state of Dy^{161}: The magnetic hyperfine interaction $g_0\beta_N H_{\text{eff}}=-806\pm20$ Mc/sec and the quadrupole interaction $\frac{1}{4}e^2qQ=420\pm20$ Mc/sec. The above values are similar to those in $DyFeO_3$ ($g_0\beta_N H_{\text{eff}}=-830$ and $\frac{1}{4}e^2qQ=435$ Mc/sec).[7]

The paramagnetic hyperfine interactions in $DyCrO_3$ may be interpreted in the effective-field approximation[7,8] as arising from an ionic ground Kramers doublet with an effective g tensor[9] $g_z=19.7$, $g_x=g_y=0$. With this g_z value we expect a quadrupole interaction of 630 Mc/sec. We conclude that -210 ± 40 Mc/sec is due to the crystalline electric-field gradient. By comparing this result to the experimental result for the direct contribution to the quadrupole interaction in dysprosium ethylsulfate,[10] we found for the crystalline electric-field constant[11] $V_2{}^0$ to be a value of 159 ± 40 cm^{-1}.

Theoretical Mössbauer spectra, which are suitable solutions of the modified Bloch equation,[12] were computed and fitted to the experimental data[13] in the region where fluctuation effects were evident. The spin-relaxation times of Dy^{3+} in $DyCrO_3$ were found to be 7×10^{-9}, 0.4×10^{-9}, 0.2×10^{-9}, and $\sim0.05\times10^{-9}$ sec at 20, 54, 66, and 78°K, respectively.

We are indebted to R. L. Cohen, G. K. Wertheim, and H. H. Wickman for useful discussions.

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[7] I. Nowik and H. J. Williams, Phys. Letters **20**, 154 (1966).

[8] I. Nowik and H. H. Wickman, Phys. Rev. **140**, A869 (1965).

[9] The free ion g_z value 19.7 should correspond to the case of magnetically ordered systems where the ground state is $|\pm J_z\rangle = |\pm15/2\rangle$, a very good approximation.

[10] H. H. Wickman and I. Nowik, Phys. Rev. **142**, 115 (1966).

[11] We used the same method and made the same assumption as in Ref. 7.

[12] H. H. Wickman, M. P. Klein, and D. A. Shirley, Phys. Rev. **152**, 345 (1966).

[13] The computing programming was kindly supplied by H. H. Wickman.

PHYSICAL REVIEW VOLUME 177, NUMBER 2 10 JANUARY 1969

Crystal-Field Studies of Fe^{2+} by the Mössbauer Effect: FeF_2†

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(Received 27 June 1968)

Mössbauer experiments on FeF_2 in the paramagnetic state are reported. The temperature dependence of the quadrupole splitting is studied experimentally, and interpreted in terms of the variations with temperature of the populations of the energy levels of the ferrous ion. From this analysis, values for the crystal-field splittings of the T_{2g} orbital levels of the Fe^{2+} ion are extracted. The best fit with experiment is obtained for $E_2-E_1=1150$°K, $E_3-E_1=1300$°K, with a certain spread in the acceptable values for these energy separations. The results agree well with values deduced previously by magnetic and optical techniques. It is shown, however, that all these results, though consistent among themselves, cannot be explained in terms of a conventional crystalline potential.

I. INTRODUCTION

The problem of the energy-level separations and eigenstates of Fe^{2+} in FeF_2 has been considered in numerous investigations.[1–5] In these previous works, the energy-level separations within the orbital T_{2g} levels of the ferrous ion were estimated from data of paramagnetic resonance (g factors), susceptibility measurements, and antiferromagnetic resonance.[6] From these, the energy separations were calculated assuming a spin Hamiltonian with appropriate point symmetry.[1,2,4] Such calculations have inherent limitations in that they contain estimated parameters which are not known with great accuracy. It is therefore of interest to compare them with the values which can be calculated for the same energies in an independent manner from other experimental data, utilizing a different technique.

In Mössbauer experiments on ferrous (Fe^{2+}) compounds, in which the point symmetry at the site of the Fe^{2+} ion is lower than cubic,[7] one usually observes a quadrupole splitting (ΔE_Q) of the Mössbauer spectrum. In the following discussion, we shall deal with ferrous compounds in the paramagnetic state, so that magnetic hyperfine interactions will not be considered.

The pertinent interaction, leading to the existence of the splitting ΔE_Q, can be generally written as[8]

$$\mathcal{H}_Q=\sum_{j,k} Q_{jk}V_{jk} \quad (j,k=x,y,z). \tag{1}$$

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† Research sponsored in part by the Air Force Materials Laboratory Research and Technology Division AFSC through the European Office of Aerospace Research, U. S. Air Force Contract No. F61052-67C-0040.

