

Mössbauer Effect in MgO:Fe⁺²; Low-Temperature Quadrupole Splitting*

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Mössbauer spectra of absorbers of Fe⁺² in MgO have been measured from room temperature (RT) down to liquid-helium temperature. At the higher temperatures, the spectrum consists of a single narrow peak ($\Gamma=0.25$ mm/sec at RT). Below 20°K, the absorption peak becomes broader and non-Lorentzian, and finally resolves into a close quadrupole doublet, $\Delta E=0.33$ mm/sec. This splitting arises from the combined effect of random strains which lift the degeneracy of the ground state, and relaxation between the ground levels by an Orbach process through the next higher spin-orbit level. The exponential dependence of the relaxation frequencies derived from the spectra is characterized by a value of $\Delta=93$ cm⁻¹. Measurements in a large applied field agree with predictions of the random-strain model.

I. INTRODUCTION

DETAILED measurements of Mössbauer spectra of dilute ferrous iron, Fe⁺², in MgO, made from room temperature down to 4.2°K, are reported here.¹ It is well known that ions of the iron-group transition metals can be incorporated into MgO at substitutional sites.² Such a site has cubic symmetry and is at the center of an octahedron of nearest-neighbor oxygen ions. Since divalent impurities in MgO do not require charge compensation, and since the ionic size of Fe⁺² is close to that of Mg⁺²,³ it is expected *a priori* that Mössbauer spectra of Fe⁺² in MgO do not show a quadrupole splitting. This should be particularly true for dilute crystals where Fe⁺² ions should be well separated, each ion having a uniform environment. This is indeed the case for measurements made at room temperature, but at sufficiently low temperature (<21°K) the sudden appearance of a small quadrupole interaction is observed.

In the octahedral crystalline field of a lattice site in MgO, spin-orbit coupling leaves the ground state of Fe⁺² threefold degenerate, the ground level being Γ_{5g} from the ⁵T_{2g} term.⁴ It was previously suggested,¹ therefore, that the quadrupole splitting might be due to the onset of a dynamic Jahn-Teller (JT) effect. ESR spectra of Fe⁺² in MgO have certain features which are not consistent with strict cubic symmetry.⁵⁻⁷ For one, a resonance is seen corresponding to forbidden (in cubic symmetry) $\Delta M=2$ transitions, and the allowed $\Delta M=1$ resonance is found to be unusually broad. However, the spin-resonance spectra are seen to be inde-

pendent of crystal orientation, which would not be the case if a static JT distortion occurred, since preferential orientation of a distortion is expected.⁸ An interpretation of the ESR results has been presented which explains the observations in terms of local departure from cubic symmetry due to a random distribution of strains arising from crystalline imperfections.⁶

Only a weak JT effect is predicted for Fe⁺² in an octahedral field,^{9,10} and an argument has been made that a strong JT effect is contrary to experiment.¹¹ In any case, it has been shown that a dynamic JT effect, by itself, will not cause a quadrupole splitting.¹²

Ham¹² has proposed a theory which explains the Mössbauer results solely on the basis of crystal-field theory. He shows that the presence of random strains lifts the degeneracy of the ground state, and that the low-temperature spectra are explained by slow electronic relaxation between these levels. It will be seen that Ham's theory accurately describes our observations, and has predicted phenomena which we have subsequently observed.

II. SAMPLE PREPARATION

Samples were prepared from thin plates of MgO cleaved from larger crystals, which were obtained from Semi-Elements, Inc. The thickness was typically in the range 0.03 to 0.05 cm. Powdered Fe₂O₃ (92% enriched in Fe⁵⁷) was applied uniformly to the surface of a crystal by rubbing a small amount onto the plate until it had a lightly rouged appearance. The iron was then diffused into the crystal.

Diffusion was done in two ways¹³: (1) The crystal was heated at ~1500°C in an atmosphere of CO+CO₂ (1:1 ratio). In this way, diffusion occurred under a

⁸ U. Opik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957).

⁹ J. H. Van Vleck, Physica **26**, 544 (1960); Discussions Faraday Soc. **26**, 98 (1959).

¹⁰ A. D. Liehr, Bell System Tech. J. **39**, 1617 (1960).

¹¹ F. S. Ham, Phys. Rev. **138**, A1727 (1965).

¹² F. S. Ham, Phys. Rev. **160**, 328 (1967).

¹³ B. J. Wuensch and T. Vasilos, J. Chem. Phys. **36**, 2917 (1962); S. L. Blank, University of California Lawrence Radiation Laboratory Report No. UCRL-11073, 1963 (unpublished); R. Linder and G. D. Parfitt, J. Chem. Phys. **26**, 482 (1957).

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¹ D. N. Pipkorn and H. R. Leider, Bull. Am. Phys. Soc. **11**, 49 (1966).

² For example, W. Low and R. S. Rubins, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), pp. 77-89; P. Auzins, J. W. Orton, and J. E. Wertz, *ibid.* pp. 90-104.

³ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), pp. 104-106.

⁴ W. Low and M. Weger, Phys. Rev. **118**, 1119 (1960).

