Study of the vibronic effects from the Zeeman-field–induced Mössbauer spectra of Fe²⁺ ions in octahedral symmetry. I. The effective Hamiltonian formalism

T. Ray and J. R. Regnard

Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, Groupe Interactions Hyperfines, BP 85, Centre de tri, 38041 Grenoble Cedex, France

(Received 28 August 1975)

The importance of the Zeeman-field–induced quadrupole and hyperfine interactions in Jahn-Teller active ions is demonstrated with particular reference to Fe^{2+} in octahedral crystals such as CaO and $KMgF_3$. An effective electron nuclear Hamiltonian is derived from general symmetry principles, whose parameters are calculated by perturbation procedure, incorporating the vibronic effects in terms of Ham reduction factors between spin-orbit states. Relevant theoretical expressions for the Mössbauer transitions are given so that these parameters can be determined experimentally from the analysis of the Mössbauer spectra.

I. INTRODUCTION

Accurate measurements of the nuclear hyperfine and quadrupole spectra at low temperatures in paramagnetic impurities in insulating crystals give useful information about the ground electronic spin-orbit levels.[1] In systems where there are low-lying excited spin-orbit levels, one should be able to vary the amount of mixing of these levels with the ground one by suitable choice of the external magnetic field. Particularly for the case of the magnetic impurities having strong Jahn-Teller interactions with the lattice, the study of the hyperfine splitting with different orientations and magnitudes of the external field might enable one to make inference about the Jahn-Teller coupling strengths of the low-lying levels. With this idea we develop the magnetic-field-dependent hyperfine and quadrupole interaction Hamiltonians for the case of Fe^{2+} ion in octahedral symmetry. The nuclear quadrupole interaction is zero for spin-orbit (s.o.) levels in cubic crystalline fields unless any strain field[2] or magnetic field,[2,3] either applied externally or present internally due to magnetic ordering, removes the degeneracy of the s.o. levels. This leads to a net quadrupole splitting due to the difference in the thermal population in these splitted-up levels. Generally only the field-independent part of this quadrupole interaction for a particular s.o. level is considered and we shall call this part the pure quadrupole interaction (pq) to distinguish it from the part which is proportional to linear and higher powers of the field, which we call the magnetic-field–induced quadrupole interaction (iq). Similarly for the hyperfine interactions, the part due to the internal field at the nucleus and independent of the external magnetic field is called the pure hyperfine (phf) interaction and the part proportional to the external magnetic field is called the induced hyperfine effects (ihf).

The importance of these induced effects in the Mössbauer spectra was first pointed out by Ghatikar[4] in the case of hexagonal rare-earth trichlorides and by Ganiel and Shtrikman[3] in the case of Fe^{2+} ion in cubic symmetry. Ghatikar calculated the coefficient of the effective quadrupole Hamiltonian linear in the Zeeman field H_0, *viz.*, $S_i H_j [I_z^2 - \frac{1}{3} I(I+1)]$ for each of the low-lying s.o. levels of the rare-earth ions considering perturbations on these s.o. levels (i) of the second order due to the Zeeman and pure quadrupole interactions and (ii) of the third order due to the Zeeman interaction and second order in hyperfine interaction $(B\vec{J} \cdot \vec{I})$. Then taking the thermal average of the effective Hamiltonian over all the spin-orbit states, the nuclear quadrupole splitting is obtained as a function of temperature. Ganiel and Shtrikman,[3] on the other hand, have derived expressions for the temperature dependence of the field-induced (either external or internal field) quadrupole and hyperfine interactions for the particular case of Fe^{2+} in an octahedral lattice treating two different cases. In the first case, the Zeeman energy is very small compared to the spin-orbit energy and the thermal energy, which is physically realizable for magnetically ordered crystals like $KFeF_3$ near the transition temperature. In this case, Ganiel and Shtrikman estimated the temperature-dependent field gradient directly by expanding the field-gradient tensor in powers of $\mu_B H / KT$ and calculating its thermal average over all spin-orbit states. Evidently this approach is not applicable to the case of Fe^{2+} impurities in diamagnetic crystals at low temperatures. In such cases, Ganiel and Shtrikman first calculated the first-order effects of the Zeeman field on the spin-orbit states and then derived the expression for the field gradient between these perturbed states,