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[1] T. Moriya, K. Motizuki, J. Kanamori, and T. Nagamiya, J. Phys. Soc. Japan **11**, 211 (1956).

[2] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535 (1956); **A236**, 549 (1956).

[3] A. Abragam and F. Boutron, Compt. Rend. **252**, 2404 (1961).

[4] A. Okiji and J. Kanamori, J. Phys. Soc. Japan **19**, 908 (1964).

[5] R. Ingalls, Phys. Rev. **133**, A787 (1964).

[6] R. C. Ohlman and M. Tinkham, Phys. Rev. **123**, 425 (1961).

[7] In this context, cubic includes tetrahedral.

[8] A. Abragam, *Nuclear Magnetism* (Oxford University Press, London, 1961), pp. 159–166.

In (1), V_{jk} are the components of the electric-field-gradient (EFG) tensor

$$V_{jk}=\partial^2 V/\partial x_k \partial x_j \tag{2}$$

at the site of the nucleus, V being the electrostatic potential due to the surrounding charge distribution. Furthermore,

$$Q_{jk}=\frac{eQ}{6I(2I-1)}\left[\tfrac{3}{2}(I_jI_k+I_kI_j)-\delta_{jk}\mathbf{I}^2\right], \tag{3}$$

where Q is the quadrupole moment of the nucleus, e is the magnitude of the electronic charge ($e>0$), and $\mathbf{I}$ is the nuclear spin operator with components I_x, I_y, and I_z. For Fe^{57}, the ground state has $I=\frac{1}{2}$, and $\mathcal{H}_Q$ vanishes. The first excited (Mössbauer) level has $I=\frac{3}{2}$, for which $\mathcal{H}_Q$ can be written in matrix form as

$$\begin{array}{cc} I_z= & \begin{array}{cccc} \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} \end{array} \\ \mathcal{H}_Q=\frac{1}{12}eQ & \begin{bmatrix} 3V_0 & 2\sqrt{3}V_{-1} & 2\sqrt{3}V_{-2} & 0 \\ 2\sqrt{3}V_1 & -3V_0 & 0 & 2\sqrt{3}V_{-2} \\ 2\sqrt{3}V_2 & 0 & -3V_0 & -2\sqrt{3}V_{-1} \\ 0 & 2\sqrt{3}V_2 & -2\sqrt{3}V_1 & 3V_0 \end{bmatrix} \end{array}, \tag{4}$$

where $V_0=V_{zz}$, $V_{\pm 1}=V_{zx}\pm iV_{yz}$, $V_{\pm 2}=\frac{1}{2}(V_{xx}-V_{yy})\pm iV_{xy}$. This Hamiltonian can be diagonalized exactly, giving two doubly (Kramers) degenerate eigenvalues, λ_+ and λ_-:

$$\lambda_+=-\lambda_-=\tfrac{1}{4}eQ\left[V_{zz}^2+\tfrac{1}{3}(V_{xx}-V_{yy})^2+(\tfrac{4}{3})(V_{xy}^2+V_{yz}^2+V_{zx}^2)\right]^{1/2}, \tag{5}$$

whence

$$\Delta E_Q=2|\lambda_+|. \tag{6}$$

If the coordinate axes are chosen in such a manner that V_{ij} is diagonal (principal axes), (6) becomes

$$\Delta E_Q=\tfrac{1}{2}e^2qQ\left[1+\tfrac{1}{3}\eta^2\right]^{1/2}, \tag{7}$$

where

$$\eta=(V_{xx}-V_{yy})/V_{zz}, \quad q=V_{zz}/e. \tag{8}$$

Equations (7) and (8) are the well-known results for $I=\frac{3}{2}$.[9]

In ferrous compounds, ΔE_Q is generally temperature-dependent. This temperature dependence is clearly due to the temperature dependence of the EFG tensor V_{ij}, which can be conveniently separated into two contributions: the contribution from the charge distribution of the aspherical $3d$ electronic shell belonging to the ferrous ion itself, and that of the charge distribution of the surrounding ions. In ferrous ions, the latter is much smaller than the first[5] and will be neglected in the following discussion. The contribution of the valence electrons, on the other hand, is temperature-dependent in a significant manner, since its temperature dependence can be interpreted in terms of the varying population of the ionic energy levels.[5] From the temperature dependence of ΔE_Q, one can therefore deduce some crystal-field parameters which characterize the ionic states of Fe^{2+} in a given compound.[10,11]

In this paper we report the results of such a study in FeF_2. Mössbauer studies of FeF_2 were first reported by Wertheim,[9] who concentrated mainly on the low-temperature region where the compound is antiferromagnetic ($T_N \sim 78°K$) and the quadrupole coupling is approximately constant. Our measurements were taken in the paramagnetic region and at high temperatures, where a pronounced decrease in ΔE_Q with temperature is expected, and observed (Sec. II). The experimental results are interpreted in Sec. III and compared with other results on FeF_2.

