. This is a major problem at high pressures as a result of material fatigue and creep in the anvils and sample. This effect was quite noticeable in trying to elucidate the structure of the spectrum in the earlier experiment with Dy<sup>161</sup>.
A second disadvantage, of lesser importance, of this spectrometer was the difficulty observed in the $^{161}$Dy experiment in maintaining a stable velocity at very low velocities. This purely mechanical limitation arises from the difficulty of operating the spectrometer with the large reducing gears and/or the low motor speeds needed to achieve low-velocity motion. For these reasons, it was decided to develop a loudspeaker technique for Mössbauer spectroscopy on samples at very high pressures. It was felt that, after establishing the shape of the spectra at high pressures, experiments using a constant-velocity spectrometer could be performed if more precise information about particular energy shifts was desired.

The loudspeaker type of spectrometer operates by generating a voltage pulse proportional to the velocity of the absorbing foil relative to the anvils which contain the source whenever radiation transmitted through the absorber is detected. For this experiment, only transmitted 14-keV radiation is used as the electronic trigger instructing the spectrometer to "read" the velocity of the absorber. The pulses generated by the absorber are analyzed and stored in a 400-channel pulse-height analyzer. This gives a spectrum of intensity of radiation transmitted (number of counts) in a given velocity range (per channel). The spectrum has to be normalized for differences in the amount of time spent in different velocity ranges, because a sinusoidal drive is used, and for variations in channel width. The normalization is obtained by counting with the detector moved to a position at which the incident radiation does not pass through the absorber. A block diagram of the spectrometer is shown in Fig. 3.1. The spectrometer is a modification of the low-temperature spectrometer developed by Shirley et al. at this Laboratory.\(^\text{45}\)

The moving assembly of the spectrometer consists of three parts: the absorber, the velocity transducer, and a voice coil. This assembly is suspended by six 0.005-in.-diameter beryllium copper wires, whose lengths
Fig. 3.1: Block diagram of Mössbauer spectrometer.
are adjustable. These wires are attached to fixed supports by strips of 0.020 in.-thick clock-spring steel. This support system allows both for alignment of the moving assembly and for adjustment of the tension. Therefore the resonant frequency of the mechanical system can be adjusted. The total weight of the assembly is about 50 g. The assembly is quite sensitive to vibration in the laboratory. For this reason this experiment had to be conducted at night and during weekends when no other work was in progress, to minimize the distortion that random vibrations would contribute to the time-average motion of the spectrometer.

The absorber used in this experiment was a stainless steel foil that was made with iron enriched to 91.19 ± 0.05% Fe\textsuperscript{57}. The gross chemical composition of the foil was 9.6 ± 0.2% nickel, 18.4 ± 0.2% chromium, 0.15 ± 0.1% carbon, and 71.8 ± 0.2% iron. The components were melted at about 1500°C in vacuum in an induction furnace, and the melt was quenched rapidly to room temperature. After heating the steel for one hour at 1000°C to permit homogenization, the button of steel obtained did not appear to notice the presence of a small permanent magnet. Alternately, the steel was rolled and annealed at 1000°C in a vacuum until a foil 0.0007 ± 0.0001 in. thick was obtained. A 1-in.-diameter section of this foil, which was without holes or major defects, was mounted for use as the absorber.

In the spectrometer the absorber mount is connected by a 2-in.-wide aluminum yoke to the velocity transducer and voice coil. This arrangement permits a NaI(Tl) scintillation detector to be placed in line with the radiation transmitted through the foil, without interfering with the motion of the foil. A Sanborn model 6LV1 transducer is used to measure the velocity of the absorber. This unit consists of a permanent magnet
0.197 in. in diameter and 3.50 in. long moving inside a 5-in.-long solenoid. The solenoid is mounted in a fixed position with respect to the press and is shielded from external fields. The magnet is used as the axle of the moving assembly and is the only connecting member between the voice coil and the absorber. Therefore the motion of the transducer is that common to the entire moving assembly relative to the radiation source. The output of the transducer is linear within 1% over more than 1 in. of travel, which is many times the distance that the assembly moves. The electrical output from the transducer is amplified with a Kintel model 111 amplifier and applied to the input of the velocity-to-pulse-height converter.