taking account of the lowest spin-orbit triplet. This latter approach is essentially the same as the effective-Hamiltonian formalism used by Ghatikar.[4] The present work differs from these earlier works in the fact that we have analyzed the magnetically induced quadrupole interactions for the dynamical case, whereas in these earlier works they are considered in the static limit. The results of Ganiel and Shtrikman for Fe^{2+} ion in octahedral symmetry show that both the field-dependent and the field-independent parts of the quadrupole splitting ΔE_Q would be the same in magnitude but opposite in sign, as the external field is changed from the [100] to the [111] direction. The same conclusion had earlier been reached by Ham[2]— also in static limit—for the field-independent or the pure quadrupole interaction in the case of $MgO:Fe^{2+}$. Subsequently, Ham, Schwarz, and O'Brien[5] considered the dynamical case for $MgO:Fe^{2+}$ which confirmed that ΔE_Q (pure) would change in sign as the field direction is oriented from the [100] to the [111] direction and whatever difference in magnitude it might show could be attributed to the different strengths of the coupling of the impurity-ion orbital to the E_g and T_{2g} modes of vibration of the octahedral complex. The Leider Pipkorn[6] Mössbauer study of $MgO:Fe^{2+}$ with an external field $H \sim 50$ KOe shows that ΔE_Q changes sign with the orientation of the field but the magnitude remains the same. This result could be interpreted in the background of the dynamical theory of Ham, Schwarz, and O'Brien[5] as both types of the Jahn-Teller coupling—one involving the E_g mode and the other the T_{2g} mode—being of more or less equal importance for the $^5T_{2g}$ term of Fe^{2+} in MgO. That the experimental and the theoretical results tallied so well, is owing to the fact that $MgO:Fe^{2+}$ is a case of comparatively weak Jahn-Teller coupling so that the induced quadrupole effects are negligible at field strengths of the order of 50 kOe at which the experiments were done. But the expression for ΔE_Q given by Ham, Schwarz, and O'Brien[5] might not be true for the cases of $KMgF_3:Fe^{2+}$ and $CaO:Fe^{2+}$ where a survey of available experimental results indicates that in these systems the spin-orbit coupling parameter $|\lambda|$ undergoes a reduction much larger than that in MgO.[7] Since a Zeeman field of the order of 50 kOe would correspond to about 8 cm^{-1} for the Fe^{2+} ion, the ihf and iq interactions might be as important as the phf and pq interactions in these systems. Hence only by extending the Ham et al. theory to include such induced effects, could one hope to correctly deduce the Ham reduction factors from the Mössbauer studies in these systems.

In Sec. II we develop the effective Hamiltonian for the field-induced nuclear quadrupole and hyper-fine interaction and calculate by perturbation theory the parameters of this effective Hamiltonian for the lowest spin-orbit triplet ($J=1$) of Fe^{2+} in octahedral symmetry. Terms linear in H have only been calculated. The advantages of using the effective-Hamiltonian formalism is that it can be used for any relative values of the field and the thermal energy and the vibronic coupling can be introduced without much complications. In Sec. III we derive the explicit expressions for the quadrupole splitting and the hyperfine field that are observed in the Mössbauer transitions of Fe^{2+} in octahedral symmetry with the external magnetic field parallel to the direction of propagation of the γ rays. It is shown how from the study of these spectra for different magnitudes and orientations (with respect to the crystal axes) of the field, one can deduce the field independent ΔE_Q and H_{hf}, and how from these values one can derive useful information about the Ham reduction factors and the nature of the vibronic coupling of the spin-orbit states. In Sec. IV, we discuss the general implications of these theoretical results for different Jahn-Teller systems.

