Hyperfine Structure of Fe[57] in Paramagnetic and Antiferromagnetic FeF$_2$ from the Mössbauer Effect

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Measurements of the gamma-ray resonant absorption in oriented slabs of FeF$_2$ have been used to determine the magnitude and direction of the magnetic field at the iron nucleus in the antiferromagnetic state (3.40×10^5 oe at 0°K) and the quadrupole splitting in the paramagnetic state (31.2 Mc/sec) of this material. The observed electric and magnetic hfs in the antiferromagnetic state is interpretable in terms of an asymmetric electric field gradient tensor with its major axis perpendicular to the c axis, an asymmetry parameter of 0.33, and a quadrupole splitting of 30.3 Mc/sec at 45°K.

FERROUS fluoride in the antiferromagnetic state has recently been studied by Jaccarino and Walker,[1] who obtained the temperature dependence of the magnetization by observing the F[19] nuclear magnetic resonance (NMR). The susceptibility and specific heat of this material have also been studied in considerable detail.[2] However, one interesting parameter that has remained unknown is the magnitude of the hyperfine field at the iron nucleus. The Mössbauer effect[3] in[4] Fe[57] appears particularly well suited for this and other investigations not possible with magnetic resonance techniques.

FeF$_2$ belongs to the space group $P4/mnm$, i.e., it has a fourfold screw axis. The point symmetry around the iron atoms is characterized by three mutually perpendicular reflection planes, and the highest rotational symmetry is twofold. The principal axes of the electric field gradient (EFG) tensor are along the twofold axes; its magnitude is characterized by two independent components. The direction of the magnetization in the antiferromagnetic state, below 79°K, is along the c axis, which is also one of the principal axes of the EFG tensor. The Hamiltonian for the hyperfine coupling may then be written[5]

$$\mathcal{H} = -g\beta H I_z + \frac{e^2 Qq}{4I(2I-1)}[3I_z^2 - I(I+1) + \tfrac{1}{2}\eta(I_+^2 + I_-^2)], \quad (1)$$

where the z direction is taken along the magnetic field and the EFG tensor has been arbitrarily resolved into an axially symmetric component,

$$eq = \partial^2 V/\partial z^2,$$

and an asymmetry parameter,

$$\eta = \left(\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2}\right) \bigg/ \frac{\partial^2 V}{\partial z^2}.$$

The equation remains valid even if η should turn out to be less than zero or greater than one, but it is then customary to describe the EFG tensor in terms of a new set of axes chosen to make $0 \leqslant \eta \leqslant 1$.

For the $I = \tfrac{3}{2}$ excited state of Fe[57], Eq. (1) becomes

$$\mathcal{H}_e = g_e\beta H I_z + \tfrac{1}{4}e^2 Qq[I_z^2 - (5/4) + \tfrac{1}{6}\eta(I_+^2 + I_-^2)], \quad (2)$$

while for the $I = \tfrac{1}{2}$ ground state it is simply

$$\mathcal{H}_g = g_g\beta H I_z. \quad (3)$$

The eigenvalues of Eq. (2) are readily obtained by noting that it is formally identical with a spin Hamiltonian discussed by Bowers and Owen.[6] This comes about since the transformation properties of the spin Hamiltonian are the same to second order as those of the quadrupole interaction.[7] The eigenvalues of Eq. (2) are

$$E_{1,3} = \tfrac{1}{2}g_e\beta H \pm \tfrac{1}{4}e^2 Qq\left[\left(1 + \frac{4g_e\beta H}{e^2 Qq}\right)^2 + \tfrac{1}{3}\eta^2\right]^{\frac{1}{2}},$$

$$\quad (4)$$

$$E_{2,4} = -\tfrac{1}{2}g_e\beta H \pm \tfrac{1}{4}e^2 Qq\left[\left(1 - \frac{4g_e\beta H}{e^2 Qq}\right)^2 + \tfrac{1}{3}\eta^2\right]^{\frac{1}{2}}.$$

In the absence of a magnetic field this reduces to

$$E_{\pm} = \pm\tfrac{1}{4}e^2 Qq(1 + \tfrac{1}{3}\eta^2)^{\frac{1}{2}}, \quad (5)$$

which also applies in the paramagnetic state when the spin correlation time is sufficiently short to destroy the magnetic hyperfine splitting.

