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POLARIZATION OF INDIUM NUCLEI IN FERRO-MAGNETS, AND NUCLEAR MAGNETIC RESONANCE OF POLARIZED COBALT IN IRON

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Rondel James Holliday
(M. S. Thesis)
May 1967

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Polarization of Indium Nuclei in Ferromagnets and Nuclear Magnetic Resonance of Polarized Cobalt in Iron

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ABSTRACT

The hyperfine magnetic fields at In nuclei dissolved in iron and nickel were determined by low temperature nuclear orientation of $^{114m}_{\text{In}}$ in iron and nickel. $^{57}\text{Co}$ was used as the thermometer. The results are: $H_{\text{int}}(\text{In in Fe}) = -295 \pm 10 \text{ kG}$, $H_{\text{int}}(\text{In in Ni}) = 42 \pm 6 \text{ kG}$.

Nuclear magnetic resonance was observed in $^{60}\text{Co}$ nuclei polarized in iron at low temperatures. The resonance frequency is $165.75 \pm 0.15 \text{ MHz}$. 
I. INTRODUCTION

Nuclear orientation has long been used as a tool for investigating nuclear and solid state properties of the elements. Of the several ways of obtaining oriented nuclei, this thesis deals only with that involving nuclei at very low temperatures in thermal equilibrium with a ferromagnetic lattice in which they are embedded. Nuclear orientation in ferromagnetic metals was first demonstrated with cobalt. Later Samoilov et al. showed that it was possible to orient certain diamagnetic elements when dissolved in a ferromagnet. This method has been used primarily for measuring the large hyperfine magnetic field, $H_{hf}$, at the nucleus of the impurity element.

Using the techniques of perturbed angular correlations, nuclear polarization, Mossbauer spectroscopy, and NMR, accurate values of several hyperfine fields at nuclei of elements between Y(Z = 39) and Te(Z = 52) in Fe and Ni lattices have been determined. Frankel et al. have found a regular variation of $H_{hf}$ in Fe and Ni lattices with solute atomic number. Thus accurate values for these fields have acquired a new importance. This thesis describes such a measurement for indium nuclei in iron and nickel. The decay scheme of $^{114m}$In is shown in Fig. 1.

Nuclear magnetic resonance in a ferromagnet was first observed by Gossard and Portis for $^{59}$Co nuclei in cobalt metal. The strength of the nuclear resonance absorption was orders of magnitude larger than expected. This enhancement is due to the fact that the resonance is excited predominantly by the hyperfine coupling itself rather than by the externally applied rf field.

In 1953 Bloembergen and Temmer suggested the possibility of observing NMR in nuclei oriented at low temperatures. Early attempts failed because of the warming of the sample due to the rf input. This thesis describes the first successful experiment of this type. By utilizing the enhancement of a rf signal in a ferromagnet it was possible to observe nuclear magnetic resonance in polarized $^{60}$Co nuclei in an iron lattice at low temperatures. The decay scheme of $^{60}$Co is shown in Fig. 2.

The essence of this thesis may be found in Refs. 6 and 7.
Fig. 1. Decay scheme of $^{114m}$In.
Fig. 2. Decay scheme of $^{60}$Co.
II. THEORY

A. Nuclear Polarization

The theory of nuclear orientation has been discussed completely elsewhere. Only a brief outline emphasizing polarization of nuclei in ferromagnets is given here.

If a magnetic field, \( H \), is applied to a nucleus of total angular momentum (spin), \( I \), the degeneracy of the \( 2I+1 \) nuclear magnetic substates (hyperfine levels) is lifted. Each substate now has a different orientation with respect to the applied field. The substates are separated equally in energy and the difference is given by

\[
\Delta E = \mu H/I
\]  

Ordinarily at room temperature these levels are equally populated by the nuclei. In such a system the nuclei are randomly oriented. However, if by some means, a distribution is achieved so that the levels are not uniformly populated, the system of nuclei is said to be oriented.

It is useful to distinguish between alignment and polarization. Defining \( m \) as the quantum number denoting the projection of the substates on the axis given by the direction of the magnetic field so that \(-I \leq m \leq I\) and denoting the relative population of the \( m \) substates as \( W(m) \), then for polarization the degeneracy of the substates is removed so that \( W(m) \neq W(-m) \) for at least one value of \( m \) and \( \langle m \rangle \neq 0 \), where \( \langle m \rangle \) is the expectation value of \( m \). For alignment the degeneracy is not completely removed and \( W(m) = W(-m) \), i.e. \( \langle m \rangle = 0 \) but \( \langle m^2 \rangle \neq 0 \). Therefore an electric field gradient acting at the nucleus can only lead to alignment whereas a magnetic field may lead to polarization.

If there are several energy states available to a system in thermodynamic equilibrium, the states will be populated in proportion to the Boltzmann factor and the relative population of the substates will be

\[
W(m) = \frac{e^{-m\beta}}{\sum_{m} e^{-m\beta}}
\]
where $\beta = \mu H / I k T$. $\mu$ is the nuclear magnetic moment and $H$ is the magnetic field at the nucleus, thus the $m$ states with lowest energy will be preferentially populated.

To achieve appreciable polarization $\beta$ must be of the order of unity which implies, for reasonable values of $\mu$ and $I$, very large magnetic fields and very low temperatures. For example with $\mu = 4.7$ mm and $I = 5$; $H/T \approx 3 \times 10^7$ G/°K.

There are several different methods for obtaining high magnetic fields at the nucleus. The method used in this thesis was to form a dilute alloy of the nucleus under study with a ferromagnet. By applying an external field sufficient to saturate the magnetization of the ferromagnet, effective magnetic fields of several hundred kilogauss, polarized in one direction, are set up at the nuclei. The mechanism for the production of these fields is discussed in Sec. VA.