⁵ W. Low and M. Weger, Phys. Rev. **118**, 1130 (1960).

⁶ D. H. McMahon, Phys. Rev. **134**, A128 (1964).

⁷ D. H. McMahon and R. H. Silsbee, Phys. Rev. **135**, A91 (1964).

partial pressure of O_2 ($\sim 10^{-10}$ atm) in which only Fe^{+2} should be stable¹⁴; (2) the crystal was heated in air at $\sim 1500^\circ\text{C}$, in which case iron entered the lattice as Fe^{+3} . Subsequently, the ferric iron was reduced to ferrous by further heating in $\text{CO}+\text{CO}_2$, or by heating in Mg metal vapor in a sealed tantalum capsule, at pressures of $P_{\text{Mg}}=1-2$ atm.¹⁵ In no case was it possible to completely eliminate Fe^{+3} . Heating an oxidized crystal in Mg vapor generally yielded smaller amounts of Fe^{+3} , and the data presented are for a crystal prepared in this manner. This crystal is designated as $\text{MgO}:\text{Fe}^{+2}$ (sample 6), and it contains $\sim 15\%$ Fe^{+3} , as determined from computer fitting the spectra. Another possible benefit from reducing in Mg vapor is that the Mg^{+2} ions formed in converting Fe^{+3} to Fe^{+2} probably occupy formerly vacant lattice sites, enhancing the over-all perfection of the lattice. Also, if some excess Mg^{+2} enters the lattice by producing *F*-center-like trapped electrons (analogous to additive coloration in alkali halides¹⁶), the vacancy concentration may be further diminished.

The final concentration of iron was found to be ~ 0.04 at. %. Of this amount, ~ 0.01 at. % was already present as an accidental impurity in the MgO crystals. The iron content was analyzed by standard chemical colorimetric methods.

III. MÖSSBAUER SPECTROMETER AND CRYOSTATS

Mössbauer spectra were measured with a lead-screw-type, constant-velocity spectrometer. A detailed description of the apparatus has already been published.¹⁷ The electronics have been improved since that report, but the basic operation is unchanged. Velocities are determined from the time interval to traverse a measured distance between two switches, and are accurate to a few tenths of a percent. The source used for all the measurements was Co^{57} in Pd at room temperature. Measurements on thin absorbers of sodium ferrocyanide and $\text{MgO}:\text{Fe}^{+2}$ gave a linewidth of 0.22 mm/sec, extrapolated to zero absorber thickness.

From room temperature to 80°K a flow-type nitrogen cryostat was used. The temperature was measured with a thermocouple and was controlled by varying the nitrogen flow rate.

Measurements in the temperature range 80 to 4.2°K were made in a cryostat with liquid helium, hydrogen, and nitrogen used as coolants. Temperature measurements were made with a carbon resistor calibrated at the boiling points of He, H_2 , and N_2 , and should be

¹⁴ J. Byrnestead and H. Flood, *Z. Elektrochem.* **62**, 953 (1958); M. E. Fine, *J. Appl. Phys.* **35**, 3587 (1964); J. V. Coughlin, *U.S. Bur. Mines Bull.* **542**, 25 (1964). (Values for P_{02} were calculated from these tabulated free energies.)

¹⁵ J. E. Wertz, J. W. Orton, and P. Auzins, *J. Appl. Phys. Suppl.* **33**, 322 (1962).

¹⁶ J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Co., New York 1962), pp. 34-36.

¹⁷ R. Booth and C. E. Violet, *Nucl. Instr. Methods* **25**, 1 (1963).

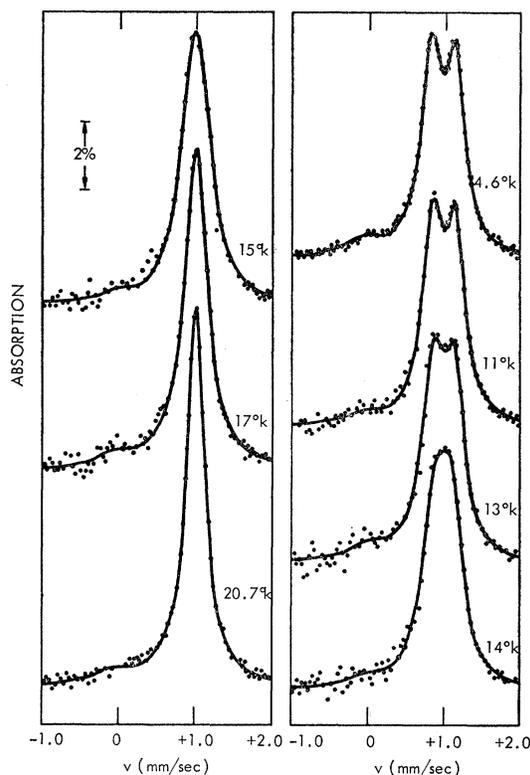


FIG. 1. Spectra of $\text{MgO}:\text{Fe}^{+2}$ (6) (~ 0.04 at. % Fe^{+2}), showing the appearance of quadrupole splitting at low temperature. In all cases, the source is Co^{57} in Pd at room temperature. Positive velocity corresponds to motion of the source towards the absorber.

accurate to several tenths of a degree below 30°K . A Zener diode provided a convenient heater to maintain the sample at temperatures above the coolant temperature. An ac bridge was used to sense the carbon resistor and to provide a feedback control for the current to the Zener diode, thus enabling precise temperature control for long periods of time.