II. EFFECTIVE ELECTRON NUCLEAR HAMILTONIAN IN THE PRESENCE OF THE ZEEMAN FIELD FOR Fe^{2+} ION IN OCTAHEDRAL SYMMETRY

In an octahedral crystal field the ground term ^5D of the Fe^{2+} ion splits into an orbital triplet $^5T_{2g}$ and an orbital doublet ^5E_g lying at about 10100 cm^{-1} above the ground triplet[8] (Fig. 1). The spin-orbit interaction splits the ground orbital triplet into a ground spin-orbit triplet Γ_{5g} with a doublet Γ_{3g} and a triplet Γ_{4g} lying at an energy -2λ above it. Higher above, at -5λ, lie a singlet Γ_{1g} and two triplets Γ_{4g} and Γ_{5g}. In the presence of the vibronic coupling between the triplet $^5T_{2g}$ and the E_g and T_{2g} modes of vibration of the molecular complex formed by the impurity ion and the surrounding ligand ions, these spin-orbit-level splittings would, in general, be more complicated. The exact nature of the vibronic spin-orbit levels can be known only by solving the total matrix $\langle |\mathcal{H}_{vib} + \mathcal{H}_{s.o.}| \rangle$ within the orbital $^5T_{2g}$ manifold. In the particular cases treated here, the s.o. splittings are much smaller than the effective frequency of vibration of the molecular complex which is usually of the order of the optical phonon frequency of the host crystal,[9] so that it might be argued that the ground and the excited vibronic s.o. levels would still be of Γ_{5g}, and Γ_{3g} and Γ_{4g} characters respectively—these latter now being the s.o. orbit states coupled to phonon states. Higher excited levels are not considered

because for the external magnetic-field strength under consideration, they are expected to have negligible mixing with the ground triplet Γ_{5g}. To

$$\mathcal{H}_{hf} = \mathcal{H}_{hf}^{(orbital)} + \mathcal{H}_{hf}^{(dipolar)} + \mathcal{H}_{hf}^{(contact)}$$

$$= -2\mu_B \mu_N g_N \langle r^{-3}\rangle_{3d} \left[(\vec{l}\cdot\vec{I}) - 9\xi \left(\sum_i l_2(\Gamma_3^i)(I,S)_2(\Gamma_3^i) - \sum_i l_2(\Gamma_5^i)(I,S)_2(\Gamma_5^i) \right) - k\vec{S}\cdot\vec{I} \right], \tag{1}$$

$$= 2\mu_B \mu_N g_N \langle r^{-3}\rangle_{3d} \left((\vec{l}\cdot\vec{I}) - 9\xi \sum_i \{\sqrt{\tfrac{2}{3}}[l_2(\Gamma_3)S(\Gamma_4)]_3(\Gamma_4^i) - [l_2(\Gamma_5)S(\Gamma_4)]_3(\Gamma_4^i)\} I(\Gamma_4^i) - k\vec{S}\cdot\vec{I} \right). \tag{2}$$

In the second form, the nuclear and the electron operators are separated and this form would be used in our perturbation calculations later. μ_B, μ_N, and g_N are the Bohr magneton, nuclear magneton, and the nuclear Landé factor, respectively. $l = 1$ is the effective orbital quantum number describing the orbital triplet T_{2g} whose real L is 2. $\xi = -\frac{1}{42}$ for Fe^{2+} ion and k is the strength of the contact interaction, $l_2(\Gamma_\alpha^i)$ and $(I,S)_2(\Gamma_\alpha^i)$ are the second rank tensor operators transforming as the ith component of the Γ_α representation as has been defined in Ref. 10.