It is possible to determine the orientation of nuclei by observing the angular distribution of radiation emitted from the nuclei, since the angular distribution is dependent on the populations of the magnetic substates involved.

The angular distribution of radiation from polarized nuclei may be represented by

$$W(\theta) = \sum_{k=0}^{\lambda} B_{k,k,k,k} U_F P_m (\cos \theta)$$

where $W(\theta)$ is defined as the number of radiations emitted by the polarized nuclei at angle $\theta$ divided by the number of radiations emitted from the unpolarized nuclei at angle $\theta$, where $\theta$ is the angle between the direction of the magnetic field and the direction of emission of the radiation. The expansion is valid for $\lambda$ equal to $2I$ or $2L$, whichever is smaller. Here $I$ is the angular momentum of the nucleus before decay and $L$ is the angular momentum carried away. For $k > 2I$, $B_k = 0$ and for $k > 2L$, $P_k = 0$. 
The $B_k$ term is the only temperature-dependent coefficient in the expansion and is determined by the population distribution between the hyperfine levels of the parent nucleus. $B_k$ is defined by the relation

$$B_k = (2k + 1)^{1/2} \sum_m C(\text{Ikm}|\text{Im}) W(m)$$

Since for alignment $W(m) = W(-m)$ and $C(\text{Ikm}|\text{Im}) = (-)^k C(\text{Ikm}|\text{Im})$ only the even terms of the expansion are nonzero, whereas for polarization both the even and odd terms appear. $B_1, B_2,$ and $B_4$ have been tabulated as functions of the Boltzmann factor $\beta$ by Blin-Stoyle and Grace. 8

The $U_k$ coefficient accounts for any reorientation occurring during transitions preceding that observed and is dependent on the angular momenta involved in the preceding transitions. $F_k$ is the Legendre polynomial of order $k$ and is the only coefficient dependent on $\theta$.

The $F_k$ coefficient depends on the multipole character of the observed transition and upon the angular momenta of the nuclear state from which the observed transition is emitted and the final nuclear state. For an unmixed $\gamma$ transition $F_k$ is given by

$$F_k = (-)^{I_f-I_i-1} (2I_i+1) C(I_{LL}|k0) W(I_i I_f LL; k I_f)$$

where $I_i$ and $I_f$ are the initial and final nuclear spins, $L$ is the angular momentum carried away by the $\gamma$ ray, and $W$ is a Racah coefficient.

Due to the conservation of parity in $\gamma$ transition the $F_k$ for odd $k$ are zero. Therefore it is impossible to differentiate between nuclear polarization or alignment by measuring $W(\theta)$ for a $\gamma$ transition. That is for a $\gamma$ transition $W(\theta) = W(\theta+\pi)$ and the direction of nuclear polarization cannot be determined, since $F_k$ even is an even function of $\cos \theta$.

Since parity is not conserved in $\beta$ transitions, it is possible to determine the direction of the magnetic field acting at the nucleus by observing the angular distribution of $\beta$ particles emitted from the polarized nucleus. The angular distribution must now include the odd
terms and for a Gamow-Teller electron decay ($\Delta I = \pm 1$), is given by

$$ W(\theta) = 1 - \frac{\sqrt{3}}{2\pi} \frac{v}{c} B \cos \theta ,$$

(3)

where $W(\theta)$ is the same as in Eq. (2), and $v/c$ is the ratio of the electron velocity to the velocity of light. Only the $k=1$ term has been included, since the higher terms vanish for allowed $\beta$ decay.

B. **Nuclear Magnetic Resonance in Ferromagnets**

When a magnetic field is applied to a nucleus, the hyperfine levels split by an energy $\Delta E$ given by Eq. (1). When radiofrequency radiation of energy equal to $\Delta E$ is applied to the nucleus, nuclear magnetic resonance is induced and transitions between the levels occur.

Nuclear Magnetic Resonance in Ferromagnets (FNR) involves nuclei in two distinct environments: domains and domain walls. This thesis deals only with FNR in domains, since in all cases reported here the ferromagnet is magnetically saturated and therefore all the walls have been swept out of the sample.

If the externally applied magnetic field is changed the resonant frequency will also be changed. In this manner it is possible to tell if the external field is parallel or antiparallel to the field at the nucleus. If an increase in the external magnetic field causes an increase in the resonance frequency then the two fields must be parallel and vice versa.

One of the most distinct characteristics of FNR is the enhancement factor. If the $z$ axis is defined by the externally applied static magnetic field, $H_o$, used to magnetically saturate the ferromagnet, then the rf field, $H_{rf}$, is applied along the $x$ axis and varies from positive to negative with the frequency of the rf field. The vector sum of these two fields forms a resultant applied field, $H_{res}$, which at a given time makes an angle $\phi$ with the static applied field, Fig. 3(a).
Fig. 3. The enhancement factor. See text for explanation.
The electronic magnetization, $M$, of the sample will follow the resultant applied field, Fig. 3(b). That is, the effect of the transverse rf field is to turn $M$, back and forth, through an angle $2\phi$ given by

$$\phi = \tan \phi = \frac{H_{rf}}{H_0},$$

since $\phi$ is small. This creates a transverse magnetization,

$$M_x = M \left( \frac{H_{rf}}{H_0} \right).$$

Since the large internal magnetic field, $H_{int}$, arises through the interaction of the electrons with the nucleus, $H_{int}$ is aligned with $M$. This gives an $x$ component to $H_{int}$, Fig. 3(c) which varies at the frequency of $H_{rf}$ and is given by

$$H_{int x} = H_{int} \left( \frac{H_{rf}}{H_0} \right).$$

Therefore the nuclei see a total transverse field

$$2H_1 = H_{rf} + H_{int} \left( \frac{H_{rf}}{H_0} \right) = \left( 1 + \frac{H_{int}}{H_0} \right) H_{rf}.$$

Thus nuclear resonance excitation in ferromagnets occurs indirectly through the response of the sample magnetization instead of by the external rf field acting directly on the nuclear moments. For cobalt nuclei in iron $H_{int} = 290kG$ and $H_0 = 1kG$, and the applied rf field is amplified by 290.

