

<sup>9</sup>In the Al-Al<sub>x</sub>O<sub>y</sub>-Al junction at  $T \approx 1.2^\circ\text{K}$  we observe a field about 30% higher than the Clogston paramagnetic criterion. This is still within the error that Clogston assigns to his estimate because of uncertainties in the estimate of the paramagnetic susceptibility.

<sup>10</sup>A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **47**, 720 (1964).

<sup>11</sup>D. Saint-James and P. G. de Gennes, Phys. Letters **7**, 306 (1963). Saint-James and de Gennes calculate the enhancement of the critical field arising from the vacuum boundary condition on a bulk sample. Abrikosov<sup>10</sup> has recently extended the treatment to cover the case of vacuum surface enhancement of a thin film. As our estimates of the properties of the region giving rise to dielectric enhanced superconduc-

tivity are meant to be correct only to order of magnitude, no attempt has been made to include combined thin-film and Saint-James-de Gennes surface superconductivity effect.

<sup>12</sup>The edges of the thin film are an ideal place for the observation of this effect since most of the edge region is not in contact with thick normal regions which would be expected to lower  $T_C$ .

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### HYPERFINE STRUCTURE OF THE 14.4-keV $\gamma$ RAY OF <sup>57</sup>Fe IN HYDRATED FERRIC AMMONIUM SULFATE AS A FUNCTION OF THE MAGNETIZATION OF THE SALT\*

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The hyperfine-structure (hfs) spectra of the 14.4-keV  $\gamma$  ray of the nucleus <sup>57</sup>Fe in the paramagnetic salt hydrated ferric ammonium sulfate have been measured through the use of the Mössbauer effect. These measurements were performed at an absolute temperature  $T$  in the liquid helium region in zero applied magnetic field, and also in the presence of applied magnetic fields  $H$  large enough to produce a substantial polarization of the unpaired electron spins of the Fe<sup>+++</sup> ions. The behavior of the Mössbauer linewidths, shapes, and spacings of the hfs spectra observed here differ from the hfs spectra found for either magnetically dense or exceedingly dilute magnetic materials.

In previous recoilless radiation studies where the magnetic materials have had a high density of magnetic ions, for example metallic iron<sup>1</sup> or  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,<sup>2,3</sup> it has been found experimentally that the individual gamma-ray lines of the hfs multiplet may show widths which are very close to  $\hbar/\tau_N$  where  $\tau_N$  is the nuclear  $\gamma$ -decay lifetime,<sup>4</sup> and that the line spacings may be very well described<sup>1-3</sup> by an approximate Hamiltonian which for either the nuclear excited or ground state has the form

$$\mathcal{H}_1 = AM I_z / g\beta + g_n \beta_n H I_z \quad (1a)$$

$$= g_n \beta_n (H_{\text{eff}} + H) I_z, \quad (1b)$$

where

$$H_{\text{eff}} = AM / g\beta g_n \beta_n. \quad (1c)$$

In Eqs. (1),  $g_n$  is a nuclear gyromagnetic ratio,  $\beta_n$  is the nuclear magneton,  $A$  is an hfs coupling constant,  $I_z$  is the  $z$  component of the nuclear spin operator  $\vec{I}$ ,  $g$  is the electron gyromagnetic ratio, and  $\beta$  is the Bohr magneton. The quantity  $M$ , the electron spin magnetization or sublattice magnetization in the case of an antiferromagnet, is the thermal average of  $S_z$ , the  $z$  component of the electron spin operator  $\vec{S}$ , and  $H_{\text{eff}}$  is an effective magnetic field. Recoilless radiation studies have also been made on dilute magnetic materials, for example by Wertheim and Remeika<sup>5</sup> on very dilute solutions of Fe<sub>2</sub>O<sub>3</sub> in Al<sub>2</sub>O<sub>3</sub>. For zero applied magnetic field, Wertheim and Remeika observed a resolved hfs spectrum in which the lines of the multiplet, as above, showed widths close to  $\hbar/\tau_N$  and where the line spacings were well described by  $A\vec{I}\cdot\vec{S}$  plus a small crystal-field term. Measurements have not been reported, but it may be expected that if this magnetically dilute material were placed in a strong magnetic field ( $g\beta H \gg A$ ),

