lation so far as the total net anisotropy energy of the film were concerned. The observed value of K_s would then be quite sensitive to the detailed nature of the film. Our model calculations thus indicate potential, possibly severe experimental difficulties. On the other hand, there is great inducement to try to make films of a thickness specified, at least predominantly, within one atomic layer. We anticipate that the change in anisotropy on changing thickness by one atomic spacing might be very dramatic. Indeed, such experiments could provide a very sensitive probe of the changes in electronic structure with thickness of ferromagnetic metal crystals.

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Magnetically Induced Electric Field Gradient at the Nucleus of High-Spin Fe²⁺ Ion in Distorted Cubic Crystal Field*

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Calculations of a magnetically induced electric field gradient (EFG) at the nucleus of a high-spin Fe²⁺ ion in an axially distorted crystal field have been made. This was done by considering the secular problem of finding eigenstates and eigenvalues for the ground state Γ_5 of the Fe²⁺ ion in an axially symmetric crystal field and then by treating the interaction between magnetic terms of the total interaction Hamiltonian with the crystal field via spin-orbit coupling as a perturbation. It is observed that the principal component of the magnetically induced EFG increases nonlinearly with the crystal-field distortion and approaches a constant value at large values of distortion. It is also seen that the magnetically induced EFG is much more sensitive to temperature in a distorted crystal field than in a cubic field. Further, the sign of the magnetically induced EFG is found to be the same as that of the zero-order EFG. The experimental results of Mössbauer experiments in RbFeF₃ in its antiferromagnetic phase are also discussed.

I. INTRODUCTION

During the past few years, the knowledge of the electric-field-gradient (EFG) tensor has played an important role in determining many important properties in the field of nuclear, solid-state, and chemical physics. Until recently, nuclear quadrupole resonance spectroscopy was the main technique used in such studies. In recent years, Mössbauer spectroscopy has been very effectively used to measure the quadrupole splitting of the nuclear levels[1] and this gives useful information about the EFG at the nucleus. Using the crystal-field theory, several authors[2-4] have worked out the expressions for the EFG in various crystal-field symmetries around an iron nucleus. All these expressions give

zero value for the EFG tensor in a cubic crystal field. In some cubic compounds like $FeCr_2O_4$ and FeV_2O_4, the presence of a static Jahn-Teller effect gives rise to a nonzero EFG.[5] Very recently, it has been observed that even in the absence of a static Jahn-Teller effect there exists the nonzero EFG at the Fe^{57} nucleus in some cubic high-spin Fe^{2+} compounds in their magnetically ordered phases.[6-9] It is also noticed that the nonzero EFG and the magnetic ordering appear simultaneously below the transition temperature. It has been shown that even in the absence of a static Jahn-Teller effect, the magnetic interactions can induce an EFG at the nucleus in the cubic crystal field.[9,10] Such attempts have been until now confined only to the cases having octahedral or tetrahedral cubic-field symmetries around the Fe^{2+} ion. In the present work, following an earlier theoretical analysis,[10] the theory for the EFG's principal component V_{zz} in an axially distorted crystal field has been considered. Two different cases are discussed: one in the magnetically ordered phase of the crystal and the other in the presence of an external magnetic field. Several important results are obtained. It is found that the presence of an axial distortion along the direction of an applied field or a molecular field enhances the value of the magnetically induced EFG. Further, this induced EFG approaches a constant value at the large crystal-field distortions. It is also seen that the variation of the magnetically induced EFG with temperature is larger in the axially distorted phase than in the cubic phase. The sign of the zero-order EFG and the magnetically induced EFG is found to be the same. An attempt is made to compare the earlier experimental results of $RbFeF_3$[6] with the theoretical results. The expected value on the basis of the existing theories is much larger than the observed value. From these anomalous results it is proposed that in $RbFeF_3$, magnetoelastic forces play an important role in the antiferromagnetic region.

In Sec. II, we review the basic theory and the expressions used to estimate the EFG for a paramagnetic Fe^{2+} ion. In Sec. III, the magnetic interactions which induce an additional EFG by changing the spatial distribution of electrons due to the magnetic perturbations are discussed. In Sec. IV, the unperturbed energy levels and the wave functions are obtained by considering the secular problem for a high-spin Fe^{2+} ion in an axially distorted octahedral field. Using these eigenstates and the second-order stationary-state perturbation theory, the results for the magnetically induced EFG's principal component V_{zz} are obtained (Sec. V).