IV. SPECTRA

Typical spectra from $\text{MgO}:\text{Fe}^{+2}$ (6) are shown in Fig. 1. A narrow single peak due to Fe^{+2} is seen at $+0.87$ mm/sec at room temperature. Figure 2 is the spectrum of the crystal prior to reduction of the iron. This measurement was made to establish the parameters for ferric ions. The Fe^{+3} absorption is associated with a broad doublet at $+0.15$ mm/sec, with a peak separation of $\Delta E=0.74$ mm/sec. This quadrupole splitting is in agreement with the value of 0.7 mm/sec reported by Gonser *et al.*¹⁸ and is attributed by them to a charge compensating vacancy in a $[110]$ orientation. The sharp unsplit peak^{1,18} for Fe^{+2} differs markedly from

¹⁸ H. Wiedersich, U. Gonser, R. W. Grant, and A. H. Muir, *Bull. Am. Phys. Soc.* **10**, 709 (1965); U. Gonser, R. W. Grant, H. Wiedersich, R. Chang, and A. H. Muir, *ibid.* **11**, 363 (1966).

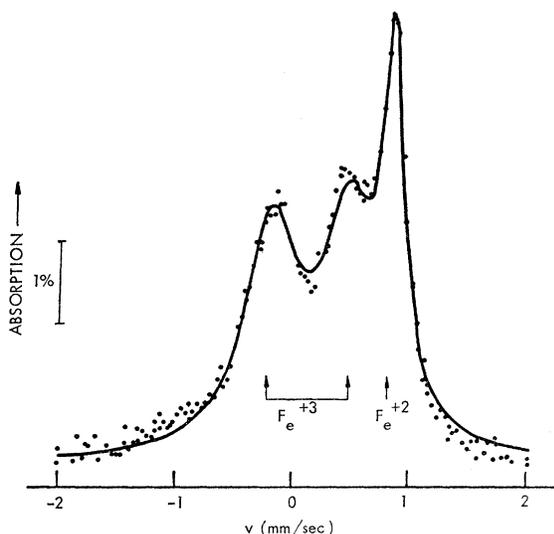


FIG. 2. Room-temperature spectrum of $\text{MgO}:\text{Fe}^{+2}$ (6) subsequent to diffusion as Fe^{+3} in air, but prior to conversion to Fe^{+2} . Note the substantial fraction of Fe^{+2} .

spectra of concentrated samples (>10 at. % iron)^{19,20} which have a quadrupole splitting of ~ 0.6 mm/sec and have rather broad lines. Identification of the peaks with Fe^{+2} and Fe^{+3} is consistent with other Mössbauer experiments,¹⁸⁻²¹ and with systematics of the isomer shift in iron compounds.²² No indication of any Fe^{+1} was found despite severely reducing conditions used in the sample preparation,¹⁵ although Fe^{+1} has been observed in sources.²³

Mössbauer parameters for Fe^{+2} and Fe^{+3} in MgO are listed in Table I, and temperature variation of the center of gravity of the Fe^{+2} spectrum is plotted in Fig. 3. Although Fe^{+2} is an impurity in a diatomic

TABLE I. Mössbauer parameters (mm/sec) for Fe^{+2} and Fe^{+3} in MgO . Positive velocity represents motion of the source towards the absorber. The source is Co^{57} in Pd at room temperature. Parameters are derived from fitting the data to theoretical spectra.

	Isomer Shift		Quadrupole splitting ΔE	Linewidth Γ
	300°K	4.2°K		
Fe^{+2}	0.87	1.00	...	0.25 ± 0.01
	± 0.01	± 0.01		
Fe^{+3}	0.15	0.29	0.74 ± 0.02	0.54 ± 0.02
	± 0.02	± 0.02		

¹⁹ G. Shirane, D. E. Cox, and S. L. Ruby, Phys. Rev. **125**, 1158 (1962).

²⁰ D. J. Simkin, P. J. Ficalora, and R. A. Bernheim, Phys. Letters **19**, 536 (1965).

²¹ G. K. Wertheim and D. N. E. Buchanan, in *The Mössbauer Effect*, edited by D. M. J. Compton and A. H. Schoen (John Wiley & Sons, Inc., New York, 1962), pp. 130-140.

²² L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

²³ R. B. Frankel and N. A. Blum, Bull. Am. Phys. Soc. **12**, 24 (1967); J. Chappert, R. B. Frankel, and N. A. Blum, Phys. Letters **25A**, 149 (1967).

lattice the temperature shift agrees with a Debye-model calculation, using $\Theta_D = 390^\circ\text{K}$ and $M = 57$. We estimate that the determination of the position and linewidth of the Fe^{+2} absorption is accurate to ± 0.01 mm/sec, although reproducibility of a given measurement has been found to be ± 0.005 mm/sec or better. The Fe^{+3} spectrum is less well defined because of its smaller intensity and because it is partially hidden under the larger Fe^{+2} features, and we estimate an uncertainty of ± 0.02 mm/sec to the Fe^{+3} parameters.