II. EXPERIMENTAL

FeF_2 in powder form was used in the present study. Three different samples were used,[12] all of which gave identical results within the experimental accuracy. The Mössbauer spectra were obtained using a constant-velocity automatic recording spectrometer.[13] The absorber was contained in a variable temperature furnace (for high-T measurements) or in a cryostat (for low-T measurements) both commercial.[14] The source, which was kept at room temperature, was Co^{57} in Pd.[15] The spectra were recorded directly on an X-Y recorder, and

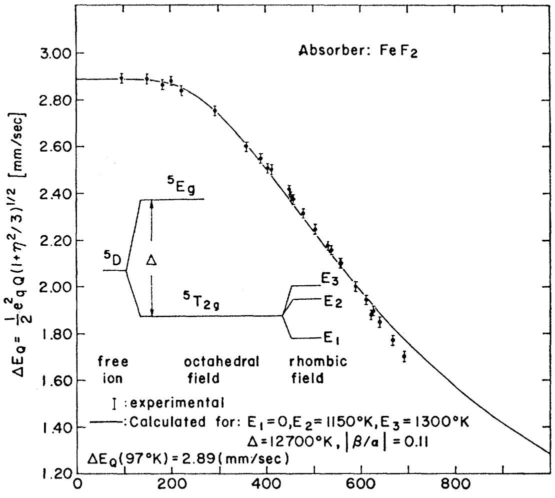

FIG. 1. Quadrupole splitting as a function of temperature in FeF_2. In the insert we show the orbital level scheme of Fe^{2+} under the influence of the crystalline field.

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[9] G. K. Wertheim, Phys. Rev. **121**, 63 (1961).

[10] M. Eibschütz, U. Ganiel, and S. Shtrikman, Phys. Rev. **151**, 245 (1966).

[11] M. Eibschütz, U. Ganiel, and S. Shtrikman, Phys. Rev. **156**, 259 (1967).

[12] Sample (a) was obtained from Dr. M. Kestigian, Sperry Rand Research Center, Sudbury, Mass. Sample (b) was purchased from Alfa Inorganics, Inc., Mass. Sample (c) was obtained from Dr. B. Sturm, Oak Ridge National Laboratory, Tennessee.

[13] Produced by "Elron," Electronic Industries, Haifa, Israel.

[14] Furnace and Cryostat produced by "Ricor," Cryogenic and Vacuum Industries, Ein Harod, Ihud, Israel.

[15] Supplied by New England Nuclear Corporation, Boston, Mass.

the quadrupole splitting was determined from the distance between the centers of gravity of the two peaks. Spectra were taken over a temperature range between 97 and 692°K. The results are shown in Fig. 1, where the experimental points give the quadrupole splitting in mm/sec versus temperature. ΔE_Q ranges from 2.89 ± 0.02 mm/sec at 97°K down to 1.70 ± 0.02 mm/sec at 692°K. This sharp decrease with temperature should be noted since from previous results,[9] in which ΔE_Q was measured only up to room temperature, it seemed that the value of ΔE_Q was rather insensitive to temperature. This in turn lead Ingalls[5] to estimate the crystal-field splitting of the Fe^{2+} ion in this compound, and these older estimates do not agree with ours, as well as with recent optical measurements[16] (see Sec. III).

III. THEORETICAL INTERPRETATION

FeF$_2$ has the rutile structure,[17] belonging to the space group $P4_2/mnm(D_{4h}^{14})$. The crystal structure is tetragonal, with two formula units per unit cell. The Fe^{2+} ions occupy the sites[18] (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the F^- ions occupy the sites $\pm(u,u,o)$, $\pm(\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2})$, with $u = 0.300 \pm 0.002$. The tetragonal unit cell has the dimensions $a = 4.6966 \pm 0.0002$Å, $c = 3.3091 \pm 0.0001$Å. A schematic drawing of the unit cell is given in Fig. 2(a). Each Fe^{2+} ion is surrounded by a distorted octahedron of F^- ions, and the point symmetry at its site is (*mmm*).