$$\mathcal{H}_{pure\,quadrupole} = -\tfrac{1}{7}e^2 Q\langle r^{-3}\rangle_{3d} \left(\sum_i l_2(\Gamma_3^i)l_2(\Gamma_3^i) - 3\sum_i l_2(\Gamma_5^i)l_2(\Gamma_5^i) \right). \tag{3}$$
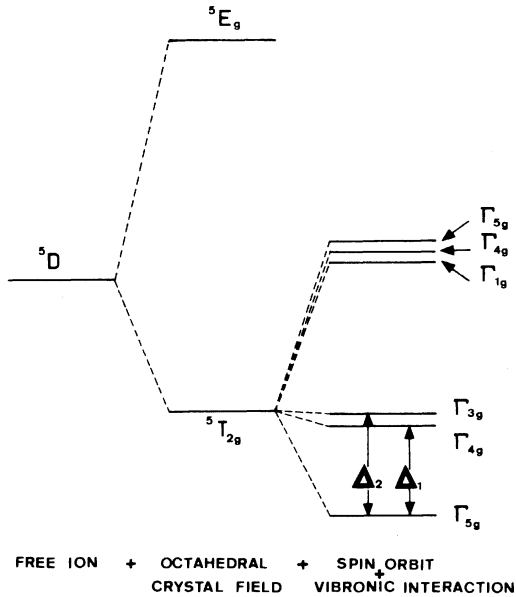

FIG. 1. Schematic diagram of the splitting of the ^5D term of Fe^{2+} in octahedral symmetry in a dynamic crystal-field model.

study the hyperfine and quadrupole splittings of the Fe^{2+} Mössbauer spectra, we have to consider the following basic interactions [Eqs. (1)-(5)]:

$$\mathcal{H}_{Zeeman} = \mu_B \vec{H}\cdot(-\vec{l}+2\vec{S}), \tag{4}$$

$$\mathcal{H}_{nuclear\,Zeeman} = -\mu_N g_N \vec{H}\cdot\vec{I}. \tag{5}$$

The first- and all higher-order effects of these basic interactions on the ground triplet Γ_{5g} can be equivalently treated by describing an effective electron nuclear Hamiltonian for this level. The effective-Hamiltonian formalism is very suitable for spectroscopic analysis as is well known in the case of the spin Hamiltonian[11] for EPR studies. For any general value of $\vec{J}$, the effective quantum number describing the ground spin-orbit level and $\vec{I}$, the nuclear spin the effective electron nuclear Hamiltonian in the presence of an external magnetic field $\vec{H}$ can be written in the following general form[12]:

$$\mathcal{H}_{eff} = \sum_{\substack{n_1,\alpha;n_2,\beta;\\n_3,\gamma}} const\,(n_1,\alpha;n_2,\beta;n_3,\gamma)$$

$$\times \sum_{i,j,k} const\,(i,j,k)$$

$$\times [J_{n_1}(\Gamma_\alpha^i)\,I_{n_2}(\Gamma_\beta^j)\,H_{n_3}(\Gamma_\gamma^k)](\Gamma_1). \tag{6}$$

The primary requisite that the Hamiltonian of any impurity ion is invariant with respect to all operations of the point-group symmetry of the host matrix as well as with respect to time reversal, has been used to decompose the electron nuclear Hamiltonian as above, in terms of the basic operators $\vec{J},\vec{I}$, and $\vec{H}$. J_{n_1}, I_{n_2}, and H_{n_3} denote tensor operators built of J, I, and H of ranks n_1, n_2, and n_3, respectively.

Individually, J_{n_1}, I_{n_2}, and H_{n_3} can belong to the Γ_α, Γ_β, and Γ_γ representations, respectively, of the point group—more precisely, corresponding to the ith, jth and kth components of these respective representations, such that the product $\Gamma_\alpha^i \times \Gamma_\beta^j \times \Gamma_\gamma^k$ is always the identity representation Γ_1. The ranks of the tensors n_1, n_2, and n_3 are limited and determined by two factors: (i) n_1 and n_2 are limited to the maximum values of $2J$

and $2I$, respectively, because for operators of orders higher than these, the matrix elements would be zero. n_3, on the other hand, is limited from the consideration of the particular problem being studied, which in our case is either 0 or 1 as we are here interested in the field-independent

and the linearly field-dependent hyperfine interactions. (ii) The invariance of the total Hamiltonian with respect to time reversal imposes the additional condition that $n_1 + n_2 + n_3$ always be even. For cubic symmetry this general expression of $\mathcal{H}_{eff}$ can be reduced to the following form:

$$\mathcal{H}_{eff} = \mu_B g_J \vec{J} \cdot \vec{H} + B_J \vec{J} \cdot \vec{I} + \left(P_3 \sum_i J_2(\Gamma_3^i) I_2(\Gamma_3^i) + P_5 \sum_i J_2(\Gamma_5^i) I_2(\Gamma_5^i) \right)$$

$$+ \left(R_3 \sum_i (J, H)_2(\Gamma_3^i) I_2(\Gamma_3^i) + R_5 \sum_i (J, H)_2(\Gamma_5^i) I_2(\Gamma_5^i) \right)$$

$$+ \left(T_0(I, H)_0(\Gamma_1) + T_3 \sum_i (I, H)_2(\Gamma_3^i) J_2(\Gamma_3^i) + T_5 \sum_i (I, H)_2(\Gamma_5^i) J_2(\Gamma_5^i) \right) - \mu_N g_N \vec{I} \cdot \vec{H}, \tag{7}$$

$$= \mathcal{H}_Z' + \mathcal{H}_{HF}' + \mathcal{H}_{PQ}' + \mathcal{H}_{IQ}' + \mathcal{H}_{NZ}'^{(2)} + \mathcal{H}_{IHF}' + \mathcal{H}_{NZ}'^{(1)} . \tag{8}$$

The first two terms are, respectively, the electronic Zeeman ($\mathcal{H}_Z'$) and the hyperfine interaction ($\mathcal{H}_{HF}'$) terms where the constants are written in the conventional form.[1] The first term on the right-hand side in large parentheses represents the pure quadrupole interaction ($\mathcal{H}_{PQ}'$), whereas the next one is the Zeeman-field–induced quadrupole interaction ($\mathcal{H}_{IQ}'$). In the third term in large parentheses the first term associated with T_0 is of the form of the direct nuclear Zeeman interaction ($\mathcal{H}_{NZ}'$) given by the last term. This is, in effect, a second-order contribution ($\mathcal{H}_{NZ}^{(2)}$) to the nuclear Zeeman interaction due to the real electron Zeeman ($\mathcal{H}_Z$) and hyperfine interactions ($\mathcal{H}_{hf}$) and this would be shown to have an important isotropic contribution to the hyperfine splitting of the Mössbauer transitions. On the contrary, no such second-order term in the electron Zeeman interaction has been taken into account because though such a term could arise owing to the second-order perturbation of the nuclear Zeeman ($\mathcal{H}_{NZ}$) and hyperfine interactions ($\mathcal{H}_{hf}$) its magnitude would be comparatively negligible. The two terms associated with T_3 and T_5 in the third expression in large parentheses obviously give the

field-induced hyperfine interactions ($\mathcal{H}_{IHF}'$) and this would give rise to an anisotropic contribution to the hyperfine splitting.

We shall now evaluate the constants of this effective Hamiltonian $\mathcal{H}_{eff}$ in terms of the parameters of the true electron and nuclear interactions defined in Eqs. (1)–(5). For this, we shall consider higher-order mixing of the excited vibronic s.o. levels T_{3g} and T_{4g} with the ground one (Γ_{5g}) due to these true interactions. We first define all possible reduction factors[5] of different electronic operators between the vibronic s.o. levels of Fe^{2+} involved in these calculations. These reduction factors indicate the degree of quenching of the different electronic operators in the spin-orbit states owing to the dynamic Jahn-Teller effect. Such calculations were first done by Ham[13] in an orbital triplet state which were extended by Ham, Schwarz, and O'Brien[5] to the case of the ground spin-orbit states of Fe^{2+}. Further extension has been done in the present work where the perturbation calculations involve excited spin-orbit states — thus making it necessary to define the quenching or the reduction factors in both the ground and the excited spin-orbit states.