As the temperature is lowered, the initially sharp Fe^{+2} peak broadens and eventually resolves into a doublet. The small linewidth measured at room temperature (0.25 mm/sec) indicates a single type of environment for Fe^{+2} . Above 21°K , all spectra are typified by one sharp peak; below this temperature, the Fe^{+2} absorption broadens until two peaks are clearly seen. This low-temperature quadrupole splitting cannot be attributed to a close vacancy. Since no charge com-

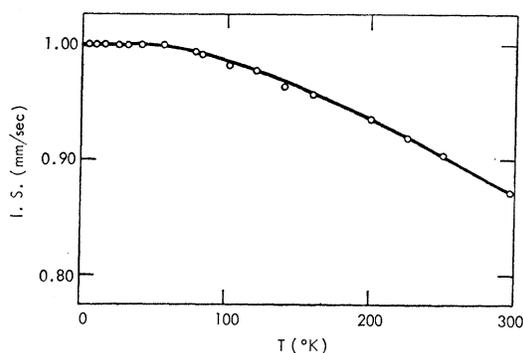


FIG. 3. Temperature dependence of the center of gravity of the Fe^{+2} spectrum. The solid curve is calculated from a Debye model for $\Theta_D = 390^\circ\text{K}$.

pensation is required, it is unlikely that a correlation will exist between Fe^{+2} ions and vacancy; moreover a nearby vacancy might be expected to produce a larger quadrupole splitting²⁴⁻²⁶ than the small value actually observed, $\Delta E = 0.33$ mm/sec. A more distant vacancy could cause a smaller splitting, as could impurities (including Fe^{+2}) and other imperfections, but it does not seem reasonable that a well-defined spectrum would result. Fe^{+2} is the major impurity, and the iron concentration is low enough that nearest neighbors are improbable if a random distribution is assumed. In more concentrated crystals (~ 1 at. % Fe), we do see a second type of ferrous site in addition to the one typical of dilute iron. This second site has a quadrupole splitting at room temperature and appears to be due to iron nearest neighbors.

A somewhat similar temperature variation of a quadrupole splitting has been reported for Fe^{+2} in silver

²⁴ D. H. Lindley and P. G. Debrunner, Phys. Rev. **146**, A199 (1966).

²⁵ G. K. Wertheim and H. J. Guggenheim, J. Chem. Phys. **42**, 3873 (1965).

²⁶ J. G. Mullen, Phys. Rev. **131**, 1415 (1963).

halides.²⁴ In these experiments, the effect is due to thermal motion of a charge-compensating vacancy. At sufficiently high temperature, the vacancy moves about the Fe²⁺ so rapidly that the field gradient averages to zero over the lifetime of the Mössbauer state. Diffusion rates are much too slow for any such process to occur in MgO,¹³ however, and a correlated vacancy in MgO:Fe²⁺ is not likely, as has been discussed above.

V. QUADRUPOLE SPLITTING

A theory has been presented by Ham¹² which successfully explains the Mössbauer spectra of Fe²⁺ in MgO. The following discussion outlines this theory.

The interaction between the valence electrons of the Fe²⁺ ion and the nuclear quadrupole moment Q of Fe^{57m} in the Γ_{5g} ground-state triplet is represented by the operator

$$H_Q = \frac{1}{4}C_3\{[3J_z^2 - J(J+1)][3I_z^2 - I(I+1)] \\ + 3[J_x^2 - J_y^2][I_x^2 - I_y^2]\} \\ + C_5\{(J_yJ_z + J_zJ_y)(I_yI_x + I_xI_y) \\ + (J_zJ_x + J_xJ_z)(I_zI_x + I_xI_z) \\ + (J_xJ_y + J_yJ_x)(I_xI_y + I_yI_x)\}. \quad (1)$$

\mathbf{I} is the nuclear spin operator ($I = \frac{3}{2}$), and \mathbf{J} is the effective spin operator ($J = 1$) for the Γ_{5g} triplet. The vector components are referred to the cubic axes of the coordination octahedron. If random strains are present (strain splitting smaller than spin-orbit splitting), the electronic eigenstates for Γ_{5g} are of the form

$$|\psi\rangle = a|\xi\rangle + b|\eta\rangle + c|\zeta\rangle. \quad (2)$$

$|\xi\rangle$, $|\eta\rangle$, and $|\zeta\rangle$ are the three states of Γ_{5g} transforming as yz , zx , and xy , respectively, and a , b , and c are real coefficients. The diagonal matrix elements of (1) with respect to such a state gives the nuclear Hamiltonian corresponding to the states (2).