II. PARAMAGNETIC ION IN CRYSTAL FIELD

The total interaction Hamiltonian for an iron-group paramagnetic ion in the absence of an external magnetic field can be expressed as[11]

$$\mathcal{H} = \mathcal{H}_f + \mathcal{H}_{cr} + \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_N + \mathcal{H}_Q , \tag{1}$$

where $\mathcal{H}_f$ is the free-ion part of the Hamiltonian and is independent of the spin variables and determines the ground-state term of the ion. $\mathcal{H}_{cr}$ is the interaction term due to the crystal field set up by the surrounding diamagnetic charges. $\mathcal{H}_{LS}$ is the energy of interaction between the orbital and spin angular momenta of the electrons. $\mathcal{H}_{SS}$ is the mutual interaction between the magnetic dipoles and is called the spin-spin interaction. $\mathcal{H}_N$ is the interaction between magnetic moment of the nucleus and the magnetic field due to the electronic orbital and the spin angular momenta. $\mathcal{H}_Q$ is the Hamiltonian for quadrupole interaction between the nuclear quadrupole moment and the EFG tensor at the nucleus and can be written in terms of the components V_{xx}, V_{yy}, and V_{zz} of the EFG tensor as[12]

$$\mathcal{H}_Q = \frac{eQ}{4I(2I-1)} \{V_{zz}[3I_z^2 - I(I+1)]$$
$$+ (V_{xx} - V_{yy})(I_x^2 - I_y^2)\} , \tag{2}$$

where Q is the quadrupole moment of the nucleus, I is the nuclear spin, $-e$ is the electronic charge, and I_x, I_y, and I_z are the components of nuclear-spin operator $\vec{I}$.

According to Hund's rule, the ground state for a free Fe^{2+} ion is ^5D. From the group-theoretical arguments it can be seen[13] that the interaction terms other than $\mathcal{H}_f$ in Eq. (1) will split the ground state ^5D into a series of orbital and spin states Ψ_n of energies E_n. Since the electrons' spatial distribution will be different for the various eigenstates, the components of EFG tensor at the nucleus will also be different for different states. The times involved in the thermal transitions between the various energy levels are generally much shorter than the quadrupole precession times,[14] and therefore in Mössbauer experiments one observes the ensemble average value of these components. The expression for V_{zz} at a temperature T is, therefore, as follows:

$$V_{zz} = \sum_n \langle \Psi_n | \underline{V}_{zz} | \Psi_n \rangle e^{-\tau E_n} \Big/ \sum_n e^{-\tau E_n} , \tag{3}$$

where $\tau = 1/kT$, k being the Boltzmann constant. Using Stevens's operator-equivalent technique,[15] Eicher[3] and a few others[4] have expressed the operator $\underline{V}_{zz}$ for $3d^6$, ^5D state as

$$\underline{V}_{zz} = \frac{2}{7} \langle r^{-3} \rangle_{3d} (L_z^2 - 2), \tag{4}$$

where $\langle r^{-3} \rangle_{3d}$ is the average of r^{-3} for $3d$ electrons.

Using Eqs. (3) and (4), if the eigenstates and eigenvalues of the Hamiltonian given in Eq. (1) are known, the average value of V_{zz} at temperature T can be estimated by evaluating the matrix elements of $(L_z^2 - 2)$ within the various eigenstates. The detailed problem of the EFG for a high-spin paramagnetic Fe^{2+} ion has been treated by Ingalls[4] for the various crystal-field symmetries. It is found that the EFG tensor is zero for the crystal field of cubic symmetry since in such a case the various interaction terms in Eq. (1) do not alter the over-all spherical distribution of electrons. In Sec. III we consider the magnetic interactions which induce an additional EFG at the nucleus.