Starting from the free ferrous ion, we deal with the configuration [Ar]$3d^6$, the lowest term of which is ^5D. In an octahedral crystal field, ^5D is split into the orbital triplet $^5T_{2g}$ and the orbital doublet ^5E_g. The orbital wave functions can be written, up to normalization factors, as[19] $\xi\eta$, $\eta\zeta$, and $\zeta\xi$ for T_{2g}, and $3\zeta^2-\rho^2$, $\xi^2-\eta^2$ for E_g. ξ, η, and ζ are the cubic axes (connecting opposite vertices of the octahedron) and $\rho^2=\xi^2+\eta^2+\zeta^2$. When the point symmetry is reduced to *mmm*, it is convenient to form the combinations $\xi\eta$, $\frac{1}{2}\sqrt{2}(\xi\eta-\eta\zeta)$, $\frac{1}{2}\sqrt{2}(\xi\eta+\eta\zeta)$, $3\zeta^2-\rho^2$, and $\xi^2-\eta^2$. Defining a new coordinate system, in which the x axis bisects the angle between the ξ and η axes, the y axis is perpendicular to x in the $[\xi\eta]$ plane, and $z=\zeta$, we have for octahedral symmetry

$$T_{2g} \equiv \left\{ \begin{matrix} |x^2-y^2\rangle \\ |yz\rangle \\ |zx\rangle \end{matrix} \right\},$$

$$E_g \equiv \left\{ \begin{matrix} |xy\rangle \\ |3z^2-r^2\rangle \end{matrix} \right\}.$$

With this choice of axes, the crystallographic c axis coincides with the y axis, and x, y, z are the three rotation axes of order 2 [Fig. 2(b)]. Hence they are also the major axes of the EFG tensor at the site of the nucleus. From symmetry considerations it is clear that only $|x^2-y^2\rangle$ and $|3z^2-r^2\rangle$ can be mixed by the crystalline field, whereas the three other functions are exact eigenstates in a crystalline field of the lower point symmetry (*mmm*), as long as spin-orbit interaction is not taken into account. We therefore have

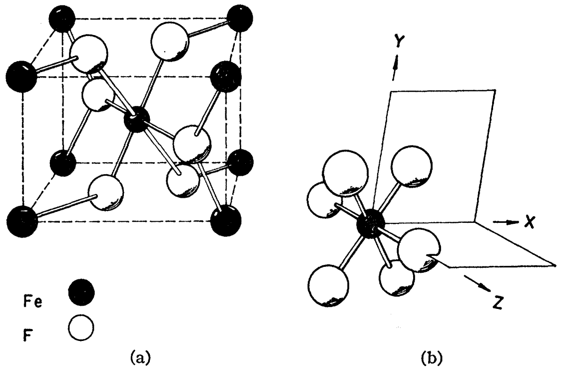

FIG. 2. (a) Schematic drawing of a crystallographic unit cell of FeF$_2$. (b) Coordinate axes x, y, z as chosen for the calculations. The x, y, z axes are twofold axes of symmetry, and hence coincide with the principal axes of the EFG tensor.

$$\begin{aligned} T_{2g}:\ & \psi_1=\alpha|x^2-y^2\rangle+\beta|3z^2-r^2\rangle, \\ & \psi_2=|yz\rangle, \\ & \psi_3=|zx\rangle; \\ E_g\ :\ & \psi_4=|xy\rangle, \\ & \psi_5=-\beta|x^2-y^2\rangle+\alpha|3z^2-r^2\rangle. \end{aligned} \tag{9}$$

Since the splitting between T_{2g} and E_g is normally of the order $\Delta \simeq 10^4$ cm^{-1},[20] it is large compared to the splittings inside T_{2g}, and hence one expects that $|\alpha| \gg |\beta|$. Tinkham[2] suggested that the orbital ground state of Fe^{2+} in ZnF$_2$ (which is isomorphous with FeF$_2$) is ψ_2 [in our notation in (9)]. Wertheim's Mössbauer studies[11] on FeF$_2$ in the antiferromagnetic region confirmed the known result[21] that the magnetic axis is parallel to the crystallographic c axis [y in Fig. 2(b)]. The major axis of the EFG tensor, however, was found to be perpendicular to the magnetic axis. Furthermore, at 45°K, the analysis of the spectrum yields $|\eta| = \frac{1}{3}$. Starting from this result, Abragam and Boutron[3] argued as follows: If one neglects the spin-orbit interaction and the magnetic exchange interaction, the states $\psi_i(9)$ are good eigenstates. Considering the valence electrons as the main cause of the EFG, only ψ_1 and ψ_5 can give rise to the observed value of η. Since 45°K is a sufficiently low temperature to allow one to assume that only the ground level is occupied, they concluded that the orbital ground state was ψ_1. By direct integration one

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[16] G. D. Jones, Phys. Rev. **155**, 259 (1967), Table I.

[17] J. W. Stout and S. A. Reed, J. Am. Chem. Soc. **76**, 5279 (1954).