Using the wave functions appropriate to $3d^6$ for the Γ_{5g} levels, Ham obtained the relationship

$$-3C_3 = +4C_5 = +\left(\frac{3}{35}\right) \frac{\langle r^{-3} \rangle (1-R) e^2 Q}{I(2I-1)}. \quad (3)$$

Here, $\langle r^{-3} \rangle$ is the one-electron expectation value of r^{-3} , and $(1-R)$ is the antishielding factor for Fe²⁺. For $I = \frac{3}{2}$ a quadrupole interaction is found, $E = \pm \frac{1}{2} \Delta E$, where

$$\Delta E = 3[C_3^2 + \frac{1}{3}(16C_5^2 - 9C_3^2)(a^2b^2 + b^2c^2 + a^2c^2)]^{1/2}, \quad (4)$$

and, from (3),

$$\Delta E = (2/70) \langle r^{-3} \rangle (1-R) e^2 Q. \quad (5)$$

ΔE is seen to be independent of the coefficients a , b , and c .

Thus, Ham shows that if random strains at a Fe²⁺ site can lift the degeneracy of the ground level by an

amount greater than the nuclear quadrupole and hyperfine interactions, three nondegenerate states result, each of which produces an *identical* quadrupole splitting ΔE . Consequently, at temperatures low enough for transitions between these levels to be slow compared to $\hbar/\Delta E$, a quadrupole splitting should be found. An estimate of $\sim 10^{-2}$ cm⁻¹ was made for the strain splitting in typical MgO crystals,¹² which is considerably larger than the nuclear hyperfine interaction²³ ($\sim 10^{-3}$ cm⁻¹).

From Eq. (5) it is seen that the size of the quadrupole splitting is expected to be one-tenth of that typical for Fe²⁺ in noncubic environments²⁷ (~ 3 mm/sec). The value derived from fitting our data to theoretical spectra gives 0.33 mm/sec, in agreement with the theory.

According to Ham, departures from the crystal-field model, such as a JT effect, would result in a small change in the ratio of C_3 to C_5 , so that the equality of (3) would no longer hold. It is expected that such a change would be no more than 10%, provided that the JT energy is less than the spin-orbit coupling.¹² The result would be a slight broadening of the spectrum in zero field. The fact that our spectra are fit by a line-width which is nearly independent of temperature implies that there is no large departure from (3). The data are not sufficiently accurate to test for a very small difference.

The only apparent discrepancy between experiment and theory is that the size of the quadrupole splitting was calculated to be ~ 0.44 mm/sec, whereas the best value derived from fitting the data is 0.33 mm/sec. Ham states that this difference is too big to be accounted for by reasonable modification of the theory, and that if the theory is correct, then the quadrupole moment of Fe^{57m} which was used,²⁷ $Q = 0.29$ b, may be too large. Values quoted in the literature for Q for Fe^{57m} vary considerably.²⁸ Our experiments favor a value close to 0.2 b, in agreement with one recent reevaluation,²⁹ $Q = 0.20$ b.

VI. QUADRUPOLE SPLITTING IN AN APPLIED MAGNETIC FIELD

In an external magnetic field large enough such that the Zeeman splitting of the ion is greater than the strain splitting, it is predicted¹² that the quadrupole splitting should change sign as the crystal is rotated from $\mathbf{H}_{\text{ext}} \parallel [100]$ to $\mathbf{H}_{\text{ext}} \parallel [111]$.

At temperatures low enough for slow relaxation, the Mössbauer spectrum consists of a superposition of three spectra from the three states of Fe²⁺, $M_s = \pm 1, 0$. The spectra for $M_s = +1$ and -1 have magnetic splitting corresponding to $H_{\text{ext}} - H_0$ and $H_{\text{ext}} + H_0$, where

²⁷ R. Ingalls, Phys. Rev. **133**, A787 (1964).

²⁸ For specific references, see *Mössbauer Effect Data Index 1958-1965*, edited by A. H. Muir, Jr., K. J. Ando, and H. M. Coogan (Interscience Publishers Inc., New York, 1966), p. 34.

²⁹ A. J. Nozik and M. Kaplan, Phys. Rev. **159**, 273 (1967).

H_0 is the nuclear hyperfine field. The $M_s=0$ spectrum is split only by H_{ext} . The quadrupole splitting for the $M_s=\pm 1$ states is given by $\frac{3}{2}C_3$ for H_{ext} along [100] and by $+2C_5$ for H_{ext} along [111]. These values are of opposite sign and are one-half the zero-field splitting. For $M_s=0$, the quadrupole splitting is $-3C_3$ and $-4C_5$ with H_{ext} along [100] and [111], respectively.

Spectra with the crystal in a superconducting solenoid at 4.2°K with $H_{\text{ext}}=50$ kG are shown in Fig. 4 for $H_{\text{ext}} \parallel [100]$ and $\parallel [111]$. The observation direction is along the field axis. For this field and temperature, the relative populations of the ion levels are 1:0.63:0.04; consequently, the most prominent spectrum is that due to the lowest state, $M_s=+1$. The presence of quadrupole splitting is clear, and it is evident that ΔE is of opposite sign in the two orientations. The size and direction of ΔE is consistent with prediction. The magnitude of the hyperfine field is 120 kG, in agreement with the determination of Frankel and Blum.²⁸ The intensity of the $\Delta m=0$ lines of the hyperfine spectrum is nearly zero, as should be the case for an axial field.