in the absence of crystal-field effects the line spacings would be described by the Hamiltonian

$$\mathcal{H}_2 = A I_z S_z + g_n \beta_n H I_z. \quad (2)$$

We note that for a given nuclear state of spin  $I$ , Eq. (1) has  $(2I+1)$  substates while Eq. (2) has  $(2S+1)(2I+1)$  substates. In the limit of dense magnetic materials, Eq. (1), the magnetization  $M$  is a parameter of the Hamiltonian, and for a paramagnetic salt  $M$  is dominantly a function of  $H/T$ . In the limit of Eq. (2) which describes exceedingly dilute magnetic substances, the spectra depend on  $H$  but are independent of  $T$ .

In obtaining the following results we have chosen to study a system with a magnetic dilution which is intermediate between the extremes described by  $\mathcal{H}_1$  and  $\mathcal{H}_2$ . Our measured spectra for the system with intermediate dilution will be compared with those for very dense and also for very dilute systems as to line spacings, Eqs. (1) and (2), and also as to line shapes and widths. This comparison is made in order to expose the difference of behavior of the line shapes, widths, and spacings which may occur at an intermediate dilution from the behavior of these properties at the two extremes of concentration of magnetic ions. In making this comparison,  $M$  or  $H/T$  will be used as a parameter. This procedure is strictly correct only in the limit of dense magnetic materials as described by Eq. (1), but the use of these parameters does provide a convenient way of showing the departure of the spectra observed here from those described by Eqs. (1) or (2).

The monochromatic gamma-ray source used for our Mössbauer measurements was prepared by diffusing about 70 mCi of  $^{57}\text{Co}$  into a 0.0003-inch-thick copper foil over an area of about 4 cm<sup>2</sup>. A Mössbauer absorption linewidth at half-height of 0.47 mm/sec was obtained with this source at 4.2°K using a  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  single-line absorber at room temperature. Thus our source of  $^{57}\text{Co}$  in Cu has a linewidth which is larger than the natural width  $\hbar/\tau_N$  by at most a factor of 2.5.

The absorber investigated in these measurements was a polycrystalline sample of hydrated ferric ammonium sulfate  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  containing 20 mg/cm<sup>2</sup> of iron. This iron had the natural isotopic abundance of  $^{57}\text{Fe}$ . Both the moving source and the stationary absorber were placed in the same liquid-helium bath, but the magnetic field was applied only to the absorber. The direction of the field was nor-

mal to the plane of the absorber and parallel to the  $\gamma$ -ray propagation direction. Measurements were made at the magnetic fields and at the temperatures given in Table I. The apparatus used for these measurements was quite similar to equipment which has been described previously.<sup>9</sup> A superconducting magnet was used to supply the external magnetic field.

Spectra observed at the highest, an intermediate, and at the lowest nonzero value of  $H/T$  are shown in Figs. 1, 2, and 3. In Table I, the observed separations of the inner and outer pairs of absorption minima  $\Delta V_i$  and  $\Delta V_0$  in mm/sec (see Fig. 1) are given for all of our measurements. In Fig. 1, at the largest value of  $H/T$ , an hfs spectrum of four well-resolved lines was observed. All four lines showed a width at half-height of about 0.85 mm/sec. This may be compared with the linewidth of 0.47 mm/sec obtained for the source and a  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  absorber as described above. Thus a large part of the observed linewidth of 0.85 mm/sec may be associated with the ferric ammonium sulfate absorber. As  $H/T$  is decreased, Figs. 2 and 3, the splittings  $\Delta V_0$  and  $\Delta V_i$  of the spectrum decrease, and the outer pair of lines appear progressively much broader, more asymmetric, and smaller in amplitude. In sharp contrast, the widths and amplitudes of the inner pair of lines appear to be independent of  $H/T$  within statistical error over the same range of  $H/T$  values.