If a rf field is applied to a system of oriented nuclei, at resonance the frequency of the rf field equals the splitting of the hyperfine levels of the polarized nuclei, and the rf induced transitions partially randomize the Boltzmann distribution, which is set up by the low temperature and the large internal field. The randomization has a destructive effect on the angular distribution, $W(\theta)$, of the emitted $\gamma$
rays, which can be detected by observing the counting rate at a specific angle as a function of frequency. The enhancement of the rf amplitude in a ferromagnet is necessary to keep the rf power at a sufficiently low level in order to avoid rapid warm up of the sample.
III. EXPERIMENTAL

A. Apparatus

The basic procedure used was to cool the alloy to a low temperature by adiabatic demagnetization of a paramagnetic salt to which the alloy was thermally linked, then to apply a sufficient magnetic field to magnetically saturate the alloy and finally to measure the intensity of radiation emitted from the polarized nuclei at various angles and compare with the intensity emitted from the unpolarized nuclei. For the resonance experiment it was also necessary to apply an rf field to the alloy.

1. Cooling System

This was essentially that described by G. A. Westenbarger and is shown schematically in Figs. 4 and 5. There are two double-walled glass dewars, D. The outer contains liquid nitrogen and the inner liquid helium. By pumping on the vapor above the liquid helium it was possible to reduce the temperature of the bath surrounding the cryostat, C, to 10 K. The dewars were tapered in order to fit between the pole pieces, P, of the large electromagnet used for adiabatic demagnetization of the paramagnetic salt, S. This magnet was capable of producing a field of 22 kG in a 2-5/8-in. gap. The salt, S, was a mixture of powdered chromium potassium alum \([\text{CrK(SO}_4\text{)}_2\cdot12\text{H}_2\text{O}]\) and glycerine. The thermal link between the salt and the alloy was accomplished by a copper fin assembly, F, made from several sheets of 5 mil copper cut to the shape shown in Fig. 5. The thermal link is necessary in order that the magnetic field at the salt can be reduced to zero in the process of adiabatic demagnetization while a magnetic field of ~2kG is applied to the alloy. If the field at the salt were not taken to zero the lowest possible temperatures would not be reached.

The cryostat, internal diameter 1-1/8-in., length 16 in., was connected to a vacuum system consisting of an oil-diffusion pump and a mechanical fore pump. There was also a provision for letting helium gas
Fig. 4. Diagram of the demagnetization apparatus. The components are described in the text.
Fig. 5. Cryostat assembly for nuclear orientation of $^{114m}$In.
into the cryostat. This was used as an exchange gas so that heat could be transferred from the demagnetization salt to the 1.3K bath and vice versa. Also included in the cryostat was a pressed pill, M, of manganous ammonium sulfate $[\text{Mn(NH}_4\text{)}_2(\text{SO}_4\text{)}_2\cdot6\text{H}_2\text{O}]$, 7/8-in. in diameter and 1/4-in. thick. This paramagnetic salt is cooled by the fringing field of the electromagnet and serves to absorb any exchange gas not pumped out by the vacuum system. This particular salt was used because of its large heat capacity and the small field needed. A field of 6kG will cool the salt to its Curie point located a little above 0.1°K.\textsuperscript{14}

2. Polarizing Magnet

This is represented in Fig. 4 by T and consisted of a tube of niobium metal 3/8 in. long, with a 1/2 in. o.d. and 3/8 in. i.d. Niobium is superconducting under the experimental conditions. When the large electromagnet is turned down in the process of demagnetizing the cooling salt, flux is trapped in the niobium ring when it goes superconducting and a field of 2.3 kG is produced. The direction of the field defines the z axis.

3. Radiation Detectors

(a) Gamma detectors. Two scintillation counters consisting of a 3 x 3 in. NaI(Tl) crystal mounted to a photomultiplier tube were used. The output from the photomultiplier went to an amplifier and then into a pulse height analyzer. For observing the 136.4 keV γ-ray of Co\textsuperscript{57} better resolution than the NaI could provide was needed and a solid state detector was used. This consisted of a 3 x 2 x 1 cm lithium-drifted germanium crystal, Ge(Li), at 77°K. The crystal was connected to a preamplifier. The output of which went to an amplifier and then to a pulse height analyser. This system had a resolution of 3 kV FWHM at the $^{57}$Co energies. A $^{57}$Co spectrum taken with the solid state detector is shown in Fig. 8. For further information about solid state detectors see Refs. 15, 16, 17, and 18.
(b) Beta detectors. A silicon surface-barrier detector,\textsuperscript{19} B in Fig. 4, mounted inside the cryostat was used. The detector was placed so that it would receive radiation emitted along the magnetization axis. The lead wire, L, was brought into the cryostat from the helium bath by means of a Kovar seal. A preamplifier, PA, was mounted on top of the apparatus. The pulses from the preamplifier went to a linear amplifier, A, and then to a pulse height analyser, PHA.