[18] J. W. Stout and R. G. Shulman, Phys. Rev. **118**, 1136 (1960).

[19] C. J. Ballhausen, *Ligand Field Theory* (McGraw-Hill Book Co., New York, 1962).

[20] For FeF$_2$, Jones (Ref. 16) has reported that $\Delta = 8800$ cm^{-1} at 290°K and $\Delta = 9050$ cm^{-1} at 77°K.

[21] R. A. Erickson, Phys. Rev. **90**, 779 (1953).

obtains

$$\begin{aligned}\langle\psi_1|V_{xx}|\psi_1\rangle&=(-\alpha^2+\beta^2+2\sqrt{3}\alpha\beta)(2/7)e\langle r^{-3}\rangle_d\,,\\ \langle\psi_1|V_{yy}|\psi_1\rangle&=(-\alpha^2+\beta^2-2\sqrt{3}\alpha\beta)(2/7)e\langle r^{-3}\rangle_d\,,\quad(10)\\ \langle\psi_1|V_{zz}|\psi_1\rangle&=2(\alpha^2-\beta^2)(2/7)e\langle r^{-3}\rangle_d\,,\end{aligned}$$

where $\langle r^{-3}\rangle_d$ is the average of r^{-3} for a d orbital. Hence,

$$\eta(\psi_1)=2\sqrt{3}\alpha\beta/(\alpha^2-\beta^2)\,. \qquad (11)$$

This type of analysis when repeated for the recent results of Wertheim and Buchanan,[22] which yield $|\eta|=0.4$ at 4.2°K, leads to $|\beta/\alpha|=0.11$.

Up to now the spin-orbit interaction has not been considered. This is done by adding a term $\lambda(\mathbf{L}\cdot\mathbf{S})$ to the Hamiltonian which describes the Fe^{2+} ion in the crystalline field. The ionic eigenstates will now be of the form

$$\phi_\alpha=\sum_{i,\sigma}\alpha_{i\sigma}\psi_i\chi_\sigma\,, \qquad (12)$$

where χ_σ are spinors of $S=2$. Since V_{jk} does not operate in spin space, we have

$$\langle\phi_\alpha|V_{jk}|\phi_\alpha\rangle=\sum_{i,i'}\alpha_{i}{}^*{}_\sigma\alpha_{i'\sigma}\langle\psi_i|V_{jk}|\psi_{i'}\rangle \qquad (13)$$

and the objects $\langle\psi_i|V_{jk}|\psi_{i'}\rangle$ are calculated by direct integration.

From here we proceed by making the following assumptions: (a) We neglect the contribution of the surrounding ions to the EFG. This contribution is much smaller than that of the valence shell of the ferrous ion itself,[5] so that this approximation should not affect our analysis considerably.[10,11] (b) We take the EFG in which the Fe nucleus is situated to be the thermal average over its values in the various electronic states. This is justified since the electronic relaxation times are much shorter than $\Delta E_Q/h(\sim10^{-8}\text{ sec})$. Hence we write

$$V_{jk}(T)=\sum_\alpha\left[\langle\phi_\alpha|V_{jk}|\phi_\alpha\rangle\exp\left(-\frac{E_\alpha}{kT}\right)\right]\Big/\sum_\alpha\exp\left(-\frac{E_\alpha}{kT}\right), \qquad (14)$$

where E_α is the energy of the state $\phi_\alpha(\alpha=1,\cdots,25)$. $\Delta E_Q(T)$ is then given by (5) or (7). In this calculation, $\Delta E_Q(T)$ will contain a factor of $Q\langle r^{-3}\rangle_d(1-R)$, in which $1-R$ is the Sternheimer factor, to correct for the polarization of the ferriclike core ($3d^5$,^6S) by the valence electrons.[5] Since the above factor is not too well known, we obtain it indirectly by calibrating our calculation to the measured result at low temperatures (97°K), where $\Delta E_Q(T)$ already reaches its saturation value.

The parameters which are included in $\Delta E_Q(T)$ are the orbital energy levels $E(\psi_i)=E_i$, and the spin-orbit interaction parameter λ.