Since the measurements for the two crystal orientations determine C_3 and C_5 separately, their ratio can be compared with the crystal-field value. Any difference, if one exists, is within experimental uncertainty, so that more accurate measurements will be required to test for a deviation.

VII. RELAXATION

A model for describing a quadrupole interaction with relaxation has been developed by Blume and Tjon.³⁰

The shape of the Mössbauer spectrum is given by

$$P(\omega) = \frac{2}{\Gamma} \text{Re} \int_0^\infty dt \exp[i\omega t - (\Gamma/2)t] \langle \langle H^{(-)} H^{(+)}(t) \rangle \rangle_{\text{av}}, \quad (6)$$

where $H^{(+)}$ is the operator for emission of a γ ray by the nucleus, Γ is the linewidth, and ω is a frequency measured from the center of gravity of the spectrum. The $()_{\text{av}}$ represents an average over a random function, $f(t) = \pm 1$, which describes the changes in the electric field gradient in the Hamiltonian

$$\mathcal{H}(t) = f(t) \frac{1}{6} (\Delta E) (3I_z^2 - I^2). \quad (7)$$

The field gradient is along the Z axis and changes sign randomly. The same result is obtained if the field gradient changes randomly among the four configurations of equal magnitude, either $+$ or $-$, along the X or Y axes.

$$\langle \langle H^{(-)} H^{(+)}(t) \rangle \rangle_{\text{av}} \propto \{ \cos XWt + (1/X) \sin XWt \} \times \exp(-Wt), \quad (8)$$

where

$$X = (\omega_1^2/W^2 - 1)^{1/2},$$

$$\omega_1 = \frac{1}{2} \text{ the quadrupole splitting,}$$

$$W = \text{relaxation frequency.}$$

Performing the integral leads to the expression

$$P(\omega) = (2\Gamma)^{-1} \left(\frac{-(1-i/X)}{i(\omega+XW) - (W+\frac{1}{2}\Gamma)} - \frac{(1+i/X)}{i(\omega-XW) - (W+\frac{1}{2}\Gamma)} - \frac{(1-i/X^*)}{-i(\omega-X^*W) - (W+\frac{1}{2}\Gamma)} - \frac{(1+i/X^*)}{-i(\omega+X^*W) - (W+\frac{1}{2}\Gamma)} \right), \quad (9)$$

where $P(\omega)$ is real and positive for all values of X , and can be written

$$P(\omega) = \frac{2}{\Gamma} \left(\frac{2\omega^2(W+\frac{1}{2}\Gamma) + (2W+\frac{1}{2}\Gamma)(\omega_1^2 - \omega^2 + W\Gamma + \frac{1}{4}\Gamma^2)}{4\omega^2(W+\frac{1}{2}\Gamma)^2 + (\omega_1^2 - \omega^2 + W\Gamma + \frac{1}{4}\Gamma^2)^2} \right). \quad (10)$$

The term $P(\omega)$ approaches a sum of two Lorentzians of width Γ , centered at $\pm\omega_1$ when $W \ll \omega_1$ (slow relaxation) and as $W \rightarrow \infty$ (fast relaxation), $P(\omega)$ approaches a single Lorentzian centered at $\omega=0$. Although the

case in which the field gradient changes along three axes is more appropriate to the experiments, it is not expected that any major difference from the present results will occur.³⁰

Equation (10) was used to fit the spectra for MgO:Fe^{+2} and to define the relaxation frequency W as a function of temperature. An iterative method was used in which the minimum of the sum of the squares of the deviations of the theoretical spectrum from the data was found by systematically varying the parameters. The data include contributions from both Fe^{+3}

³⁰ M. Blume and J. Tjon, Brookhaven National Laboratory Report No. BNL-11654 (unpublished); J. Tjon and M. Blume, Brookhaven National Laboratory Report No. BNL-11655 (unpublished); M. Blume, Phys. Rev. Letters **18**, 305 (1967). Subsequent to having fit our spectra, the solution for the three-axis case was worked out by Blume and Tjon. This equation has the same form as Eq. (10) with W replaced by $:W$. The factor has been incorporated into the results shown in Fig. 5.

and Fe^{+2} ions. The Fe^{+3} spectra were represented by two Lorentzian lines to a good approximation.³¹ Fitting was most sensitive in the region $W \leq 5\omega_1$. We found it necessary to constrain some parameters, however, since the fitting procedure was very sensitive to Γ and ω_1 . By fitting several sets of data to a range of fixed Γ and ω_1 , we were able to arrive at values for these two quantities which essentially minimized the squares of the deviations from the theoretical spectra for all of the measurements. These values, $\Gamma = 0.26$ mm/sec and $\omega_1 = 0.165$ mm/sec, were used to determine W . The solid curves in Fig. 1 are calculated spectra, and the plot of relaxation frequency W as a function of temperature is shown in Fig. 5.