EXPERIMENTAL

The experiments were performed using the Mössbauer effect of the 14.4-kev gamma ray of Fe[57]. Two single-crystal slabs of FeF$_2$, 0.013 cm thick, one oriented with

[1] V. Jaccarino and L. R. Walker (to be published).

[2] J. W. Stout and E. Catalano, Phys. Rev. **92**, 1575 (1953); J. W. Stout and L. M. Matarrese, Revs. Modern Phys. **25**, 338 (1953).

[3] R. L. Mössbauer, Z. Physik **151**, 124 (1958); Naturwissenschaften **45**, 538 (1958); Z. Naturforsch. **14a**, 211 (1959).

[4] R. V. Pound and G. A. Rebka, Jr., Phys. Rev. Letters **3**, 554 (1959); J. P. Schiffer and W. Marshall, Phys. Rev. Letters **3**, 556 (1959).

[5] M. H. Cohen and F. Reif, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 321.

[6] K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 304.

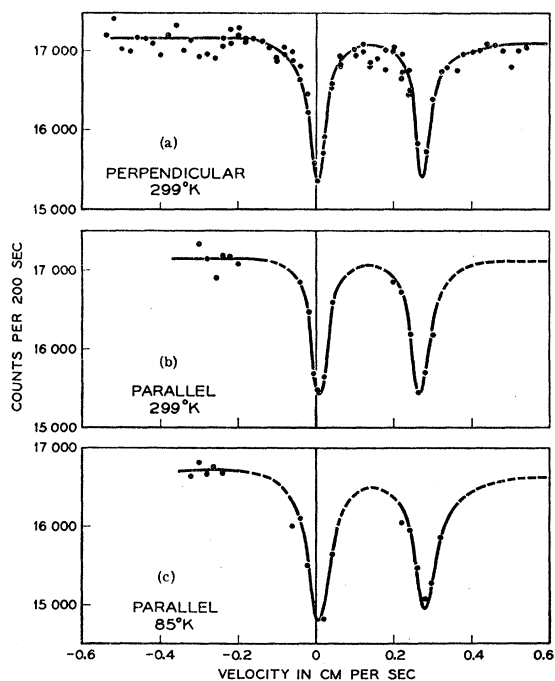[7] J. C. Burgiel, V. Jaccarino, and A. L. Schawlow (to be published).

FIG. 1. Resonant absorption of the 14.4-kev gamma ray of Fe[57] in paramagnetic FeF$_2$ at 299° and 85°K.

linearity of the setup were checked with an iron absorber whose absorption spectrum was known.

RESULTS AND DISCUSSION

Data taken at room temperature [Fig. 1(a), (b)], where the crystal is paramagnetic, show two absorption lines of equal intensity, consistent with pure quadrupole splitting. The separation of the lines is 0.268 cm/sec, equivalent to 31.2 Mc/sec. There is no observable difference between the two crystal orientations insofar as the splitting or the intensity of the absorption is concerned. The fact that the two absorption lines are not symmetrically disposed about zero Doppler velocity indicates that there is a large "chemical shift," which will be discussed further below. Data taken just above the Néel temperature [Fig. 1(c)], at 85°K, do not differ significantly from those taken at room temperature.

Data taken below the Néel temperature, at 45°K, show a complex hyperfine pattern (Fig. 2), as well as a significant difference between the two crystal orientations. The data taken with the c axis parallel to the plane of the absorber show absorption at the expected six energies, but those taken with the c axis perpendicular show absorption at only four. This feature confirms directly that the c axis is the direction of the magnetization, since the only case for which two hyperfine components vanish is when the direction of observation is along the field. In this case, the relative intensities of the hyperfine components are 3:0:1:1:0:3, while when the direction of observation is perpendicular to the field, the relative intensities are 3:4:1:1:4:3. (These intensities are strictly valid only in the absence of quadrupole interaction, but the amount of quadrupole coupling present is not sufficient to perturb them seriously.)