Taking after Jones[20] $\Delta=12800$°K, we performed a least-squares search for the values of λ, E_2-E_1, and E_3-E_1, which will give the best fit of $\Delta E_Q(T)$ to the experimental data. We adopt the eigenfunctions (9), with the values for α and β which are dictated by the argument above ($|\beta/\alpha|=0.11$). Inherent in such a fit is the assumption, often made in similar cases,[5,10,11] that the parameters themselves do not change appreciably with temperature, so that the calculation can be performed assuming E_2, E_3, and λ to remain constant with temperature. For the present case we found that the best fit is obtained for $E_2=1150$°K and $E_3=1300$°K. Furthermore, the dependence on λ is very weak, so that no reliable value for λ can be extracted from this calculation. This can be understood, since in Fe^{2+} $|\lambda|\lesssim100$ cm^{-1}, with even lower values found in compounds. The orbital splitting within T_{2g} is therefore large compared to $|\lambda|$.[23] The finer details of the level structure, which depend on λ, cannot be analyzed in this case on the basis of the high temperature dependence of $\Delta E_Q(T)$, since this quantity is a result of various averaging processes which tend to integrate out this "fine structure." The curve in Fig. 1 was calculated for $\lambda=0$ and for the values of E_2 and E_3 as given above.

It should be noted that the fit obtained is not sensitive to the structure of the orbital functions, i.e., to the values of α and β. To check this point we performed similar calculations for different values of α and β, taking $\alpha=1$ and $\beta=0$ in the extreme case which at low temperature would lead to $\eta=0$ in the above picture (11). The values of E_2 and E_3 obtained are nearly the same as before, although at each temperature the values of $V_{ij}(T)$ are, of course, different. This shows that the temperature dependence of $\Delta E_Q(T)$ in the paramagnetic state cannot be used for the determination of the eigenstates, and so we have adopted the low-temperature value of η which is found in the presence of the magnetic interaction.[22]

There remains the important question of the possible spread of the values of E_2 and E_3 obtained in this manner.

The values of E_2 and E_3 obtained above are those which minimize the sum[24] $\sigma^2=\sum_i[\Delta E_Q(\text{calc.},i)-\Delta E_Q(\text{obs.},i)]^2$, where i goes over all the experimental points. As a criterion to allow for a spread of the parameters, we form contours of equal σ^2 in the $[E_2,E_3]$ plane, and allow for all $[E_2,E_3]$ pairs for which σ^2 is within twice its minimum value. In the close vicinity of the minimum region, such a contour will obviously have the shape of an ellipse, and for larger deviations it can deviate to arbitrary forms. Such a behavior is actually found for these contours. The value of σ^2 is very sensitive to deviations in E_2+E_3 (namely, the "average" splitting within the T_{2g} multiplet) and much less sensitive to

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[22] G. K. Wertheim and D. N. E. Buchanan, Phys. Rev. **161**, 478 (1968).

[23] A similar "λ independence" was found in $\mathrm{GeFe_2O_4}$ (Ref. 10), presumably for the same reason.

[24] Since the experimental error is the same for all the points, they are all equally weighted in this sum.

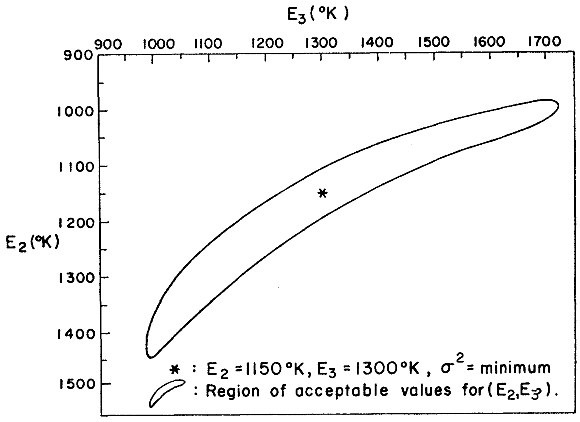

FIG. 3. Region of $[E_2,E_3]$ plane within which the pair $[E_2,E_3]$ gives value $\sigma^2<2(\sigma^2)_{\min}$ (see text).

deviations in E_3-E_2. In Fig. 3 we show the contour in $[E_2,E_3]$ plane, which encloses the region of $[E_2,E_3]$ pairs acceptable by the above criterion. We find that in the extreme case it is possible to have $E_2=1000$°K, $E_3=1700$°K and still obtain quite a good fit to our experimental data.

IV. DISCUSSION

It is of interest to compare the values obtained for the orbital energy levels in the present study to those calculated on the basis of different experimental data.[2,4]

Let us write a spin Hamiltonian for the ground orbital singlet state (ψ_1) which operates within the spin quintet of $S=2$. In the absence of an external magnetic field we have[19]

$$\mathcal{H}_{\text{spin}}=D_xS_x^2+D_yS_y^2+D_zS_z^2. \tag{15}$$

For rhombic symmetry, and remembering our choice of axes [Fig. 2(b)], we can rewrite this as

$$\mathcal{H}_{\text{spin}}=DS_y^2+E(S_z^2-S_x^2). \tag{16}$$

Here,

$$\begin{aligned} D&=-\lambda^2[\Lambda_{yy}-\tfrac{1}{2}(\Lambda_{zz}+\Lambda_{xx})],\\ E&=-\lambda^2[\tfrac{1}{2}(\Lambda_{zz}-\Lambda_{xx})], \end{aligned} \tag{17}$$

where the Λ_{ij}'s are defined by

$$\Lambda_{ij}=\sum_{n\neq 1}\frac{\langle\psi_1|L_i|\psi_n\rangle\langle\psi_n|L_j|\psi_1\rangle}{E_n-E_i}. \tag{18}$$