III. MAGNETIC INTERACTIONS

Below the magnetic transition temperature, the spin ordering takes place in a crystal which gives rise to a spontaneous magnetization. The origin of spontaneous magnetization, according to Heisenberg theory,[16] is the exchange interaction between the neighboring spins. This interaction term can be expressed as

$$\mathcal{H}_{ex} = -\sum_{ij} J_{ij}\, \vec{S}_i \cdot \vec{S}_j , \tag{5}$$

where J_{ij} is the effective exchange integral between atoms i and j having total spins $\vec{S}_i$ and $\vec{S}_j$, respectively. In the molecular field approximation, this equation can be written as

$$\mathcal{H}_{ex} = 2ZJ\langle S_{zn}\rangle_T S_z = \mu_B h_z S_z , \tag{6}$$

where Z is the coordination number of Fe^{2+} ion, z is the direction of the sublattice magnetization, $\langle S_{zn}\rangle_T$ is the thermal expectation value of the z component of the spin at the neighboring sites, h_z is the molecular field which is temperature dependent and has a nonzero value only below the magnetic transition temperature, and μ_B is the Bohr magneton.

In the presence of an external magnetic field, an additional term is to be included in Eq. (1) owing to the Zeeman interaction between the external magnetic field and the electrons. This term can be expressed by the well-known relation

$$\mathcal{H}_m = \mu_B(\vec{L} + 2\vec{S}) \cdot \vec{H} , \tag{7}$$

where $\vec{H}$ is the applied magnetic field.

The presence of the magnetic interaction $\mathcal{H}_{ex}$ or $\mathcal{H}_m$ perturbs the eigenstates of the unperturbed Hamiltonian [Eq. (1)] and, therefore, the spatial distribution of the electrons is altered. The change in the spatial distribution of the electrons results in a different EFG at the nucleus. Thus, even in the case of a cubic ligand symmetry, the presence of magnetic interaction $\mathcal{H}_{ex}$ or $\mathcal{H}_m$ will, in general, result in a

nonzero EFG. This magnetically induced EFG in the cubic ligand field was discussed recently by Ganiel and Shtrikman[10] for an octahedral arrangement of ligands and by Hoy and Singh[9] for an octahedral as well as a tetrahedral arrangement of ligands. The case of axially distorted symmetry is of additional interest since in this case, even in the absence of the magnetic interactions, the EFG is nonzero. The EFG in such a case consists of two parts: one due to the unperturbed Hamiltonian and the other due to the magnetic interactions. We have calculated the magnetically induced EFG for the axially distorted octahedral symmetry by first evaluating the eigenstates and eigenvalues for high-spin Fe^{2+} ion in an axially symmetric crystal field.

IV. ENERGY LEVELS AND EIGENFUNCTIONS IN ABSENCE OF MAGNETIC INTERACTIONS

The interaction Hamiltonian, in the presence of an axially symmetric crystal field, can be expressed as[11,17]

$$\mathcal{H}_0 = \mathcal{H}_f + \mathcal{H}_C + \mathcal{H}_T + \lambda(\vec{L} \cdot \vec{S}), \tag{8}$$

where $\mathcal{H}_f \gg \mathcal{H}_C \gg \mathcal{H}_T$ and $\lambda(\vec{L} \cdot \vec{S})$ and $\mathcal{H}_T = \Delta(1 - l_z'^2)$.[18,19] Here, λ is the well-known spin-orbit coupling parameter, and for the high-spin Fe^{2+} ions in the absence of covalency effects and dynamic Jahn-Teller effect, λ is approximately equal to -100 cm^{-1}. The excited states corresponding to the interaction term $\mathcal{H}_f$ are much farther from the ground state ^5D and therefore the influence of excited states on the ground state is negligible.[17] The perturbation $\mathcal{H}_C$ splits the fivefold orbital degenerate level into two levels $^5\Gamma_5$ and $^5\Gamma_3$ (in Bethe's notation) with the energy difference of $10Dq$. The presence of the axial distortion represented by $\mathcal{H}_T$ further splits the triply degenerage Γ_5 level and the doubly degenerate Γ_3 levels into two levels each. The magnitude of Δ is the measure of the axial-field distortion, and for the $3d^6$ ion its value lies between 100 and 2000 cm^{-1}. The spin-orbit coupling $\lambda(\vec{L} \cdot \vec{S})$ lifts the spin degeneracy. Since $10Dq$ is much larger than both Δ and λ, the levels corresponding to Γ_3 are much above the ones corresponding to Γ_5. We therefore neglect the admixture of Γ_3 states with Γ_5 states. It has been shown[19] that in the presence of axial octahedral symmetry, the 15 eigenfunctions corresponding to 9 energy levels should be considered. The detailed energy-level scheme in an axial crystal field is shown in Fig. 1.