In order to explain the rapid temperature variation of the quadrupole splitting below 20°K, Ham proposed that relaxation between the levels of the ground-

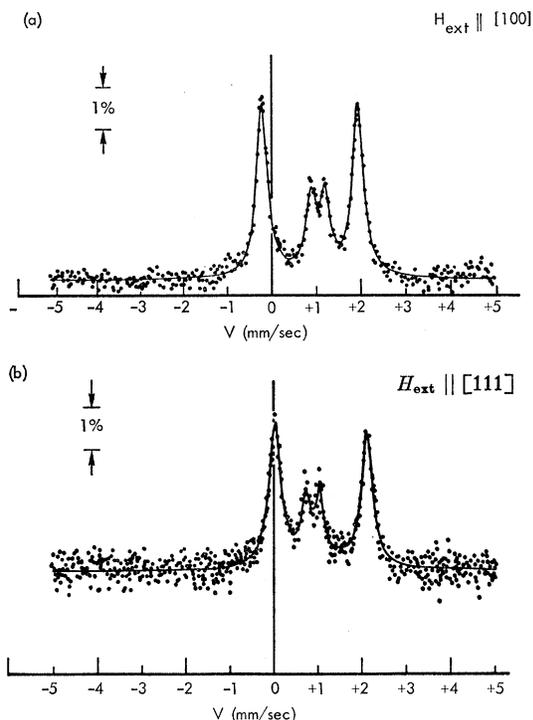


FIG. 4. (a) $\text{MgO}:\text{Fe}^{+2}$ (6) in an external magnetic field of 50 kG at 4.2°K. External field \parallel [100]. (b) Same as 4(a) except that the external field \parallel [111].

³¹ At first, the Fe^{+2} spectra were also fitted to a pair of Lorentzian lines whose separation varied with temperature. These happened to fit rather well in this instance because the linewidth and the peak separation are about the same, and the characteristic relaxation line shapes observed when the splitting is larger than the linewidth [see Ref. 30 and also P. W. Anderson, *J. Phys. Soc. Japan* **9**, 316 (1954); M. Blume, *Phys. Rev. Letters* **14**, 96 (1965); F. van der Woude and A. J. Dekker, *Phys. Status Solidi* **9**, 775 (1966); E. Bradford and W. Marshall, *Proc. Phys. Soc. (London)* **87**, 731 (1966); H. H. Wickman, M. P. Klein, and D. A. Shirley, *Phys. Rev.* **152**, 345 (1966)] were not apparent. The fit to the data is even better when relaxation spectra are used, however.

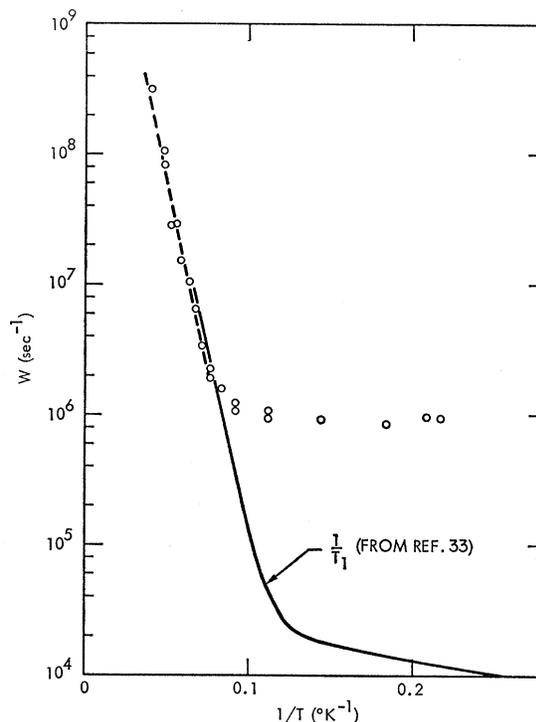


FIG. 5. Relaxation frequency versus $1/T$, as derived from computer fitting the spectra of $\text{MgO}:\text{Fe}^{+2}$ (6). The Mössbauer relaxation frequencies are plotted as angular frequencies to be compatible with $1/T_1$. The solid line shows the values of the spin-lattice relaxation frequency, $1/T_1 = 2.5 \times 10^8 T + 6.5 \times 10^{10} \exp(-133/T)$, from ESR measurements in the temperature range 1.2–15°K (Ref. 33). The dashed line is a fit of W to an exponential dependence on $1/T$ for the points above 12°K.

state triplet occurs by an Orbach mechanism via the next higher spin-orbit level. To account for an estimated relaxation time $\sim 5 \times 10^{-8}$ sec at 14°K, he calculated that the required separation from the next spin-orbit level had to be ~ 95 cm^{-1} . This value is much smaller than the free-ion value (~ 200 cm^{-1}), but such a reduction was attributed to a combination of covalent bonding and Jahn-Teller displacement of the higher spin-orbit levels.¹²

The temperature dependence of the relaxation frequency derived from our Mössbauer data above $\sim 13^\circ\text{K}$ conforms to an exponential form, as is required for an Orbach mechanism. A least-squares fit of W to an exponential dependence on $1/T$ for the points in the range $T \geq 13^\circ\text{K}$ gives a slope which corresponds to a level at 93 cm^{-1} above the ground state, in good agreement with Ham's estimate. We find that

$$W = \omega_1 (= \Delta E/\hbar) = 2.4 \times 10^7 \text{ sec}^{-1} \text{ at } 17.5^\circ\text{K}.$$