4. Apparatus for Resonance Experiment

The apparatus for the resonance experiment was essentially the same as described above. The only difference in the cooling system was that the shape of the copper fins was changed. See Fig. 6. This was necessary since the source had to be exposed to the rf field. For the same reason the Nb ring had to be modified. This was accomplished by using two Nb rings, one on either side of the fins, in an arrangement similar to a Helmholtz coil. This produced a field of approximately 1 kG at the source. The rf input consisted of 50 ohm shielded cable running down through the helium bath to the top of the cryostat, then of \#20 copper wire (.035 in. diameter). This was wrapped around the outside of the cryostat to form a two turn coil. See Fig. 6. There was no beta detector used in the resonance experiment.

The rf circuitry and detection system are shown in Fig. 7. Using this counting system it was possible to set the window of the single channel analyzer on the photopeak of interest and have the total number of events in the window summed and printed on a typewriter. The oscillator used was a Hewlett-Packard Model 608B. The frequency meter was a Hewlett-Packard 5245L Electronic Counter.
Fig. 6. Cryostat assembly for NMR in polarized $^{60}$Co.
Fig. 7. RF circuitry and detection system for the NMR of polarized $^{60}\text{Co}$. 
B. Thermometry

The temperatures of the In alloys were determined by observing W(O) for the 136.4-keV γ ray of $^{57}\text{Co}$, which was included in the alloys. This method of measuring the temperature of the alloy is more accurate than measuring the temperature of the salt by the change of its susceptibility, since there is a thermal gradient between the salt and alloy.

$^{57}\text{Co}$ was chosen because of the low intensity of potentially interfering high-energy radiations and because the moment and internal fields of Co in iron and nickel are known. The decay scheme and γ-ray spectrum of $^{57}\text{Co}$ are shown in Fig. 8. Table I gives the calculated intensity of the 136.4-keV γ ray vs. temperature, for $^{57}\text{Co}$ oriented in Fe and Ni. These calculated values are based on the nuclear moment of 4.6 nm $^{20}$ for $^{57}\text{Co}$ and magnetic fields at the Co nucleus of -286 kG and -120 kG in Fe and Ni respectively. $^{21}$ The $^{57}\text{Co}$ anisotropies have been shown to obey the calculated relationship by comparison with a $^{60}\text{Co}$ thermometer. $^{22}$ No thermometer was used in the resonance experiments.

C. Procedure

1. Nuclear Orientation of $^{114m}\text{In}$

All radioisotopes were obtained as chlorides in HCl solution. The In-Co-Fe alloys were made by evaporating the $^{114m}\text{In}$ and $^{57}\text{Co}$ as the chlorides in small iron crucibles (~4 g) and then heating to 1600° for 5 minutes in an electric resistance furnace. Alloy #1 was heated in an argon atmosphere and #2 in an evacuated quartz ampule.

The In-Co-Ni alloys (again two were made) were formed by plating $^{114m}\text{In}$ from an HCl solution onto a thin strip (5 mil) of Ni metal, then evaporating a solution containing $^{57}\text{Co}$ onto the surface of the strip. This was folded several times, melted at 1500°C for 10 minutes in a sealed evacuated quartz ampule. Bright metallic alloys were obtained in every case. The second Fe alloy was checked for homogeneity by
Fig. 8. Gamma-ray spectrum of $^{57}$Co as recorded with a Ge(Li) detector. The decay scheme of $^{57}$Co is also shown.
Table I. \( W(\theta) \) vs \( 1/T \) for the \( ^{57}\text{Co} \) \( \gamma \)-ray thermometers.

<table>
<thead>
<tr>
<th>( 1/T (\text{K}^{-1}) )</th>
<th>Fe lattice</th>
<th>Ni lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( W(0) )</td>
<td>( W(\pi/2) )</td>
</tr>
<tr>
<td>10</td>
<td>0.980</td>
<td>1.010</td>
</tr>
<tr>
<td>20</td>
<td>0.927</td>
<td>1.036</td>
</tr>
<tr>
<td>30</td>
<td>0.851</td>
<td>1.070</td>
</tr>
<tr>
<td>40</td>
<td>0.767</td>
<td>1.106</td>
</tr>
<tr>
<td>50</td>
<td>0.682</td>
<td>1.138</td>
</tr>
<tr>
<td>60</td>
<td>0.602</td>
<td>1.165</td>
</tr>
<tr>
<td>70</td>
<td>0.531</td>
<td>1.185</td>
</tr>
<tr>
<td>80</td>
<td>0.465</td>
<td>1.202</td>
</tr>
<tr>
<td>90</td>
<td>0.404</td>
<td>1.216</td>
</tr>
<tr>
<td>100</td>
<td>0.353</td>
<td>1.225</td>
</tr>
</tbody>
</table>
cutting the alloy into several pieces and counting the activity of each. When count rate was plotted against weight, all points fell on a straight line.

The alloys were pounded down to a thickness of ~10 mils and cut to the desired shape (2mm x 5mm). The Ni alloys were annealed at 400°C for one hour at this point. The Fe alloys were not annealed. Each alloy was then cleaned with acid to remove any residual surface activity and soldered into a slit in the snout of the copper fin assembly, Fig. 5. Next the chrome alum slurry was made up. This was done by mixing equal volumes (~3 ml) of glycerine and a saturated aqueous solution of chrome alum. Then powdered chrome alum was added until the slurry had the consistency of jelly which was then spread between the fins of the copper thermal link. The fins were then placed in a glass tube (3-1/4 in. long, 3/4 in. diameter) and additional slurry added to fill the tube. Care was taken to make sure no slurry crept up between the fins, since there it would not be in the maximum magnetic field. The slurry was used so that good thermal contact would be made with the fins and also to improve the thermal conductivity of the salt itself at low temperatures.