The diagonalization of the 15×15 matrix for the interaction Hamiltonian $\mathcal{H}_0$ has been carried out earlier.[19] However, on reconsidering this problem, it was found that 3 of the 15 eigenfunctions used were not reported correctly. This can be seen by taking the limiting case of $\Delta \to 0$. On evaluating the matrix elements of $(L_z^2 - 2)$ and then calculating

FIG. 1. Energy-level scheme for the high-spin Fe^{2+} state in the presence of an axially symmetric crystal field and spin-orbit coupling.

V_{zz} using Eq. (3), we find that the value of V_{zz} does not come out to be zero for $\Delta = 0$, which is in contradiction to the well-established result that in a cubic field V_{zz} should be zero. Further, on computing the matrix elements of L_z and S_z within the manifold of 15 states for Fe^{2+} ion in a cubic octahedral crystal field, it was observed that the results did not agree with an earlier work.[20] It was therefore necessary to reevaluate the correct eigenfunctions. Since the procedure for setting the matrix elements and solving the secular problem for Fe^{2+} ion has already been described by Low and Weger,[17] the detailed treatment is omitted here for brevity and only the final results are given in Table I. The eigenfunctions Ψ_n^0 and the energy levels E_n^0 given in Table I are used in Sec. V to evaluate V_{zz} at various temperatures as a function of Δ.

TABLE I. Energy levels and eigenfunctions for the ground state of Fe^{2+} ion in an axial field in the order of increasing energy. The equations for the coefficients α, β, and γ and for the energies E_n as a function of Δ and λ are given in the Appendix.

Energy levels	Eigenfunctions
E_1	$\Psi_1 = \alpha(1,\ 0) + \beta(0,\ 1) + \gamma(-1,\ 2)$ $\Psi_2 = \alpha(-1,\ 0) + \beta(0,\ -1) + \gamma(1,\ -2)$
E_2	$\Psi_3 = \alpha_1(1,\ -1) + \beta_1(0,\ 0) + \alpha_1(-1,\ 1)$
E_3	$\Psi_4 = \alpha_1'(1,\ -1) + \beta_1'(0,\ 0) - \alpha_1'(-1,\ 1)$
E_4	$\Psi_5 = \alpha'(1,\ 0) + \beta'(0,\ 1) + \gamma'(-1,\ 2)$ $\Psi_6 = \alpha'(-1,\ 0) + \beta'(0,\ 1) + \gamma'(1,\ -2)$
E_5	$\Psi_7 = \alpha_2(1,\ 1) - \beta_2(0,\ 2)$ $\Psi_8 = \alpha_2(-1,\ -1) - \beta_2(0,\ -2)$
E_6	$\Psi_9 = (1,\ 2)$ $\Psi_{10} = (-1,\ -2)$
E_7	$\Psi_{11} = \beta_2(1,\ 1) + \alpha_2(0,\ 2)$ $\Psi_{12} = \beta_2(-1,\ -1) + \alpha_2(0,\ -2)$
E_8	$\Psi_{13} = \alpha''(1,\ 0) + \beta''(0,\ 1) + \gamma''(-1,\ 2)$ $\Psi_{14} = \alpha''(-1,\ 0) + \beta''(0,\ -1) + \gamma''(1,\ -2)$
E_9	$\Psi_{15} = \alpha_1''(1,\ -1) + \beta_1''(0,\ 0) + \alpha_1''(-1,\ 1)$