The field at the nucleus can be obtained in two essentially independent ways from these data. (I) The spacing of lines (2) and (4) or (3) and (5) directly reflects the splitting of the ground state, which is equal to $2\mu_g H$. The ground-state moment is known from

the c axis perpendicular, the other with the c axis parallel to the plane of the slab, were used as absorbers. Each absorber was mounted on a thin Mylar backing in a copper sample holder attached to the bottom of a vacuum Dewar; its temperature was measured with a thermocouple attached to the backing.

The source was a 0.6×0.6×0.0025 cm piece of type 310 stainless steel[8] into which radioactive Co[57] was diffused at 950°C in vacuum. This source was mounted on a polyfoam post 7 cm long, attached to a loudspeaker voice coil which was driven at fixed amplitude by a symmetrical sawtooth wave of adjustable frequency. The amplitude of the motion was 0.05 cm; the frequency ranged from 0.01 to 5.0 cps. The calibration and

TABLE I. Summary of data and derived quantities.[a]

Data	
Doppler velocities for resonant absorption at 299°K (cm/sec)	+0.006; +0.274
Doppler velocities for resonant absorption at 45°K (cm/sec)	−0.425; −0.140; +0.140; +0.224; +0.512; +0.647
Derived quantities	
Ground-state splitting at 45°K (cm/sec)	0.368
Excited-state spectrum shifted for zero average value at 45°K (cm/sec)	−0.389; −0.103; +0.177; +0.315
Results	
Magnetic field at Fe nucleus at 0°K	3.40×10^5 oe
Quadrupole splitting	31.2 Mc/sec
Direction of maximum electric field gradient	Normal to c axis
Asymmetry parameter	0.33

[a] Energies expressed in cm/sec, the natural unit for the Mössbauer effect, may be converted to electron volts by multiplying by 4.80×10^{-7}, or to Mc/sec by multiplying by 1.16×10^2.

[8] G. K. Wertheim, Phys. Rev. Letters 4, 403 (1960).

FIG. 2. Resonant absorption of the 14.4-kev gamma ray of Fe^{57} in oriented single-crystal slabs of FeF_2 below the Néel temperature.
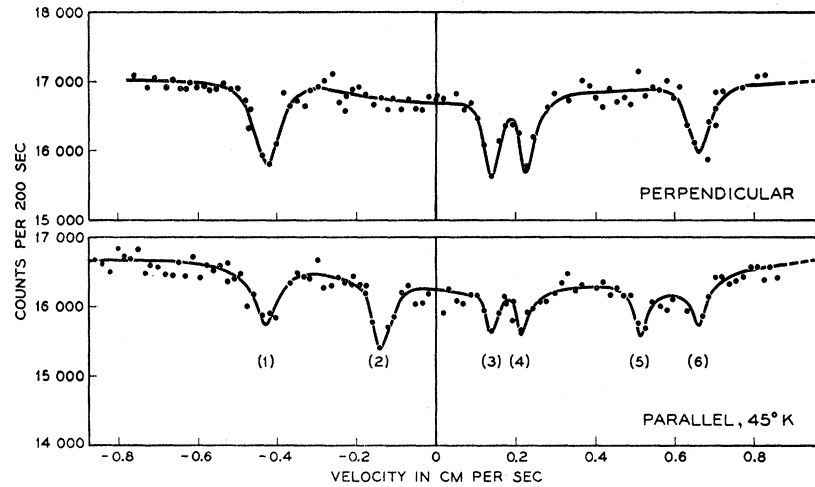
electron-nuclear double resonance experiments[9] and allows direct determination of the local field, which is thus found to be 3.10×10^5 oe at 45°K. (II) The hyperfine splitting of the $I=\frac{3}{2}$ excited state can be constructed by taking lines (1), (2), and (3) in their normal positions plus line (6) displaced toward the center of the pattern by the ground-state splitting. If these four lines (Table I) are then shifted by a common additive constant so as to make their sum equal to zero, the resulting values can be used directly to solve Eq. (4) for $g\beta H$, $\frac{1}{4}e^2Qq$, and η. The moment of the $I=\frac{3}{2}$ state of Fe^{57} is known from the study of the Mössbauer effect in metallic iron.[10] This analysis gives a value of 3.17×10^5 oe for the field at the nucleus, which is consistent with the value obtained using the ground-state moment. The best value for the field at 45°K is $(3.13\pm0.06)\times10^5$ oe, where the uncertainty is based on the errors inherent in the counting statistics, in the measurement of velocity, and in the values of the nuclear moments used in the calculations. The corresponding field at 0°K, using the data of reference 1, is 3.40×10^5 oe.