Furthermore, the g factor is given by[25]

$$g_y=2(1-\lambda\Lambda_{yy}). \tag{19}$$

There is an additional contribution to (16), of the form ρS_y^2 (spin-spin interaction), but this is rather small ($\rho\lesssim 1$ cm^{-1}) and will be neglected.[2] D, E, and g_y are known from magnetic resonance and susceptibility measurements,[2,6] and hence the Λ_{ij} can be estimated. On the other hand, a straighforward calculation gives

$$\begin{aligned} \Lambda_{xx}&=(\alpha+\sqrt{3}\beta)^2/(E_2-E_1),\\ \Lambda_{yy}&=(\alpha-\sqrt{3}\beta)^2/(E_3-E_1),\\ \Lambda_{zz}&=4\alpha^2/(E_4-E_1), \end{aligned} \tag{20}$$

so that the orbital energies E_2, E_3, E_4 can be estimated. Using Tinkham's[2] results, $D=-7.3\pm0.7$ cm^{-1}, $E=0.70\pm0.04$ cm^{-1}, and the value $g_y=2.25\pm0.05$ reported by Ohlman and Tinkham,[6] Okiji and Kanamori[4] calculated the energy values E_i. They assumed certain reduction factors on the matrix elements appearing in (18) to correct for covalency effects. Furthermore, they took values for α and β which would give $|\eta|=\frac{1}{3}$. In an alternative calculation they show that if α and β are varied so that one would obtain $|\eta|\simeq0.53$, the values for E_i are also changed considerably. Within their reported accuracy (±300 cm^{-1}) for E_2 and E_3, and remembering the more recent value[6] for D ($D=-9\pm2$ cm^{-1}), and the more accurate value of $|\eta|=0.4$,[22] their estimates agree with the values that we find, and are contained in the "allowed" region we defined in Sec. III (Fig. 3).

Although all the results of the investigations mentioned above, as well as the present results, seem to be understood in terms of a straightforward formulation, using the orbital wave functions (9) and a spin Hamiltonian (16), there is a central difficulty in understanding the whole picture. In order to explain in a consistent manner the low-temperature Mössbauer[22] results ($|\eta|=0.4$), the values for the anisotropy constants (D,E), and the observed g value,[2,4,6] we have to impose such a noncubic crystalline field which will reproduce the orbital wave functions (9) with $|\beta/\alpha|\simeq0.1$. The crystalline field consistent with the point symmetry of the ferrous ion (mmm) can be expressed as

$$V=V_c+V_a+V_r. \tag{21}$$

Here V_c is the cubic term which is dominant, and V_a and V_r are the axial and rhombic terms, respectively. V_a and V_r can be treated as perturbations to V_c, which has the eigenfunctions (9) with $\alpha=1$, $\beta=0$. We write V_a and V_r in the form

$$V_a=a'(3z^2-r^2), \tag{22a}$$

$$V_r=b'(x^2-y^2). \tag{22b}$$

In (22), fourth-order terms in the potential have been neglected.[26] A first-order perturbation calculation yields

$$\begin{aligned} E_2-E_1&=6a-2b,\\ E_3-E_1&=6a+2b,\\ E_4-E_1&=\Delta,\\ E_5-E_1&=\Delta+8a, \end{aligned} \tag{23}$$

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[25] Our g_y is the usual g_z, since we chose the y direction parallel to the crystallographic C axis.

[26] This does not affect the essential features of the argument which follows, as can be checked by writing explicitly all the possible terms. (See, e.g., Ref. 1.)