The voice coil consists of about 70 turns of copper wire mounted on a rigid fiberglass cone. The coil fits between the pole pieces of a cylindrical permanent magnet that produces a field of about 3000 G. The coil is driven through a matching transformer with the output of a Krohn-Hite model 446 stable-amplitude oscillator which has a rated short-term output stability of 0.01%. The spectrometer was driven at 15.0 cps for this experiment, which was quite close to the mechanical resonance of the apparatus. The mechanical assembly is pictured in Figs. 3.2, 3.3, and 3.4.

2. Electronics

The electronics associated with the spectrometer serve three purposes: to detect the 14-keV radiation, to use this radiation to generate an intensity-vs-energy spectrum, and to record the spectrum. The γ-ray detection equipment used is standard laboratory counting equipment. A NaI(Tl) scintillation crystal 1 in. in diameter and 1 mm thick (obtained from the Harshaw Chemical Company) is used to detect the radiation. The crystal is mounted on the face of a DuMont 5292 phototube, selected for its low noise level. This arrangement allows the crystal to be inserted
Fig. 3.2 The drive capsule viewed from the absorber end.
Fig. 3.3 Rear view of the drive capsule with the permanent magnet removed, shown together with the mold on which the loudspeaker cone was fabricated.
Fig. 3.4 The permanent magnet for the drive capsule during assembly.
behind the absorber foil at an angle of about 45 deg to the incident radiation.

The phototube output is amplified by using a Model VI linear amplifier (LRL 3X9494) operating in a double-delay clipping mode to minimize amplifier distortion due to amplifier overload. The amplifier and phototube are operated such that the noise level corresponds to γ-ray energies somewhat lower than the iron 8-keV x ray. The amplifier output feeds a single-channel analyzer and pulse-gate generator (LRL 4X6953). This generates an 18-V positive square pulse for each input pulse passing the single-channel analyzer. This analyzer is set to pass the 14-keV γ-ray peak. After passing through a 2-μsec delay line terminated by a cathode follower, the square pulse serves to inform the velocity-to-pulse-height converter of the detection of a transmitted 14-keV photon.

The velocity-to-pulse-height converter (LRL- 4X9021) is a blocked linear amplifier in which the pulse from the single-channel analyzer is used to unblock the amplifier for 1 μsec. With no input to the amplifier, a positive-going 1-μsec square pulse of the order of 10 V in amplitude is generated by the converter to serve as the zero-velocity base line. The voltage from the velocity transducer is added to this base voltage so that all velocities are represented with a positive-going pulse. The zero-velocity base voltage is adjustable over a 10-V range and the blocked amplifier is linear over a 20-V range.

The velocity pulses are fed to a pulse-height analyzer which records the intensity observed in different velocity ranges by discriminating the pulse voltages corresponding to different velocity ranges. A Victoreen model ST800M pulse-height analyzer was used in this experiment as a 400-channel analyzer. The analyzer was modified to accept a positive 10-V pulse as a full-scale signal by changing a resistor at the input of the
inverter amplifier. Because the analyzer measures the sum of the base level generated by the velocity-to-pulse-height converter and the output of the velocity transducer, the spectrum is sensitive to shifts in the reference level of the velocity-to-pulse-height converter. Two factors are found to contribute appreciably to such shifts in the converter. These are poorly regulated dc supply voltages and IR losses due to appreciable power drains at the output emitter-follower stage of the converter at high counting rates. Any dc ripple in the base line is reduced to less than 2 mV by use of a Zener-diode-regulated transistorized power supply. Experimentally, it is observed that average counting rates below 10 kc produce negligible power drain; thus, the counting rate is maintained in this range. As a further precaution, all of the electronics are powered from a common 117-V regulated ac power supply to reduce the regulation requirements placed on the individual components.