V. EFG IN PRESENCE OF MAGNETIC INTERACTIONS

The Hamiltonian in the presence of an external magnetic field or in a magnetically ordered crystal can be written as

$$\mathcal{H} = \mathcal{H}_f + \mathcal{H}_C + \mathcal{H}_T + \lambda(\vec{L} \cdot \vec{S}) + \mathcal{H}' = \mathcal{H}_0 + \mathcal{H}' , \qquad (9)$$

where $\mathcal{H}'$ is $\mathcal{H}_{ex}$ or $\mathcal{H}_m$ and $\mathcal{H}_0 \gg \mathcal{H}'$. On combining Eqs. (3) and (4), the ensemble average of V_{zz} over 15 eigenstates can be expressed as

$$V_{zz} = \tfrac{2}{7}\langle r^{-3}\rangle_{3d} \sum_{n=1}^{15} \langle \Psi_n | (L_z^2 - 2) | \Psi_n \rangle\, e^{-\tau E_n} \Big/ \sum_{n=1}^{15} e^{-\tau E_n} . \qquad (10)$$

In the presence of perturbation $\mathcal{H}'$, the eignestates and the energies E_n^0 are no longer the same as given in Table I. Using a stationary-state perturbation theory, E_n is given by

$$E_n = E_n^0 + E_n' + E_n'' + \cdots , \qquad (11)$$

where E_n' and E_n'' are the first- and second-order changes, respectively, in E_n^0 due to $\mathcal{H}'$. We restrict the calculations up to second-order effects only and assume that (i) $\mu_B h_z$ and $\mu_B H$ are much smaller than both λ and T, and (ii) the z axis is the direction of axial-field distortion and of sublattice magnetization. Based on these assumptions and Eq. (11), V_{zz} can be written as the sum of three parts: the zero order V_{zz}, the first order V_{zz}, and the second order V_{zz}, such that

$$V_{zz} = \langle V_{zz}\rangle^0 + \langle V_{zz}\rangle' + \langle V_{zz}\rangle'' . \qquad (12)$$

Using Eq. (10) and the unperturbed eigenfunctions (Ψ_n^0) along with their corresponding energies (E_n^0), the zero order V_{zz} is evaluated at various temperatures from 40 to 200 °K. The lengthy calculations required to get $\langle V_{zz}\rangle^0$ is performed on an ICT 1909 computer. It is convenient to define a reduction factor F_0 as

$$F_0 = \left(\tfrac{2}{7} e \langle r^{-3}\rangle_{3d}\right)^{-1} \langle V_{zz}\rangle^0 . \tag{13}$$

It is obvious from this definition that F_0 represents $\langle V_{zz}\rangle^0$ in units of $\tfrac{2}{7} e \langle r^{-3}\rangle_{3d}$. The values of F_0 as a function of Δ are shown in Fig. 2. For a crystal field of cubic symmetry ($\Delta = 0$), as expected $\langle V_{zz}\rangle^0$ turns out to be zero. On calculating the first-order perturbation of $\mathcal{H}'$ on the partially degenerate unperturbed levels E_n^0, we get

$$\langle V_{zz}\rangle' = 0. \tag{14}$$

Equation (14) shows that the magnetic interactions do not induce an EFG in the first order in the case of an axial crystal field. Also, in the cubic crystal-field Ganiel and Shtrikman[10] have observed that the first-order effect of magnetic perturbation of the type $\mathcal{H}_{ex}$ is zero. On considering the second-order perturbation, we found that $\langle V_{zz}\rangle''$ is nonzero in an axially distorted symmetry of ligands. It was observed that like in a cubic crystal field it is possible to express $\langle V_{zz}\rangle''$ in the axially symmetric field as

$$\langle V_{zz}\rangle'' = \left(a_1(T)\frac{h_z^2}{T^2} + a_2(T)\frac{h_z^2}{\lambda T} + a_3(T)\frac{h_z^2}{\lambda^2}\right) , \tag{15}$$