where

$$a=(1/7)\langle r^2\rangle_d a',$$

$$b=(1/7)\langle r^2\rangle_d b'.$$

Furthermore, the same calculation directly gives

$$\beta/\alpha=4b/\Delta\sqrt{3}. \tag{24}$$

In terms of this presentation, the previous results are rather difficult to understand.[27] If we start from the measured value for η at low[22] temperatures ($|\eta|=0.4$) and infer from it $|\beta/\alpha|\simeq 0.11$ as explained in Sec. III, the present analysis (24) would lead to $b\simeq 470$ cm^{-1}, or $E_3-E_2\simeq 1900$ cm^{-1}. Such a large splitting is in complete disagreement with all the results mentioned above, both of the various magnetic measurements[4] and of our Mössbauer studies which indicate that $|E_3-E_2|\lesssim 500$ cm^{-1}. Alternatively, we could start from our data, and then (23) would lead to $b\lesssim 100$ cm^{-1}. This, however, would lead to $\beta/\alpha\lesssim 0.02$, by (24). It is worth mentioning here that we tried to examine this possibility. The main point which needs to be clarified, if this line of thought is pursued, is the value found for $\eta(\simeq 0.4)$ at 4.2°K,[22] since by (11) we obtain $\eta\simeq 0$ for $\beta\simeq 0$. However, (11) was derived neglecting the effect of the magnetic-exchange interaction, which can modify the EFG tensor via the spin-orbit interaction.[28] The magnetic-exchange interaction can be taken into account by adding a term of the form $-hS_y$ to the ionic Hamiltonian,[29] where h describes the molecular field. Assuming $|h|\gg|\lambda|$,[30] we add the spin-orbit interaction as a perturbation, and calculate η for the ground state (i.e., ψ_1, with $S_y=2$), by a direct perturbation calculation. The result obtained is

$$\eta(\text{ground state})=\left[4\sqrt{3}\alpha\beta+3(\alpha+\sqrt{3}\beta)^2\left(\frac{\lambda}{E_1-E_2-h}\right)^2-12(\alpha-\sqrt{3}\beta)^2\left(\frac{\lambda}{E_1-E_3}\right)^2\right]\Big/$$
$$\left[2(\alpha^2-\beta^2)-(\alpha+\sqrt{3}\beta)^2\left(\frac{\lambda}{E_1-E_2-h}\right)^2-4(\alpha-\sqrt{3}\beta)^2\left(\frac{\lambda}{E_1-E_3}\right)^2\right]. \tag{25}$$

For $\lambda=0$, (25) reduces to (11), as required.

This result shows clearly, that a value $\eta\neq 0$ can be "induced magnetically" even for $\alpha=1$, $\beta=0$. However, quantitatively, our problem is not resolved this way, since in such a case, and with the observed values for E_2-E_1, E_3-E_1 and the known value for λ, one cannot obtain $|\eta|$ larger than ~ 0.1. We therefore arrive at the conclusion that the large value $|\eta|=0.4$, observed experimentally, must be due to a large mixing ratio $|\beta/\alpha|\gtrsim 0.1$ in the orbital eigenfunctions (9), which is also consistent with other experimental data available.[4] The origin of this rather large mixing, however, is not clearly understood by us presently.

After this work was completed, we learned of a recent study by Stout *et al.*,[31] in which both susceptibility and optical studies of FeF$_2$ were performed. They report an optical transition at 1115 cm^{-1}, which (in our notation) corresponds to the difference E_3-E_1. This value is somewhat larger that our "best value" (1300°K$\simeq$900 cm^{-1}), but is still within the "acceptable" values, in the sense defined earlier (Fig. 3). Furthermore, these measurements were made at low temperatures ($\sim$15°K). It is most probable that the crystal-field splittings vary somewhat with temperature, as in fact reported by Jones[20] for Δ (9050 cm^{-1} at 77°K, 8800 cm^{-1} at room temperature). Our values necessarily represent some average over a wide temperature range, so that Stout's results do in fact conform with the results of our analysis.

ACKNOWLEDGMENTS

We would like to thank Dr. M. Kestigian and Dr. B. Sturm for sending us samples of FeF$_2$. We are also grateful to Dr. G. Wertheim for communicating to us his recent results on FeF$_2$ prior to their publication. We have benefited from an interesting discussion with Professor A. Abragam, concerning some aspects of this study.

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[27] In fact, this type of analysis (24) has led to Ingalls's (Ref. 5) estimate $\Delta\simeq 3200$ cm^{-1}, which is too small by about a factor of 3 (Ref. 20).

[28] That this effect is of importance is manifested most clearly in the extreme case of Fe^{2+} in a site of cubic symmetry, where above the magnetic transition $\Delta E_Q=0$, and below such a transition there appears a magnetically induced EFG; see U. Ganiel and S. Shtrikman, Phys. Rev. **167**, 258 (1968).

[29] y is the direction of the magnetic axis.

[30] This is not the case for FeF$_2$, where $h\sim kT_N$, so that roughly $|h|\sim|\lambda|$. However, the assumption $|h|\gg|\lambda|$ represents the extreme case for which the effect of the magnetic exchange interaction on the EFG tensor should be greatest.

[31] J. W. Stout, M. I. Steinfeld, and M. Yuzuri, J. Appl. Phys. **39**, 1141 (1968).