To test the stability of the spectrometer, the output of the Kintek amplifier is monitored by a Tektronix Type Z differential preamplifier and a Tektronix Type 535 oscilloscope. This permits the amplitude of the velocity oscillations to be controlled to within 0.2%, assuming the gain of the Kintek amplifier to be constant with time. In his work, Shirley has found this to be a good assumption. As the pulse-height analyzer also measures the peak-to-peak amplitude of oscillation in terms of the velocity range, the oscilloscope and analyzer serve to cross-check the behavior of the electronics.

3. **Calibration**

Because of the great number of variables involved in the conversion of the velocity spectrum to electrical waveforms, it was necessary to provide a calibration for the spectrometer. The most direct calibration
that could be used was the 1-atm Mössbauer spectrum of Fe\textsuperscript{57} in iron. The spectrum obtained is shown in Fig. 3.5. The fine structure of the iron spectrum was spread over more than 200 channels while the velocity range used extended over more than 390 channels, in order to minimize any distortion due to variations in the amplitude of oscillation. As it proved desirable to average the normalized data on ten adjacent channels to smooth out the high-pressure spectra, the same averaging process was used here. This averaging made the spectrum less sensitive to fluctuations in individual channels; however, because of the large line width, presumably due to the high concentration of Fe\textsuperscript{57} in the absorber, the spectrum was not distorted appreciably. With the value of 10.64 mm/sec given by Dash et al.\textsuperscript{17} for the splitting of the outer lines, which were separated by 168 ± 2 channels, the width of one channel was determined to be 0.063 ± 0.001 mm/sec (0.302 ± 0.005 x 10\textsuperscript{-8} eV). The apparent line half-width at half-maximum was 0.82 ± 0.07 mm/sec (3.9 ± 0.3 x 10\textsuperscript{-8} eV). In this spectrum the statistical accuracy in the intensity at each channel was ± 0.3\% of full scale.

Because of the overlap of the broad lines, it was necessary to separate the contributions of the different lines where they contributed to a common channel, in order to locate the position of the lines. For the 1-atm spectrum, this was accomplished by locating the maximum absorption for the most intense outside line and by constructing a symmetric absorption line around this channel. The contribution of this line to channels shared with the adjacent line could then be subtracted. The line width was fixed by the absorber and was the same for all lines. Thus, because no more than two lines contributed to any one channel, the separation was achieved easily. The quality of this separation could be tested by the ability to
Fig. 3.5 The 1-atm Mössbauer spectrum of Fe$^{57}$ in metallic iron used to calibrate the spectrometer. The statistical error is indicated every tenth channel. The solid lines indicate the positions and intensities of the absorptions.
account for the spectrum near zero velocity by working inward from both extremes independently; the fit was quite good. A less sensitive test was the agreement of the intensities with the theoretical 3:2:1 ratio. This agreement was fair, and the differences could be attributed to saturation of the absorber.

A similar procedure was used to analyze the spectra obtained at high pressures except that, because of reduced intensities, it was difficult to locate the weak center lines with high precision. The location of these lines was not necessary to obtain the chemical shift or the parameters of the fine-structure splittings. Having located the positions of the four outer lines, the chemical shift $V_c$ and the magnetic $A$ and quadrupole $B$ splitting parameters [see (2.7) to (2.10)] were calculated from

$$V_c = \frac{1}{4} (V_1 + V_2 + V_3 + V_4), \quad (3.1)$$
$$A = \frac{1}{5.43} (V_6 - V_1), \quad (3.2)$$
$$B = \frac{1}{4} (V_1 + V_6 - V_2 - V_5), \quad (3.3)$$

where $V_i$ denotes the position of the $i$th line, higher numbers referring to lower-energy transitions.
IV. RESULTS OBTAINED FROM THE EXPERIMENT