The quadrupole coupling constant obtained from this analysis is $\frac{1}{4}e^2Qq=0.0425$ cm/sec with $\eta=5.0$, which shows that the field-gradient ellipsoid has its major axis *perpendicular* to the c axis. For a comparison with the quadrupole coupling in the paramagnetic state, these quantities may be combined according to Eq. (5), yielding a splitting of 0.260 cm/sec, in satisfactory agreement with the measured value for the paramagnetic state. Since the magnitude of η indicates that the major axis of the EFG tensor is not in the c direction, the diagonal elements of the EFG tensor are obtained from the parameters $\frac{1}{4}e^2Qq$ and η. If this tensor is then resolved in such a way as to make the axially symmetrical component as large as possible, the values $\frac{1}{4}e^2Qq=0.127$ cm/sec and $\eta'=0.33$ are obtained. The

value of η' indicates that the EFG ellipsoid deviates significantly from axial symmetry. A point-charge calculation considering only the nearest neighbors suggests that the major axis of the ellipsoid is in the [110] direction, but this is not conclusive, since an appreciable fraction of the EFG tensor may arise from the electronic configuration of the iron atom itself.

An estimate for the magnitude of the field gradient, using Bersohn's value of $\sim0.3\times10^{-24}$ cm² for the Fe^{57} quadrupole moment,[11] yields $eq'=80\times10^{16}$ volts/cm².

It is apparent in Fig. 1 and also true in Fig. 2 that the center of the absorption pattern is shifted from zero velocity; this implies that there is a difference between the energy of the nuclear gamma ray from the stainless steel source and the resonant absorption energy in FeF_2. The observed effect is very much larger than can be accounted for by a second-order Doppler shift due to thermal motion.[12] The fact that the displacement does not change between room temperature and 85°K also argues against this interpretation. The shift is then most probably related to the "nuclear isotope shift" discussed by Kistner and Sunyar,[13]
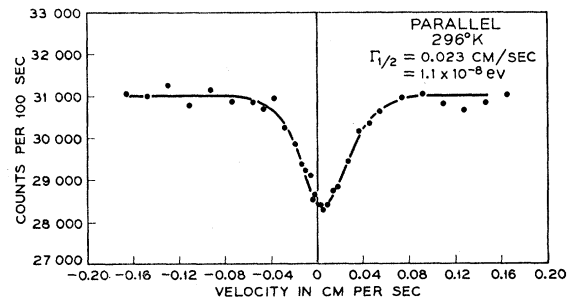

FIG. 3. Line shape of the resonant absorption in paramagnetic FeF_2 at room temperature. Only the line near zero Doppler velocity is shown.