where $a_1(T)$, $a_2(T)$, and $a_3(T)$ are the functions of Δ, λ, and T. Again as before, we define reduction factors F_{ex} and F_m for a magnetically ordered crystal and for a paramagnetic ion under the influence of an external magnetic field, respectively, as
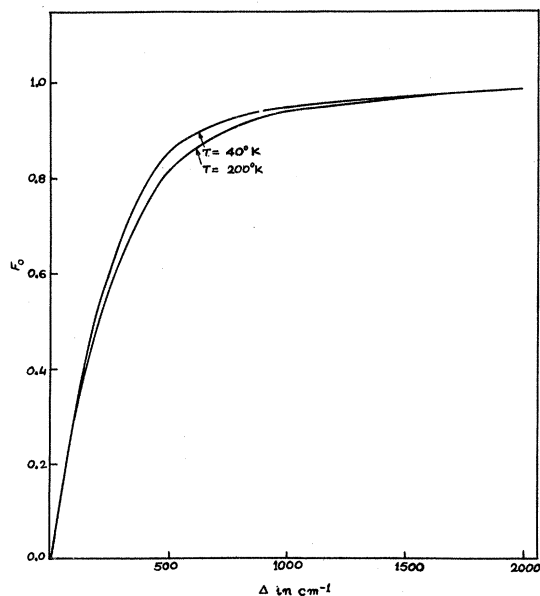
FIG. 2. F_0 as a function of Δ at $T = 40$ °K and $T = 200$ °K ($\lambda = -100$ cm^{-1}).
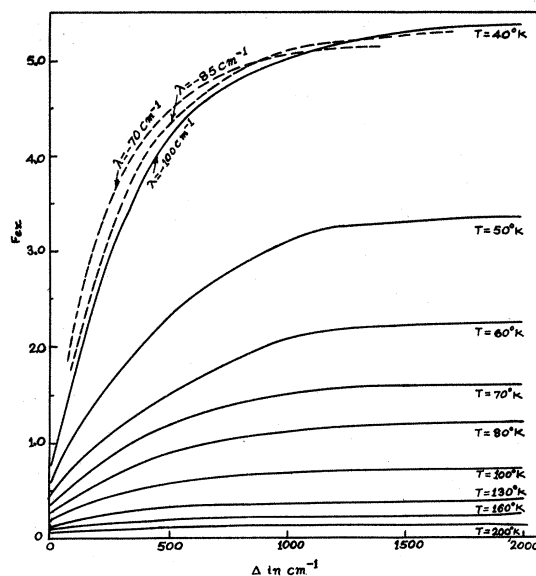

FIG. 3. F_{ex} as a function of Δ at various temperatures between 40 and 200 °K ($\lambda = -100$ cm^{-1}). At 40 °K the variation with λ is also shown.

$$F_{ex} = \left[\tfrac{2}{7} e \langle r^{-3}\rangle_{3d}\, h_z^2 \times 10^{-8}\right]^{-1} \langle V_{zz}\rangle'' \tag{16}$$

and

$$F_m = \left[\tfrac{2}{7} e \langle r^{-3}\rangle_{3d}\, H_z^2 \times 10^{-8}\right]^{-1} \langle V_{zz}\rangle'' , \tag{17}$$

where h_z and H_z are the molecular field and external magnetic field, respectively, in units of kOe. Using an ICT 1909 computer, we have calculated $a_1(T)$, $a_2(T)$, and $a_3(T)$ as a function of Δ at various temperatures and have obtained the parameters F_{ex} and F_m. Since the method of setting the secular problem for second-order perturbation theory for degenerate levels is well known and since it is not possible to give here for 15 eigenstates the detailed treatment and the final expressions for $\langle V_{zz}\rangle''$, we present the results in a numerical form in terms of F_{ex} and F_m, as shown in Figs. 3 and 4. At very low temperatures, the assumption that $\mathcal{H}'$ is much smaller than kT is not strictly valid. At the same time at higher temperatures, the large influence of upper eigenstates onto the lower ones will result in a much smaller temperature dependence of the magnetically induced V_{zz}. The calculations for F_{ex} and F_m are therefore restricted to the temperature range of 40 to 200 °K. These results are shown in Figs. 3 and 4, and the several interesting aspects of these results are discussed in Sec. VI.