After the spectrometer had been calibrated, the sample was pressurized and spectra were obtained at loads of 50, 60, 90, 105, 120 and 140 kbar. An attempt was made to obtain the Mössbauer spectrum of iron at 160 kbar, but no absorption more intense than the statistical error of 0.5% per channel was observed. Failure to observe the spectrum at a load of 160 kbar was not due to the disappearance of recoilless radiation emitted at this pressure. Rather it could be attributed to a gradual loss of the intensity of the recoilless 14-keV radiation passing through the walls of the pressure chamber. This is evidenced by the gradual loss of intensity of the absorption peaks from 13% absorption for the uncovered sample at 1 atm to nearly 2% absorption at 140 kbar. If decreasing intensity of the recoilless 14-keV radiation was the only problem, it should have been possible to observe the Mössbauer spectrum by going to longer counting periods. However, a reasonable amount of higher energy radiation appeared electronically in the 14-keV region. This became dominant as the attenuation of the recoilless radiation increased due to the closing of the anvils and the increased density of the pyrophyllite. For the same reason, it was impossible to obtain an estimate of the change of the recoil-free fraction with pressure.

When the pressure was removed the sample and anvils were examined for evidence of a blowout. The impression of the sample on the anvil faces indicated that the anvils had been well centered and the sample well aligned. No cracks were discovered in the carbides. The spectrum was rerun after the sample had been at 1 atm for one week, and was found in good agreement with the 1 atm spectrum obtained before compression.
During the first high-pressure run, the sample had been held at high pressures for nearly 16 days. It was decided that a spectrum might be obtained at a load higher than in the first run in a quick run that involved going directly to a pressure of the order of 100 kbar. A new set of anvils was used. It was thought that by reducing the time that the anvils spent at lower pressures, the amount of creep and deformation might be reduced, and a spectrum in the 150-kbar pressure range might be observed. The 100-kbar spectrum showed agreement with the corresponding spectra of the first run; however, the intensity of the spectrum was reduced. No absorption lines more intense than the statistical error of 0.5% were found in a 48-hour counting period at 150 kbar. Failure of this attempt was attributed to flow of the sample during both pressurizations, which moved some of the activity from the edge to a region from which it could not be detected outside the anvils. It would be necessary to prepare a more active sample in order to observe the spectrum at these pressures.

In the first run, detailed spectra were observed at pressures of 50, 60, 90, 105, 120 and 140 kbar. These spectra are shown in Figs. 4.1 through 4.6. The average statistical error per channel in the intensity is indicated in these spectra. This error ranges from ±1% of full scale in the 90 kbar spectrum to ±0.5% of full scale in the 120- and 140-kbar spectra. In the higher-pressure spectra, the statistical error became a significant fraction of the total intensity of the absorption intensity. The agreement between the observed and theoretical 3:2:1 ratio of intensities in these spectra was not so good as at lower pressure.

The spectra observed at pressure up to 120 kbar consisted of six lines characteristic of Fe$^{57}$ in ferromagnetic α-iron. In most of the
Fig. 4.1 The Mössbauer spectrum of Fe$^{57}$ in metallic iron at 50 kbar. The solid lines indicate the positions of the absorptions. The positions of the two inner lines of the six-line α-iron spectrum is calculated at every pressure. The height of these lines indicates the theoretical intensity based on the intensity of lines 1 and 6 of the α-iron spectrum. The statistical counting error is indicated on every tenth channel.
Fig. 4.2 As Fig. 4.1 but at 60 kbar.
Fig. 4.3 As Fig. 4.1 but at 90 kbar.
Fig. 4.4 As Fig. 4.1 but at 105 kbar.
Fig. 4.5 As Fig. 4.2 but at 120 kbar.
Fig. 4.6 As Fig. 4.1 but at 140 kbar. The center absorption is attributed to the high-pressure phase of metallic iron.
THIS IS A BLANK PAGE.
spectra it was possible to locate the positions of the four outer lines to within ±1 channel. In some spectra, however, the weak inner lines were poorly resolved. It is not necessary to locate the inner lines to calculate the splitting parameters, and values of A and V_0 could be obtained with good precision. Values of B represent small differences in large numbers and are less precisely known. Only in the 120-kbar spectrum was B nonzero within the estimated error. These data are tabulated in Table IV.1.