In Fig. 4 the splittings  $\Delta V_0$  and  $\Delta V_i$  are plotted versus  $M/g\beta$ . In making this graph we seek

Table I. The observed separations of the absorption minima for the outer and inner line pairs  $\Delta V_0$  and  $\Delta V_i$  (see Fig. 1) are given in columns 3 and 4, respectively, and the corresponding external magnetic field  $H$  and temperature  $T$  at which the measurements were made are given in columns 1 and 2. In column 5 the  $\beta H/kT$  values are listed, and the magnetization values  $M$  calculated from Eq. (3) are given in column 6 as the ratio  $M/g\beta$ . The gyromagnetic ratio  $g$  was taken equal to 2 for this calculation.

$H$ (kOe)	$T$ (°K)	$\Delta V_0$ (mm/sec)	$\Delta V_i$ (mm/sec)	$\beta H/kT$	$M/g\beta$
24.0	1.70	16.69 ± 0.17	2.66 ± 0.10	0.946	2.31
24.0	2.25	15.8 ± 0.3	2.31 ± 0.10	0.715	2.18
18.9	2.25	15.0 ± 0.4	2.27 ± 0.10	0.564	2.01
27.3	4.20	14.1 ± 0.4	2.11 ± 0.10	0.437	1.79
24.0	4.20	13.7 ± 0.4	1.75 ± 0.10	0.384	1.67
18.0	4.20	12.3 ± 0.5	1.57 ± 0.10	0.289	1.39
12.0	4.20	11.0 ± 0.5	0.97 ± 0.10	0.192	1.01

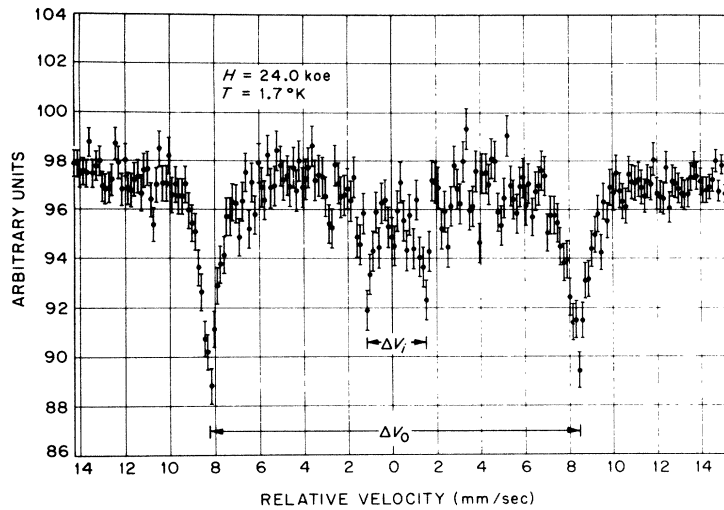


FIG. 1. The hfs spectrum for hydrated ferric ammonium sulfate is shown for an external magnetic field  $H = 24$  kOe and a temperature  $T = 1.70^\circ\text{K}$ . The separations of the absorption minima for the outer and inner pairs of lines  $\Delta V_0$  and  $\Delta V_i$  are shown for this figure. Similar determinations were made for Figs. 2 and 3 but are not indicated on the figures. All of the four lines have widths at half-height of about  $0.85$  mm/sec.