[9] G. W. Ludwig and H. H. Woodbury, Phys. Rev. 117, 1286 (1960).
[10] S. S. Hanna et al., Phys. Rev. Letters 4, 609 (1960).
[11] R. Bersohn, Phys. Rev. Letters 4, 609 (1960).
[12] R. V. Pound and G. A. Rebka, Jr., Phys. Rev. Letters 4, 274 (1960).
[13] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters 4, 412 (1960).

although it is much larger than those previously reported. We have observed similar large shifts in other divalent iron compounds, which has led to the suggestion by Blumberg and Jaccarino[14] that the exchange polarization of inner s electrons by the d shell causes a charge rearrangement of the s-electron wave functions at the nucleus. This effect is apparently considerably larger than the bonding effects (chemical shift) on the outer valence s electrons, and may account for the large shifts observed.

The linewidth of the absorption in the paramagnetic state, Fig. 3, allows an upper limit to be put on the spin correlation time, τ. This quantity is related to the linewidth, $\Delta\nu$ ($\frac{1}{2}$ width at $\frac{1}{2}$ amplitude), through the equation

$$\tau \leqslant 2\pi\Delta\nu(\hbar/IA)^2, \qquad (6)$$

where A is the hyperfine coupling of the Fe^{57} nucleus. The measured linewidth for the stainless steel source and the FeF$_2$ absorber is 0.023 cm/sec, while that obtained when the absorber is replaced by a piece of

stainless steel identical to the source is 0.026 cm/sec. From these a linewidth of 0.010 cm/sec is deduced for the FeF$_2$ alone. This is about twice the natural width of the gamma ray, and yields a correlation time of less than 3×10^{-11} second for FeF$_2$ at room temperature, on the assumption that linewidths are additive. It should be recognized, however, that the difficulty of combining linewidths arising from various mechanisms is such that the uncertainty in the spin correlation contribution may be as large as a factor of two or three. In view of this, no correction has been made for the broadening due to the finite absorber thickness, which would amount to 30% for a line of natural width in the absorber used.

[14] W. E. Blumberg and V. Jaccarino (private communication).

Magnetic Studies on Single-Crystal Chrome Potassium Alum Below 1° Kelvin*

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The magnetic susceptibility of a spherically shaped single crystal of chrome potassium alum has been measured as a function of entropy and applied external field along the [100], [110], and [111] directions in the crystal at temperatures below 0.1°K. Zero-field measurements of the static susceptibility were made with a moving coil apparatus and longitudinal field measurements were made using the conventional ballistic bridge method. A ballistic galvanometer with period 4.6 seconds was used in both circuits. Drop coil measurements indicate no long-time effects in the magnetization and show no appreciable difference from the susceptibility measured by the ballistic method. The isentropic susceptibility measured in fields up to 300 gauss indicates definite anisotropy below the Néel point in fields from 50 to 300 gauss.

INTRODUCTION

CHROME potassium alum has been one of the most widely investigated of the alums used in the production of temperatures below 1° Kelvin. In order to understand the mechanisms leading to the ordered state which occurs in these crystals well below 1°K, it is important to obtain a great deal of accurate quantitative and reproducible data. In recent years a large amount of information about the low-temperature properties of this salt has been obtained at the Leiden University, Oxford University, and National Bureau of Standards laboratories.[1-4] Magnetic susceptibiltiy measurements have indicated rather unusual behavior below the Néel point where magnetic ordering sets in. The susceptibility was found to depend on both the measuring field employed in the measurements and the time constants of the measuring circuit. Further, a secondary maximum in the susceptibility was observed at one laboratory.[4] These measurements indicate similarities between the properties of this salt and chrome methylamine alum. Using a moving coil apparatus it was found[5] that a long relaxation time is associated with the magnetization in the methylamine alum and a very pro-

[1] J. A. Beun, A. R. Miedema, and M. J. Steenland, Physica 23, 1 (1957).

[2] J. A. Beun, M. J. Steenland, D. De Klerk, and C. J. Gorter, Physica 21, 651 (1955).

[3] J. M. Daniels and N. Kurti, Proc. Roy. Soc. (London) A221, 243 (1954).

[4] E. Ambler and R. P. Hudson, Phys. Rev. 95, 1143 (1954).

[5] C. W. Dempesy and R. C. Sapp, Phys. Rev. 110, 332 (1958).