The variation of the observed magnetic splitting with pressure is compared in Fig. 4.7 with the more precise results obtained by nuclear magnetic resonance to 65 kbar by Litster and Benedek. The agreement is quite good considering the lower precision and accuracy of this Mössbauer technique. Furthermore, now that the gross details of the effect of pressure on the Fe^{57} Mössbauer spectrum in iron are known, additional experiments with greater velocity resolution and accuracy can be performed with a constant-velocity spectrometer to study the detailed behavior.

The observed volume dependence of H(0) at constant σ, discussed in Sec. II, means that the variation of H(0) with pressure cannot be used alone to study the variation of the magnetic behavior of ferromagnets. However, these results demonstrate the effectiveness of the Mössbauer effect for magnetic studies at high pressures. A much smaller amount of material was needed in this Mössbauer experiment than for the nmr study or for a determination of σ. This permits much greater flexibility in the pressure and temperature range than can be studied with the Mössbauer effect than with other techniques.
Table IV.1. Experimental values for A, B, and V (see Eqs. 2.7 through 2.10) for the α-iron spectrum. $V_c$ is measured with reference to the absorber energy.

<table>
<thead>
<tr>
<th>Pressure (kbar)</th>
<th>A = $\mu_0 H(0)$ (eV x $10^3$) ± 0.10</th>
<th>B = $\frac{\pi e^2}{4} qQ$ (eV x $10^8$) ± 0.5</th>
<th>$V_c$ (eV x $10^8$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001 (1 atm)</td>
<td>9.43 ± 0.10</td>
<td>0.0</td>
<td>+ 0.45 ± 0.15</td>
</tr>
<tr>
<td>50</td>
<td>9.24 ± 0.10</td>
<td>0.0</td>
<td>+ 0.27 ± 0.17</td>
</tr>
<tr>
<td>60</td>
<td>9.19 ± 0.10</td>
<td>0.0</td>
<td>+ 0.57 ± 0.29</td>
</tr>
<tr>
<td>90</td>
<td>9.34 ± 0.10</td>
<td>0.0</td>
<td>- 0.03 ± 0.15</td>
</tr>
<tr>
<td>105</td>
<td>9.34 ± 0.10</td>
<td>0.0</td>
<td>- 0.33 ± 0.15</td>
</tr>
<tr>
<td>120</td>
<td>9.24 ± 0.10</td>
<td>1.0</td>
<td>- 0.54 ± 0.15</td>
</tr>
<tr>
<td>140</td>
<td>8.96 ± 0.10</td>
<td>0.5</td>
<td>+ 0.12 ± 0.17</td>
</tr>
</tbody>
</table>
Fig. 4.7 The variation of the magnetic coupling constant with pressure for Fe$^{57}$ in iron metal. The straight line is calculated from the nuclear magnetic-resonance results of Litster and Benedek. The bars indicate the probable error in the determination of $A$. 
In Fig. 4.8, the variation of the chemical shift with pressure is shown together with an indication of the variation obtained by Pound et al.\textsuperscript{20} at lower pressures. Up to 120 kbar there is a gradual shift of the spectrum to lower energy which seems to become more rapid with increasing pressure. However, as the spectrometer does not measure the absolute velocity directly, the precision of this measurement is not high. A minor variation in the voltage of the pulse from the velocity-to-pulse-height converter corresponding to zero velocity shifts the entire spectrum. This contribution can be checked by observing the location of the ends of the velocity spectrum on the pulse-height analyzer; however, the precision in this correction is of the order of a channel width.