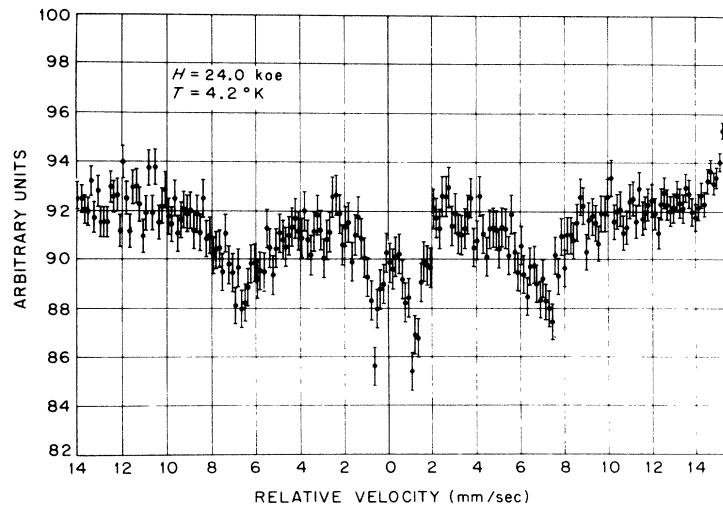


FIG. 2. The hfs spectrum for hydrated ferric ammonium sulfate is shown for  $H = 24.0$  kOe and  $T = 4.20^\circ\text{K}$ . For this magnetic field and temperature the outer lines of the spectrum are much broader, more asymmetric, and smaller in amplitude than the corresponding lines of Fig. 1; the inner lines, however, do not show any additional broadening within statistical error.

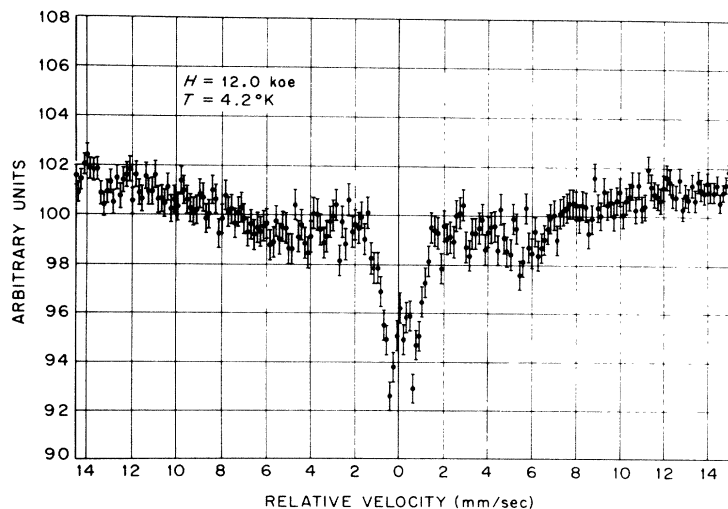


FIG. 3. The hfs spectrum for hydrated ferric ammonium sulfate is shown for  $H = 12.0$  kOe and  $T = 4.20^\circ\text{K}$ . At this magnetic field and temperature the outer lines are very broad and small in amplitude. Analysis of the spectrum indicated that  $\Delta V_0 = 11.0 \pm 0.5$  mm/sec. The inner lines again have a width of about  $0.85$  mm/sec which is the same as the widths of the corresponding lines shown in Figs. 1 and 2 within statistical error.