The slurry assembly and the manganous ammonium sulfate pill were then suspended, by means of six nylon threads, inside a brass cage support assembly which bolted to the bottom of the cryostat vacuum line. Next the glass cryostat was soldered into place around the brass cage. This was accomplished by using a housekeeper seal at the top of the cryostat which could be soldered to the bottom of the vacuum line and thus make the cryostat chamber, C in Fig. 4, vacuum tight.

The outer surface of the cryostat was coated with an aqueous suspension of graphite mixed with acetone. This prevented black-body radiation from entering the cryostat and warming the contents.

The inner helium dewar was then filled with liquid nitrogen and helium exchange gas was introduced into the cryostat in order to keep the pressure at one atmosphere. This was done to freeze the chrome alum before pumping on it. After approximately 30 minutes the pumping was
started on the cryostat and continued overnight. When the pressure reached \(\sim 10^{-6}\) mm Hg, nitrogen was put in the outer dewar and the liquid nitrogen in the inner dewar was blown out and liquid helium transferred. Helium exchange gas was then let into the cryostat, bringing the pressure to \(\sim 0.03\) mm. The helium bath temperature was then lowered to 1\(^\circ\)K by pumping on the helium vapor.

The paramagnetic salt was then magnetized with a field of 22 kG. After thermal equilibrium had been reached, that is, all the heat of magnetization had left the salt (10 minutes), the exchange gas was pumped out. When the pressure reached \(\sim 10^{-6}\) mm, the magnetic field was slowly and as reversibly as possible turned down. The large electromagnet was rolled away and the table on which the detectors were placed was moved into position and counting started. Four-minute counts were taken for 30 minutes and then exchange gas was introduced in order to warm the alloy to 1\(^\circ\)K and several warm counts were made. Each spectrum was printed out, giving the number of counts in each channel of the pulse height analyser. Several demagnetizations were done with each alloy.

The \(\beta^+\) spectrum of \(^{114}\)In was observed using one of the In-Co-Ni alloys. The alloy was cooled as above and the detector in the cryostat, B in Fig. 4 was used. Counts were taken both at 0\(^\circ\) and 180\(^\circ\), by reversing the polarity of the electromagnet, in order to determine the sign of the internal magnetic field.

2. Resonance in \(^{60}\)Co

It is necessary to use thin foil alloys in order that most of the nuclei can feel the rf field. The skin depth in iron is given by

\[
\delta = (\pi \nu \mu \sigma)^{-1/2}
\]

where \(\nu\) is the frequency in cycles per second, \(\mu\) the permeability, \(\sigma\) the conductivity in \(\text{ohm-m}^{-1}\), and \(\delta\) is the skin depth in meters. At a depth equal to \(\delta\) the rf amplitude has decreased to \(1/e\) its value at the surface.
Two $^{60}$Co alloys were made by plating $^{60}$Co onto thin Fe foils (1.7 x $10^{-4}$ cm) and then diffusing, in a vacuum, the activity into the foil, (alloy I at 950°C for 80 hrs., alloy II at 950°C for 48 hrs.). The alloys were soldered to the fin system using Wood's metal (m.p. 70°C). After the alloy was soldered to the fin system the apparatus was assembled and the alloy cooled as described in the previous section. Using the electronics shown in Fig. 7, the total number of counts per minute in the $^{60}$Co photopeaks was printed out on the typewriter. Both the 1.173 MeV and 1.333 MeV γ rays were included in the window since $W(0)$ is identical for both. The rf input was kept constant at 0.5 volts peak-to-peak and the frequency was changed at the end of each counting period.

D. Treatment of Data

1. Solid Angle Correction

It is necessary to account for the fact that the detectors are not at a specific angle but subtend an angle proportional to the size of the active surface of the detector. This is accounted for by including another coefficient, $Q_k$, in Eq. (2). Explicit values of $Q_2$ and $Q_4$ have been tabulated as a function of γ-ray energies by Yates for various NaI crystal sizes. For the Ge(Li) detector it was necessary to use the following equation:

$$Q_2 = \frac{1}{2}(1+\mu) \quad Q_4 = \frac{1}{8}(1+\mu)(7\mu^2-3)$$

where $\mu$ is the cosine of the half angle of the cone of radiation accepted by the counter. $\mu$ was calculated assuming the Ge(Li) crystal was circular with an area equal to the actual area.

2. 191 keV γ-ray of $^{144m}$In

The number of counts in the photopeak was summed and the background subtracted. The number to subtract for background was calculated
by determining the number of counts in the same number of channels as used for the photopeak only some distance from the peak. Then by comparing the area under these channels and the area under a line drawn in as a continuation of the background under the peak, the background was accounted for. Next $W(0)$ was calculated by dividing the cold count rate by the warm count rate. $W(\pi/2)$ was not accurately calculated since it is one half the size of $W(0)$ and therefore less accurate. $W(\pi/2)$ was used as a check to make sure the alloy was good and that the anisotropy seen was due to the magnetic field at the In nucleus.

$W(0)$ for the 136.4 keV $\gamma$ ray of $^{57}\text{Co}$ was calculated in the same manner described above. Since the magnetic moment and the internal field at the $^{57}\text{Co}$ nucleus is known, it was possible to plot $W(0)$ vs. $1/T$. Then by referring to this, the temperature of the alloy could be determined for each counting period and thus $W(0)$ vs. $1/T$ could be plotted; then by comparing with the experimental points it was possible to determine $|H|$ for In in Fe and Ni. See Figs. 9 and 10.