VI. RESULTS AND DISCUSSIONS

From Figs. 3 and 4, it is seen that the magnetically induced EFG increases nonlinearly with the crystal-field distortion and at large crystal-field
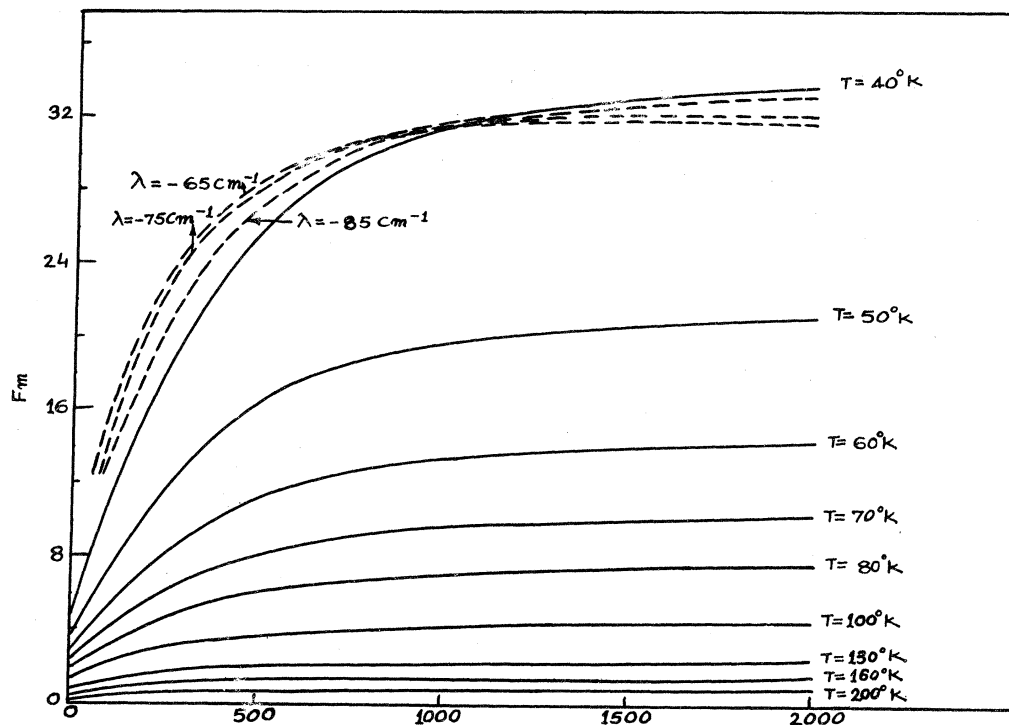
FIG. 4. F_m as a function of Δ at various temperatures taking $\lambda = -100$ cm^{-1}. At $T = 40\,°K$ the effect of variation with λ is also shown.

distortions this induced EFG appears to approach a constant value. In Fig. 2 the zero-order EFG at two temperatures, 40 and 200 °K, is plotted as a function of Δ. It is seen that at very small as well as at very large crystal-field distortions, F_0 and hence V_{zz} is almost the same at these two temperatures. In the intermediate region, however, the value of $\langle V_{zz}\rangle^0$ differs at these two temperatures. On comparing the temperature dependence of F_0 for various values of the crystal-field distortions with that of F_{ex} (Fig. 3) and F_m (Fig. 4), we obtain two significant results. First, the magnetically induced effects are far more sensitive to the temperature than the zero order V_{zz}. This result is also supported experimentally by the observation of a large temperature dependence of quadrupole splitting in RbFeF$_3$ in antiferromagnetic phase.[6] Second, V_{zz} is found to be more sensitive to the temperature in the presence of axial distortion than in cubic crystal field (Figs. 3 and 4). This can be explained by the fact that the nonadmixture between Γ_5 levels is quite small in an axial crystal field compared to the one in a cubic field (Fig. 1). The large admixture among various eigenstates of Γ_5 enhances the second-order effects. It is also seen that the sign of both $\langle V_{zz}\rangle^0$ and $\langle V_{zz}\rangle''$ are the same. On the basis of this result and the results mentioned above, we now discuss the experimental results of RbFeF$_3$.

Wertheim et al.[6] using Mössbauer technique have studied the variation of quadrupole splitting with temperature in antiferromagnetic phase of RbFeF$_3$.