According to the estimates of Walker et al.\textsuperscript{18} (see Fig. 2.2), the change in the chemical shift from 1 atm to 120 kbar corresponds to an increase of about 8 to 10\% in the 4s electron density at the nucleus for a 3d\textsuperscript{5} s\textsuperscript{3} configuration. Bancroft et al.\textsuperscript{38} have measured the compression of iron by dynamic methods to pressures of the order of 200 kbar near room temperature. They report that the volume of \(\alpha\)-iron at the 131-kbar transition is reduced about 8\% from 1 atm, which is in excellent agreement with the change predicted from the chemical shift. The qualitative agreement between the bulk compressibility of the lattice and the compressibility of the 4s electron density at the nucleus suggests that the approximation of a uniform compressibility of the conduction-electron density throughout the core can be used to establish a relationship between \(H_{\text{cond}}\) and the indirect exchange coupling. However, the magnitude of \(H_{\text{cond}}\) still is undetermined; and the contribution of indirect exchange to the ferromagnetic coupling cannot be evaluated.
Fig. 4.8 The variation of the chemical shift with pressure, compared with the results of Pound et al. 20 (dashed line) obtained at lower pressures. The bars indicate the probable error in the determination of the chemical shifts.
The 140-kbar spectrum is shown in detail in Fig. 4.6. The most
striking feature of this spectrum is the appearance of a seventh line at
- 0.6 ± 0.3 \times 10^{-3} \text{ eV} in addition to six lines that are characteristic of
\(\alpha\)-iron. The constants calculated for the six-line spectrum are given in
Table IV.1. The values seem consistent with the values for \(\alpha\)-iron at
lower pressures, although the variation with pressure is not so smooth as
at lower pressures. In particular, the chemical shift of the \(\alpha\)-iron
spectrum is positive with respect to 105- and 120-kbar, and \(A\) has dropped
abruptly. The chemical shift also is positive with respect to the position
of the seventh line; this shift is in the same direction, but slightly
larger, than the shift observed at the \(\alpha\)-\(\gamma\) transition at high temperatures.\(^9\)

Although the statistical error per channel of 0.5\% is an appreciable
fraction of the intensity of the three center absorption peaks, the
channel-to-channel variation in the intensity is quite smooth. Even the
least intense peak extends over at least eight channels. The positions of
the three center peaks are separated by 4.8 ± 0.6 \times 10^{-3} \text{ eV}; and the posi-
tions of the two of these peaks associated with the \(\alpha\)-iron spectrum are
in good agreement with the positions calculated from the location of the
other peaks in the spectrum, as indicated by the solid lines in Fig. 4.6.
The position of the seventh peak does not correspond to the energy of
either of the higher multipolarity transitions of the \(\alpha\)-iron spectrum
which are not observed.

The most plausible explanation of the seventh peak is that it belongs
to the spectrum of the \(x\)-phase of iron, which is beginning to appear in
this pressure range. Coexistence of an \(x\)-phase spectrum with the six-
line \(\alpha\)-phase spectrum can be explained by the observed coexistence of
\(\alpha\)-phase and \(x\)-phase lines in the x-ray patterns observed in this pressure
range by Jamieson and Lawson.\textsuperscript{42} If this explanation is correct, with increasing pressure, the intensity of the \(x\)-phase spectrum should increase relative to the \(\alpha\)-phase spectrum at higher pressures, if the spectra could be detected.