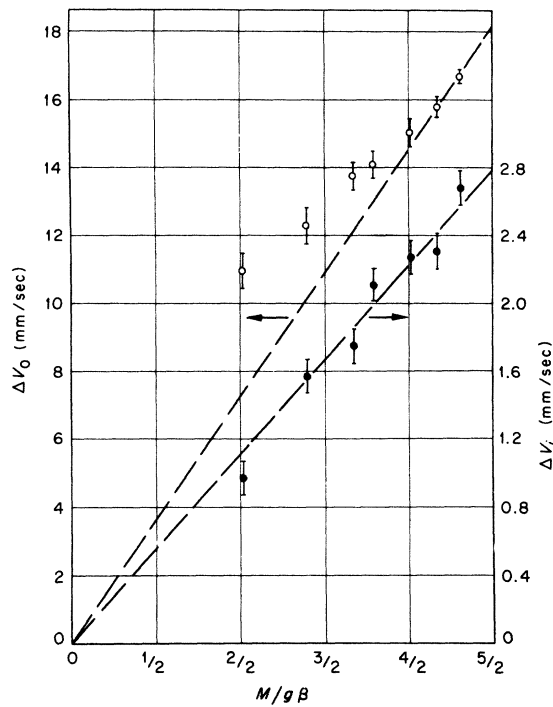


FIG. 4. The quantities  $\Delta V_0$ , which are shown as open circles, and  $\Delta V_i$ , which are shown as closed circles, are plotted versus  $M/g\beta$  (see Table I). The extrapolation of the dashed curves to magnetic saturation ( $M/g\beta = \frac{5}{2}$ ) yields  $\Delta V_0(\frac{5}{2}) = 18.01$  mm/sec and  $\Delta V_i(\frac{5}{2}) = 2.77$  mm/sec. The effective internal magnetic field estimated from these saturation values of  $\Delta V_0$  and  $\Delta V_i$  is  $|H_{\text{eff}}|_{5/2} = 563 \pm 30$  kOe. See text for a discussion of the  $\pm 30$ -kOe range of uncertainty in this value.

to give at least a rough comparison of the spacings of the absorption minima found here for intermediate magnetic dilution with the line spacings which would occur for a magnetically dense system as described by Eq. (1). The splittings  $\Delta V_0$  and  $\Delta V_i$  contain a contribution from the interaction of the externally applied magnetic field with the nucleus. If, for the purpose of obtaining an estimate of its magnitude, this contribution from the nuclear Zeeman effect is assumed tentatively to give an additive contribution to  $\Delta V_0$  or  $\Delta V_i$ , this contribution is found to be small, of the order of 5% of  $\Delta V_0$  or  $\Delta V_i$ . The comparison in Fig. 4 is made, not with the expectation that  $\Delta V_0$  or  $\Delta V_i$  should be a function of  $M/g\beta$ , but rather to show at least in a qualitative way the departures from Eq. (1) which can arise when the magnetic material has an intermediate magnetic dilution.

For the purpose of making the graph, Fig. 4, the salt magnetization  $M$  was estimated using

the Brillouin function,

$$M = g\beta \frac{\text{Tr}[S_z \exp(-g\beta H_z S_z / kT)]}{\text{Tr}[\exp(-g\beta H_z S_z / kT)]}. \quad (3)$$

In justification of this use of the Brillouin function to estimate the expectation value of the magnetization of an ion in a powder sample, the following points should be noted: Ferric iron has a half-filled 3d electron shell. Correspondingly, in hydrated ferric ammonium sulfate the ferric ion has a spin of  $\frac{5}{2}$ . The electron-spin  $g$  factor, which has been measured for example in very dilute solutions of  $\text{Fe}^{+++}$  ion in the isomorphous salt  $\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , is found<sup>7</sup> to be isotropic and very close to 2. In the calculation of  $M$  we have assumed  $g = 2$ . All crystal-field terms in the spin Hamiltonian measured on these dilute solutions of  $\text{Fe}^{+++}$  ion in  $\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  are at least an order of magnitude smaller than the interaction energy of the electron spin with the applied magnetic fields ( $H \geq 12.0$  kOe) used in these measurements and also are at least an order of magnitude smaller than  $kT$ . It is assumed that these crystal-field terms are similarly small for  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . For this paramagnetic salt the fact<sup>8</sup> that the Néel temperature is only  $0.04^\circ\text{K}$  shows that the electron spin-spin interactions are similarly small compared to  $kT$  and to the electron spin energy in the applied magnetic fields. Since  $g\beta H_z S_z$  is the dominant term in the spin Hamiltonian for the magnetic field values used, and because all terms other than  $\langle g\beta H_z S_z \rangle$  are small compared with  $kT$ ,  $M$  will be within a few percent of the actual magnetization of the salt.<sup>9</sup>

It now may be seen from Fig. 4 that, within statistical error,  $\Delta V_i$  is approximately proportional to  $M$  over the range of  $M$  values studied. However, while  $\Delta V_0$  decreases with decreasing  $M$ , it is not proportional to  $M$ . Thus  $\Delta V_0$  appears to have a different dependence on  $H$  and  $T$  and a different relationship to  $M$  from  $\Delta V_i$ . Then neither Eq. (1) nor in fact Eq. (2) which give satisfactory descriptions of magnetically dense and very dilute systems can give an adequate description of the results given in Table I.