In a molecular field approximation, Ganiel et al.[8] have made a rough estimate of h_z as 70 °K[21] for RbFeF$_3$. Assuming for the time being that RbFeF$_3$ is a cubic antiferromagnet as was assumed by earlier workers,[6,8] the value of h_z that one gets at 92 °K using the experimental results of quadrupole splitting[6] between 86 and 97 °K in conjunction with our results in Fig. 3 is 58.3 °K. The antiferromagnetic compound RbFeF$_3$ which was previously believed to have cubic structure[6,8] has been recently shown by Testardi et al.[22] to exhibit a tetragonal structure between 86 and 97 °K. Even if we assume that this crystal-field distortion is small ($\Delta = 100$ cm^{-1}), the expected quadrupole splitting in the absence of any magnetically induced effect is approximately equal to 0.05 cm/sec. Since the sign of $\langle V_{zz}\rangle^0$ and $\langle V_{zz}\rangle''$ is theoretically the same, after taking the magnetically induced effects into account, one should expect a value for the quadrupole splitting four to ten times larger than the experimentally observed values.[6] It is also seen that even if we take a much smaller value of h_z, say, of the order of 10 °K, the expected value of the quadrupole splitting, because of finite tetragonal distortion, is quite large compared to the one observed experimentally. In a cubic tetrahedral normal spinel FeCr$_2$S$_4$ also, the existing theory[9,23] does not explain the experimental results satisfactorily. The significant difference for RbFeF$_3$, as pointed out above, may presumably be due to the presence of magnetoelastic strains.

APPENDIX

In this Appendix, we present the equations for the energies and the coefficients α, β, and γ (used in Table I) in terms of Δ and λ:

$$E_2 = \tfrac{1}{2}\{(\Delta + \lambda) - [(\Delta - \lambda)^2 + 24\lambda^2]^{1/2}\}, \tag{A1}$$

$$E_3 = \lambda, \tag{A2}$$

$$E_5 = \tfrac{1}{2}\{(\Delta - \lambda) - [(\Delta + \lambda)^2 + 8\lambda^2]^{1/2}\}, \tag{A3}$$

$$E_6 = -2\lambda, \tag{A4}$$

$$E_7 = \tfrac{1}{2}\{(\Delta - \lambda) + [(\Delta + \lambda)^2 + 8\lambda^2]^{1/2}\}, \tag{A5}$$

$$E_9 = \tfrac{1}{2}\{(\Delta + \lambda) + [(\Delta - \lambda)^2 + 24)^2]^{1/2}\}. \tag{A6}$$

$E_1, E_4,$ and E_8 are the roots of a cubic equation

$$E^3 - (2\lambda + \Delta)E^2 + (2\Delta - 5\lambda)\lambda E + 6\lambda^3 = 0, \tag{A7}$$

$$\beta_1 = \left(1 + \frac{6\lambda^2}{(\lambda - E_2)^2}\right)^{-1/2}, \quad \alpha_1 = \frac{\sqrt{3}\,\beta_1\lambda}{\lambda - E_2}, \tag{A8}$$

$$\beta_1' = \left(1 + \frac{6\lambda^2}{(\lambda - E_3)^2}\right)^{-1/2}, \quad \alpha_1' = \frac{\sqrt{3}\beta_1'\lambda}{\lambda - E_3}, \tag{A9}$$

$$\beta_1'' = \left(1 + \frac{6\lambda^2}{(\lambda - E_9)^2}\right)^{-1/2}, \quad \alpha_1'' = \frac{\sqrt{3}\,\beta_1''\lambda}{\lambda - E_9} \tag{A10}$$

$$\beta_2 = \left(1 + \frac{2\lambda^2}{(\Delta - E_5)^2}\right)^{-1/2}, \quad \alpha_2 = \frac{\sqrt{2}\,\lambda\beta_2}{\Delta - E_5}, \tag{A11}$$

$$\gamma = \left(1 + \frac{(2\lambda - E_1)^2}{2\lambda^2} + \frac{3(2\lambda - E_1)^2}{2E_1^2}\right)^{-1/2}, \tag{A12}$$

$$\beta = (\tfrac{1}{2})^{1/2}\gamma(2\lambda - E_1)/\lambda, \tag{A13}$$

$$\alpha = (\tfrac{3}{2})^{1/2}\gamma(2\lambda - E_1)/E_1 . \tag{A14}$$

$\alpha', \beta',$ and γ' can be obtained by replacing E_1 by E_4 in Eqs. (A12)–(A14) for $\alpha, \beta,$ and γ, respectively; $\alpha'', \beta'',$ and γ'' can similarly be obtained by replacing E_1 by E_8 in the same Eqs. (A12)–(A14).

These Eqs. (A1)–(A14) have been used by us to estimate the unperturbed energy levels and the eigenfunctions for various values of Δ.

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