Recent measurements³² of the far-infrared absorption of $\text{MgO}:\text{Fe}^{+2}$ show a level at 105.0 cm^{-1} , and in addi-

³² J. Y. Wong and A. L. Shawlow, *Bull. Am. Phys. Soc.* **12**, 655 (1967), and private communication.

tion, ESR studies³³ on the relaxation time for the $\Delta M=1$ transition of Fe^{+2} in MgO also indicate an Orbach process with $\Delta=92.5\text{ cm}^{-1}$. The discrepancy in the value for Δ measured by optical methods as compared with ESR (and Mössbauer) evaluation may be explained by the effect of finite width of the excited level.³⁴

Our derived relaxation frequencies (Fig. 5) deviate from the exponential dependence on $1/T$ at $\sim 12^\circ\text{K}$. The spin-lattice relaxation time for Fe^{+2} in MgO determined by ESR experiments³³ was found to be described by a one-phonon direct process at the lowest temperatures, but the direct process is not dominant until $T < 8^\circ\text{K}$ (the solid curve in Fig. 5). The origin of the difference is not explained, but it may be as-

³³ R. L. Hartman, E. L. Wilkinson, and J. G. Castle, Jr., *Bull. Am. Phys. Soc.* **12**, 642 (1967).

³⁴ B. A. Young and H. J. Stapleton, *Phys. Letters* **21**, 498 (1966).

sociated with the concentration of iron in the MgO , or some other sample-dependent effect.

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Hyperfine Fields and Electronic Structure of CsCl-Type Ternary Alloys of the First Transition Series

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The ^{59}Co Knight shift K and the ^{57}Fe isomer shift have been measured in $\text{TiFe}_{1-x}\text{Co}_x$ alloys over most of the composition range $0 \leq x \leq 1$. The experimental results are discussed in terms of correlations with electron concentration and s admixture in the d bands. At room temperature, K varies from a maximum of $(3.2 \pm 0.2)\%$ at $x \approx 0.8$, and roughly follows the electronic specific heat as the composition is varied, with a minimum of $K = (0.8 \pm 0.2)\%$ near $x = 0$. K increases substantially as the temperature is lowered for x near 1, and decreases somewhat for x near 0. The maximum K measured is $(4.7 \pm 0.2)\%$ for $x \approx 0.8$ at 120°K . The slopes of K versus susceptibility vary from $+86\text{ kG}/\mu_B$ per formula unit for $x = 0.8$ to $-47\text{ kG}/\mu_B$ per formula unit for $x = 0.05$. The isomer-shift variation, from -0.15 ± 0.01 (mm/sec relative to pure Fe) at TiFe to -0.19 ± 0.02 at TiCo , is similar to that of Fe in Cr-Mn. The $^{47,49}\text{Ti}$ Knight shift in TiFe is $(0.26 \pm 0.04)\%$ at room and at liquid-nitrogen temperatures.

I. INTRODUCTION

THE CsCl-type pseudobinary alloy system $(\text{TiFe})_{1-x}(\text{TiCo})_x$ formed from the two transition-metal intermetallic compounds TiFe and TiCo exhibits a variety of surprising features. Although neither TiFe nor TiCo is ferromagnetic above 1°K , ferromagnetism with paramagnetic Curie points of about 50°K is observed¹ in the composition range $0.3 \leq x \leq 0.7$ with the exception of $x = 0.5$. The alloy $\text{TiFe}_{0.5}\text{Co}_{0.5}$ does not order magnetically above 1.2°K but exhibits a superconductive transition¹ at about 3°K . The electronic specific

heat values γ for these alloys² display a remarkable parallelism, as shown in Fig. 1, with the values of γ appropriate to the first transition series bcc alloys having the same average conduction (or "valence") electron concentration per atom n_e . The terms electron concentration and electron-to-atom ratio (often abbreviated e/a), are used interchangeably.

The Mössbauer effect for ^{57}Fe in $\text{TiFe}_{1-x}\text{Co}_x$ shows³

² E. A. Starke, Jr., C. H. Cheng, and P. A. Beck, *Phys. Rev.* **126**, 1746 (1962); C. H. Cheng, C. T. Wei, and P. A. Beck, *ibid.* **120**, 426 (1960); C. H. Cheng, K. P. Gupta, E. C. Van Reuth, and P. A. Beck, *ibid.* **126**, 2030 (1962).

³ L. H. Bennett and L. J. Swartzendruber, *Phys. Letters* **24A**, 359 (1967); L. J. Swartzendruber and L. H. Bennett, *Bull. Am. Phys. Soc.* **12**, 349 (1967). Note that the designation of the alloys and the isomer shift reference and sign convention are different in this paper.

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† Supported by U.S. Atomic Energy Commission.

¹ B. F. DeSavage and J. F. Goff, *J. Appl. Phys.* **38**, 1337 (1967).