Additional lines in the \(x\)-phase spectrum might be detected with greater energy resolution. However, a single-line spectrum can easily be understood if there is no aligned localized magnetic moment on the iron atom in the \(x\) phase. The observed increase of the resistance by a factor of four through the \(\alpha-x\) transition\textsuperscript{39,41} suggests that a major electronic rearrangement occurs which might delocalize the magnetic electrons. Observation of an unsplit spectrum does not necessarily imply that the \(x\) phase is paramagnetic as unsplit Fe\textsuperscript{57} Mössbauer spectra have been observed in ferromagnetic alloys\textsuperscript{48} and for Fe\textsuperscript{57} as an impurity in antiferromagnetic chromium.\textsuperscript{49} Experiments in which an external magnetic field is used are necessary to distinguish between these possibilities.
V. CONCLUSIONS

The experiment reported herein has only scratched the surface of the possible applications of the Mössbauer effect to high-pressure research. However, it suggests a number of experimental approaches which could be followed in future work. Observation of a seventh line in the spectrum at very high pressures demonstrates the effectiveness of the Mössbauer effect for detection of new phases. This application is not limited to iron, or even to metals, but can be widely used to study the phase behavior of all varieties of solids.

The suggestion made concerning the magnetic behavior of the high-pressure phase, however, must be regarded as tentative. Additional experiments are necessary to determine that this line becomes more intense with respect to the α-phase lines with increasing pressure, before it can be attributed to the new phase with certainty. Also, experiments should be performed with an external magnetic field to distinguish between a paramagnetic or ordered magnetic structure as well as to aid in establishing the symmetry of the new phase.

The degree to which the magnetic properties of the α-phase vary almost linearly with pressure is somewhat surprising. The magnitude of the variation of H(0) agrees with Patrick's observation\textsuperscript{37} of a slow variation of the Curie temperature with pressure. This suggests that further experiments following the Curie temperature to the α-γ phase boundary should be performed.

More precise measurements over wider pressure ranges may detect appreciable deviations from low-pressure results. Large deviations in the ferromagnetic coupling also might be masked by the large core contribution to the
magnetic field. However, such effects would require a major modification of the interpretation of the results. As suggested in Sec. II, the temperature dependence of \( H(0) \) should be measured over wide temperature ranges at a number of elevated pressures to determine the variation of the ferromagnetic coupling with pressure. These measurements, related to \( \frac{dJ}{dP} \) determined from \( (d\ln\gamma/dP)_T \), also would be very useful in understanding the contribution to the magnetic field at the nucleus.

The present experiment has concerned only pure iron. However, if the interpretation is correct, exchange polarization by conduction electrons should be important in the cores of impurity atoms in ferromagnets as well. A systematic study of the magnetic field at the nucleus of those impurities to which direct d exchange is prohibited should be especially fruitful in understanding the ferromagnetic coupling process. Some work has appeared in the literature along these lines, and it is beyond the scope of this discussion to review the implications of this work in detail. However, the problem appears to be far from solved, and a number of Mössbauer isotopes are reasonable impurity atoms for such a study.
ACKNOWLEDGMENTS

I wish to express my most sincere gratitude to Professor George Jura for the guidance, direction, and encouragement he has provided throughout my graduate career. His unceasing alertness to both novel and extremely useful approaches to the multitude of problems of this research is a continuing source of inspiration.

The counsel of Professor David A. Shirley also has been most useful with respect to the development and application of Mössbauer-effect studies. This experiment could not have been performed without the valuable assistance of the many support groups at the laboratory. Mitch Nakamura and George Kilian made major contributions to the development of the spectrometer electronics.

Within the high-pressure group, nothing is accomplished without the advice and aid of Duane Newhart. From construction of the press and the high-pressure apparatus to the details of the spectrometer design, his influence is felt throughout the experiment.

The pulse-height analyzer used in this experiment was kindly loaned by the Victoreen Instrument Company.

For the past year, I have received the support of the DuPont Teaching Assistant Award.

This work was done under the auspices of the United States Atomic Energy Commission.
REFERENCES

12. D. A. Shirley (Department of Chemistry, University of California, Berkeley, California), private communication.


46. D. A. Shirley (Department of Chemistry, University of California, Berkeley, California), private communication.
This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.