3. $\beta^-$ Particles of $^{114}\text{In}$

It is possible to determine the direction of the internal field by observing $W(0)$ for $\beta$ particles. The $\beta$ spectra obtained were not corrected for background or solid angle since only a rough measurement of $W(0)$ was needed to determine the direction of the internal field.

4. 1.333 and 1.172 MeV $\gamma$ ray of $^{60}\text{Co}$

The cold count rate of the two $\gamma$ ray peaks of $^{60}\text{Co}$ was determined as a function of the frequency of the applied rf. No background or solid angle corrections were made.
IV. RESULTS

A. The Sign of the Internal Magnetic Field at Nuclei of In in Ni and Fe

The internal field is defined as positive if the internal field is parallel to the external field and negative if antiparallel. From Eq. (3) it is seen that if \( W(0) \) is known the sign of \( B_\parallel \) is determined. The sign of \( B_\parallel \) is dependent on the ordering of the hyperfine levels and since the ordering of the levels is determined by the sign of \( \mu H_{\text{int}} \), the determination of the sign of \( B_\parallel \), also gives the sign of \( \mu H_{\text{int}} \).

It was found that \( W(0) \) and \( W(\pi) \), implying \( \mu H_{\text{int}}(0) \). To deduce the sign of \( H_{\text{int}} \) from the above data, the sign of the nuclear moment, \( \mu \), must be known. Kogan et al.\textsuperscript{26} assumed that reorientation occurs in the 72-sec ground state of \( ^{114}\text{In} \), and that the magnetic moment of this state, \( \mu_{114} \), is therefore the one in question. If this is correct, the moment can be theoretically estimated as \( +3.4 \text{ mm} \), using the nuclear shell-model single particle states \( g_{9/2} \) (proton) and \( g_{7/2} \) (neutron). This estimate is based upon Schmidt-limit values for the single-particle moments, and more sophisticated methods of calculation would reduce its magnitude somewhat, but if the proton has mainly \( g_{9/2} \) character a positive sign for \( \mu \) is inescapable.

If thermal equilibrium is not established in 72-sec \( ^{114}\text{In} \); that is if the nuclear orientation induced in \( ^{114m}\text{In} \) is retained in \( ^{114}\text{In} \), then the interpretation is even simpler. The magnetic moment has been measured as \( \mu_{114m} = +4.75 \text{ mm} \).\textsuperscript{20} Fortunately either interpretation yields the same result: \( H_{\text{int}} \) for In in Ni is negative.

The sign of \( H_{\text{int}} \) for In in Fe has been previously determined and found to be negative.\textsuperscript{26,27}
B. The Magnitude of the Internal Field at Nuclei of In in Ni and Fe

Figure 9 shows the results for In in Fe. Each point represents one demagnetization. The results for In in Ni are shown in Fig. 10. Each point in this figure is the average of several demagnetizations. The values obtained are

\[ |H_{\text{int}}| = 295 \pm 5 \text{ kG (In in Fe)} \]

\[ |H_{\text{int}}| = 42 \pm 3 \text{ kG (In in Ni)} \]

The above statistical errors are the root mean square values. They should be doubled in both cases to include miscellaneous systematic errors.

Recent NMR values for the above give

\[ |H_{\text{int}}| = 288 \text{ kG (In in Fe)} \]

\[ |H_{\text{int}}| = 33 \text{ kG (In in Ni)} \]

where the experimental errors are within 2%. The value for In in Fe agrees well with the value obtained from nuclear orientation when the difference in concentration and temperature are considered. For In in Ni the agreement is not as good. The NMR results were done at 4°K with a concentration of \( \sim 1 \) at. % whereas the concentration of the nuclear orientation alloys was less than 0.1 at. %.
Fig. 9: \( W(0) \) for 191-keV \( \gamma \) ray from \(^{114m}\text{In} \) in Fe as a function of temperature. Each point represents one demagnetization. Curves are for various values of the hyperfine field. □-source 1[NaI(Tl)], O-source 2[Ge(Li)], .-source 2[NaI(Tl)].
Fig. 10. W(0) for 191-keV $\gamma$ ray from $^{114m}$In in Ni as a function of temperature. Each point represents the average of several demagnetizations. Curves are for various values of the hyperfine field. □-source 1[Ge(Li)], ○-source 2[Ge(Li)], •-source 2[NaI(Tl)].
C. Nuclear Magnetic Resonance in Polarized $^{60}\text{Co}$

In Figs. 11 and 12 are shown the results of the first successful attempt to observe NMR in oriented nuclei in thermal equilibrium. The resonant frequency is $165.75 \pm 0.15$ MHz. With a magnetic moment of $\mu = 3.754 \pm 0.008$ nm,\textsuperscript{14} this gives an effective magnetic field of $|H| = 289.6 \pm 0.7$ kG. Assuming that the demagnetization factor for a thin foil is negligible, and correcting for the polarizing field ($1.0 \pm 0.5$ kG), the value $|H_{\text{int}}| = 290.6 \pm 0.9$ kG is obtained for the internal magnetic field of very dilute Co in Fe (less than 0.1 at. %) at 0.03°K. This agrees well with the value of 289.7 kG measured by NMR for 1\% Co in $^{29}\text{Fe}$ and 4 to 17\% Co in Fe.\textsuperscript{30} A more recent measurement gives $-290.07 \pm 0.09$ kG.\textsuperscript{31}
Fig. 11. Warm up curves for $^{60}$Co in Fe (alloy II) at $\theta = 0^\circ$. In the upper part the frequency was varied with time and the resonance effect appears at 165.8 MHz. The lower curve was taken with a fixed frequency off resonance but with the same rf amplitude as in the upper case.
Fig. 12. Resonance effect at 0° and 90° for two different alloys (I and II) of $^{60}$Co in Fe.
V. DISCUSSION