A measurement was made at zero applied magnetic field at  $4.20^\circ\text{K}$  and thus for  $M = 0$ . Here a rather broad unresolved line was observed with a width at half-height of approxi-

mately 2.0 mm/sec. This behavior, where a single line is observed rather than a resolved hyperfine structure, is more similar to that found for the dense than for the extremely dilute magnetic materials. For  $M=H=0$ , Eq. (1), which describes dense magnetic systems, would predict a single line while the operator  $A\vec{I}\cdot\vec{S}$  which describes very dilute systems would predict a resolved hfs spectrum.

The Mössbauer spectrum for metallic iron in a magnetic field which is parallel to the  $\gamma$ -ray propagation direction consists of four lines.<sup>10</sup> These correspond to transitions for which  $\Delta m_I = \pm 1$ . If we define  $\Delta V_0$  and  $\Delta V_i$  for this spectrum in a manner analogous to Fig. 1, then it is found that the ratio  $(\Delta V_0/\Delta V_i)_{\text{Fe}}$  has the value<sup>3</sup>  $6.15 \pm 0.09$ . Insofar as Eq. (1) describes the spectrum, this ratio is independent of  $(H_{\text{eff}}+H)$ , and does depend only on the gyromagnetic ratios of the excited and ground nuclear states.

With increasing  $H/T$ , in the limit of magnetic saturation where  $M/g\beta = \langle S_z \rangle = S$ , it should be possible to describe the hfs coupling for  $\text{Fe}^{+++}$  in  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  in terms of an effective field. The ratio  $(\Delta V_0/\Delta V_i)$  should again be independent of applied field and should have a value close to that for metallic iron. Referring to Fig. 4, the ratio  $\Delta V_0/\Delta V_i$  extrapolated to magnetic saturation ( $M/g\beta = \frac{5}{2}$ ) has the value  $6.5 \pm 0.3$ . This agrees within error with the corresponding ratio for effective field from the intercepts of  $\Delta V_0$  and  $\Delta V_i$  at  $M/g\beta = \frac{5}{2}$ . Thus a value of  $|H_{\text{eff}}|_{5/2} = 563 \pm 30$  kOe is obtained. This value has an uncertainty due to the approximately 5% contribution of the applied field to  $\Delta V_0$  and  $\Delta V_i$ . The indicated error of  $|H_{\text{eff}}|_{5/2}$  contains a contribution of  $\pm 24$  kOe due to this.

A theoretical investigation of the notably different behavior of the splittings  $\Delta V_0$  and  $\Delta V_i$  and also of the line shapes of the inner and outer pairs of lines as a function of  $H$  and  $T$  may be of interest in the study of electron spin-spin interactions in magnetic solids. Some of the line broadening observed in Figs. 1, 2, and 3 will be due to the small crystal-field and possible nuclear-quadrupole terms in the spin Hamiltonian along with the fact that a powdered sample was used. It is suggested, however, that the major behavior of the line shapes and splittings may be described in terms of the nuclear lifetime  $\tau_N$  and in terms of an approximate spin Hamiltonian involving (a) the interaction of the applied field with the electron spins  $g\beta\vec{H}\cdot\vec{S}$ , and (b) also the interaction of the applied

field with the nuclear spins  $g_n\beta_n\vec{H}\cdot\vec{I}$ , (c) the hfs coupling  $A\vec{I}\cdot\vec{S}$ , and (d) the exchange and dipole-dipole interactions of the electron spins among themselves. These terms in the spin Hamiltonian may be represented as characteristic times. In this sense, three characteristic times are of importance in the description of these results: the nuclear lifetime, the nuclear precession time, and the electron spin-spin relaxation time. Although no theoretical discussion directly applicable to our measurements is as yet available, it should be possible to describe these results in terms of a correlation-function treatment. In taking the data shown in Figs. 1, 2, 3, and 4,  $g\beta H$  has been made large compared to other terms in the spin Hamiltonian. The thermal energy  $kT$  was comparable to  $g\beta H$  and similarly was large compared to these other terms in the Hamiltonian. These facts may simplify the theoretical description of these results.

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