A. The Internal Field

The total magnetic field, H, acting at the nucleus may be written as

\[ H = H_o + H_{\text{int}} \]

where \( H_o \) is the external, applied field and \( H_{\text{int}} \) is the internal field. The internal field at the nucleus is given for cubic symmetry by

\[ H_{\text{int}} = H_{\text{hf}} - DM + \frac{4}{3} \pi M \]

where \(-DM\) is the demagnetizing field depending on the shape of the sample, (for a thin slab with the field, \( H_o \), along an axis in the plane, \( D = 0 \)), \( \frac{4}{3} \pi M \) the Lorentz field and \( H_{\text{hf}} \) the hyperfine magnetic field. For a complete discussion of hyperfine interactions in magnetic materials see Ref. 32.

The hyperfine field may be written for cubic symmetry as

\[ H_{\text{hf}} = \frac{8\pi}{3} \mu_B S |\psi(0)|^2 + \mu_B L \left( \frac{1}{2} \right) \]

where the first term arises from the Fermi contact interaction.\(^{33}\) \( |\psi(0)|^2 \) is the unpaired s electron density at the nucleus. The second term is due to the electron orbital angular momentum, L, and will be considered negligible with respect to the contact term. Marshall\(^{34}\) has shown that the orbital angular momentum term for the unquenched part of the orbital moment in a ferromagnet is \( -50 \) kG.

The problem in understanding \( H_{\text{hf}} \) is in determining the main contribution to \( |\psi(0)|^2 \). It has been shown by Collins and Low\(^{35}\) using neutron diffraction that there is a 3d moment of 2.1 \( \mu_B \) at the impurity site for Co and Fe. There are three main contributions to \( |\psi(0)|^2 \) due to this large 3d moment:
(a) Spin polarization, which occurs by exchange between electrons of the same spin, of the inner or core s electrons. Thus since the 3d electrons have a majority of spin of one sign, the s electrons of the core with the same sign will be attracted outwards toward the 3d electrons and thereby cause a net contribution to $|\psi(0)|^2$ by the core s electrons of opposite spin.

(b) Spin polarization of the 4s or conduction electrons occurs in the same manner as for the core s electrons except in this case the 4s electrons are on the other side of the 3d electrons and the effect on $|\psi(0)|^2$ is in the opposite direction.

(c) The admixture of the 4s conduction electrons with the 3d electrons causes the 3d electrons to have a partly 4s nature, which thus contributes to $|\psi(0)|^2$.

Contribution (a) would lead to a negative value of $H_{hf}$ whereas (b) and (c) would give a positive value. Since the experimental value is $-290$ kG, the contribution due to core polarization must be dominant.

The production of $H_{hf}$ for nonmagnetic elements (such as In) dissolved in ferromagnets is more complicated. One interpretation is that the unpaired spin of the 3d electrons of the neighboring ferromagnetic atom attracts the 4s conduction electrons of like spin thus leaving a net unpaired spin density, opposite to the 3d, at the outer edge of the Fe atom. This unpaired spin density of the 4s Fe electrons interacts via a positive exchange integral with the outer s electrons of the impurity which in turn causes $|\psi(0)|^2$ to be nonzero for these electrons at the impurity nucleus. This would give rise to the negative hyperfine magnetic field for In dissolved in Fe and Ni.

Daniel and Friedel $^{36}$ have proposed a model for nonmagnetic atoms dissolved in Fe in which it is assumed that only the conduction electrons, treated as free electrons, in the alloy are responsible for the hyperfine field observed at the nucleus of the dissolved atom. The impurity atom is represented by a square potential well, the depth of which is determined by the condition that the electronic charge attracted by the well exactly neutralizes the excess ionic charge of the impurity. The
s-d exchange interaction shifts the two conduction "spin-up" and "spin-down" half bands in relation to the "initial" bottom of the band so that the effective depth of the impurity potential well is not identical for the two directions of spin. They take the s-d exchange interaction as positive, i.e. to an excess of electrons having spins parallel to those of the d shell in relation to the electrons having antiparallel spin. If the excess d spin is taken as ↑ then there are fewer conduction electrons of spin ↓ than of spin ↑. The bottom of the conduction band for electrons of spin ↓ is at a higher energy than for spin ↑, thus the effective depth of the impurity well is greater for electrons of spin ↓, and the potential of the impurity atom has a greater attraction for the electrons of spin ↑ than for those of spin ↓. Thus there is an excess of spin ↑ electron density at the impurity nucleus and therefore a negative hyperfine field by the contact interaction.

In Fig. 13 are plotted the best values to date for $H_{hf}$ at nuclei of elements between Y and Te dissolved in Fe and Ni. The open 4d shell probably contributes (via core polarization) heavily to the negative hyperfine fields above the middle of the shell. Recent measurements on local moments for Ru in Ni by Matthias et al. and the neutron diffraction work of Collins and Low support this conclusion. The continuing large negative $H_{hf}$ in Ag, Cd, and In may be understood as arising from polarization of the 5s conduction electrons as was described above.

The systematic sign change of $H_{hf}$ in the 5p shell indicates the contribution of polarized conduction electrons. A quantitative analysis, however, has yet to be given. The measurements of $H_{hf}$ for In in Fe and Ni emphasize the regularity of this trend. The Y-in-Fe point is probably another indication of the phenomenon. Any successful theory for these fields will have to explain both the regularity and trends shown in Fig. 13. Trends among fields at solutes in ferromagnets are discussed in Ref. 39.
Fig. 13. Hyperfine fields at nuclei of atoms (Z=39-52) dissolved in Fe (circles) and Ni (squares) hosts. Cases for which the sign is known are shown as filled points.
B. Comparison of Conventional Nuclear Orientation with NMR in Polarized Nuclei

1. Accuracy

The resonance type experiment has the inherent advantage of accuracy over conventional nuclear orientation, NO. This can be seen by comparing the result of this thesis for In in Fe where the error is ± 10 kG to the result of Templeton and Shirley\textsuperscript{31} for Co in Fe where the value of the hyperfine field is given as -290.07 ± 0.09 kG. The \textsuperscript{114}In is actually a very favorable case for NO due to its large anisotropy, and the error is certainly representative of conventional nuclear orientation.

The curves shown in Fig. 12 show only a 1% effect. This small effect is due to the strong inhomogeneous broadening of the resonance (linewidth 0.65 MHz) compared to the small natural linewidth. By using frequency-modulation and an amplitude, \( H_\perp \), sufficient to saturate the resonance, Templeton and Shirley have been able to observe almost complete destruction of the anisotropy, thereby greatly extending the applicability of the resonance technique.

2. Sign of \( H_{\text{int}} \) and the nuclear g Factor

As mentioned in the section on theory, the sign of the internal field may be determined directly by varying the applied field and observing the direction the resonant frequency shifts. This has recently been done by Templeton and Shirley for \( ^{60}\text{Co} \) in Fe. They found that increasing the external field decreased the resonant frequency; therefore the external field is antiparallel to the internal field.

In the resonance experiment the quantity measured is

\[
|\nu| = \frac{g\mu_N}{h} (H_o + H_{\text{int}})
\]

where \( g \) is the nuclear g factor and \( \mu_N \) the nuclear magneton. By plotting \( \nu \) versus \( H_o \); \( |g|, H_{\text{int}} \) and the sign of \( H_{\text{int}} \) can be determined provided the source is magnetically saturated.
The resonance experiment measures a frequency $|g\mu_B N/h|$ while NO using $\gamma$ rays measures an energy $|\mu H|$. Combining both techniques would determine the spin of the nuclear state.$^4$ 

3. Relaxation Times

Templeton and Shirley$^3$ have also demonstrated that this technique is well suited to observe relaxation times, $T_1$. They saturated the $^{60}$Co spin system by sweeping in the resonant frequency range and observed a dramatic increase in $W(0)$. After termination of the sweeping, $W(0)$ decayed to its equilibrium (oriented) value. They found that to within experimental accuracy, $W(0,t)$ obeyed the equation

$$W(0,t) - W_{eq}(0) = [W(0,t_0) - W_{eq}(0)] \exp\left[-(t-t_0)/T_1\right],$$

where $T_1$ depends only on the lattice temperature. They measured $T_1$ for both $^{60}$Co and $^{54}$Mn in Fe, and found for $^{60}$Co in Fe, $(\gamma_{N-T}^{2D})^{-1} \times 10^{-7} = 0.87$, and for $^{54}$Mn in Fe, $(\gamma_{N-T}^{2D})^{-1} \times 10^{-7} = 3.0$. These are the first $T_1$ measurements on ferromagnets in the millidegree range and the first such measurements for very dilute ($10^{-3}$%) solutes.

4. Temperature Scale

The resonance experiments are independent of any precise knowledge of the temperature, although the alloy must be cooled in order to produce an anisotropy in the emitted radiations. For NO the temperature must be known accurately.

5. Treatment of Data

No corrections are made to the number of counts recorded in the resonance experiment since only a relative change is being observed. For NO the absolute value of the anisotropy is of importance and therefore background and solid angle corrections must be made, as described in Sec. III-D.
6. **Use of Thin Foils**

The fact that thin foils (~10^{-4} cm) are necessary for the resonance experiments is a disadvantage, since they are very susceptible to accidents and alloy preparation is much more difficult. This handicap could be overcome however with the use of a mass separator by which it would be possible to shoot the desired isotope into the ferromagnet. The depth of penetration could also be controlled.

7. **Finding the Resonance**

If the nuclear moment of the isotope under study is not known, then it may be necessary to sweep a considerable frequency range in order to find the resonance.

NMR in polarized nuclei has the advantage over conventional NMR in that a greater number of isotopes is available to this technique at concentrations and temperatures much below that possible before. Also with the advent of 3He - 4He dilution refrigerators,^{41,42} the versatility of the NMR in polarized nuclei technique should be greatly increased, making possible the measurement of relaxation times at constant temperatures for dilute ferromagnetic alloys.
VI. CONCLUSIONS

The internal magnetic fields at nuclei of In in Fe and Ni have been measured and found to be $H_{\text{int}} = -295 \pm 5$ kG (In in Fe) and $H_{\text{int}} = -42 \pm 6$ kG (In in Ni). These values emphasize the striking regularity of the value of $H_{\text{int}}$ in ferromagnets with atomic number of the impurity.

Detection of nuclear magnetic resonance in polarized nuclei by destruction of the anisotropy of nuclear radiation is shown to be possible. This technique opens up an entire new dimension for nuclear orientation. It should now be feasible to measure with great accuracy: $H_{\text{int}}$, nuclear magnetic moments, and spin-lattice relaxation times for many radioactive nuclei, at temperatures and concentrations which were not accessible before.
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