The reduction factors within the ground vibronic s.o. triplet Γ_{5g}:

$$K_L(5,5) = i \langle \psi(\Gamma_5^1) | l_z | \psi(\Gamma_5^2) \rangle, \quad K_S(5,5) = i \langle \psi(\Gamma_5^1) | S_z | \psi(\Gamma_5^2) \rangle,$$

$$K_E(5,5) = -\tfrac{\sqrt{3}}{2} \langle \psi(\Gamma_5^3) | l_2(\Gamma_3^1) | \psi(\Gamma_5^3) \rangle, \quad K_{T_2}(5,5) = -\sqrt{2} \langle \psi(\Gamma_5^1) | l_2(\Gamma_5^3) | \psi(\Gamma_5^2) \rangle,$$

$$K_A(5,5) = i \sqrt{\tfrac{2}{3}} \langle \psi(\Gamma_5^1) | [l_2(\Gamma_3) S(\Gamma_4)]_3(\Gamma_4^3) | \psi(\Gamma_5^2) \rangle, \tag{9}$$

$$K_B(5,5) = i \langle \psi(\Gamma_5^1) | [l_2(\Gamma_5) S(\Gamma_4)]_3(\Gamma_4^3) | \psi(\Gamma_5^2) \rangle.$$

The reduction factors between the ground Γ_{5g} and the excited Γ_{3g}:

$$K_L(5,3) = i \langle \psi(\Gamma_5^3) | l_z | \psi(\Gamma_3^2) \rangle, \quad K_S(5,3) = i \langle \psi(\Gamma_5^3) | S_z | \psi(\Gamma_3^2) \rangle,$$

$$K_E(5,3) = 0, \quad K_{T_2}(5,3) = -\sqrt{2} \langle \psi(\Gamma_5^1) | l_2(\Gamma_5^1) | \psi(\Gamma_3^2) \rangle,$$

$$K_A(5,3) = i \sqrt{\tfrac{2}{3}} \langle \psi(\Gamma_5^3) | [l_2(\Gamma_3) S(\Gamma_4)]_3(\Gamma_4^3) | \psi(\Gamma_3^2) \rangle . \tag{10}$$

$$K_B(5,3) = i \langle \psi(\Gamma_5^3) | [l_2(\Gamma_5) S(\Gamma_4)]_3(\Gamma_4^3) | \psi(\Gamma_3^2) \rangle.$$

Similarly between the ground T_{5g} and the excited T_{4g}, these are:

$$K_L(5,4) = i \langle \psi(\Gamma_5^1) | l_z | \psi(\Gamma_4^2) \rangle, \quad K_S(5,4) = i \langle \psi(\Gamma_5^1) | S_z | \psi(\Gamma_4^2) \rangle,$$

$$K_E(5,4) = -\sqrt{\tfrac{3}{2}} \langle \psi(\Gamma_5^1) | l_2(\Gamma_3^1) | \psi(\Gamma_4^1) \rangle, \quad K_{T_2}(5,4) = -\sqrt{2} \langle \psi(\Gamma_5^1) | l_2(\Gamma_5^3) | \psi(\Gamma_4^2) \rangle, \tag{11}$$

$$K_A(5,4) = i \sqrt{\tfrac{2}{3}} \langle \psi(\Gamma_5^1) | [l_2(\Gamma_3) S(\Gamma_4)]_3(\Gamma_4^3) | \psi(\Gamma_4^2) \rangle, \quad K_B(5,4) = i \langle \psi(\Gamma_5^1) | [l_2(\Gamma_5) S(\Gamma_4)]_3(\Gamma_4^1) | \psi(\Gamma_4^2) \rangle.$$

In the effective Hamiltonian $\mathcal{H}_{\text{eff}}$ [Eq. (8)], the electron Zeeman ($\mathcal{H}_Z'$), the hyperfine ($\mathcal{H}_{\text{HF}}'$) and the pure quadrupole ($\mathcal{H}_{\text{PQ}}'$) interactions are all first-order terms and for these within the ground manifold we have the following equivalent relationship:

$$\langle \phi_i(\Gamma_5) | \mathcal{H}' | \phi_j(\Gamma_5) \rangle \equiv \langle \psi_i(\Gamma_5) | \mathcal{H} | \psi_j(\Gamma_5) \rangle. \tag{12}$$

where $\mathcal{H}$ is the corresponding true interaction term defined in Eqs. (1)–(5). It should be noted that on the left-hand side of Eq. 12 the matrix elements of the effective Hamiltonian are to be evaluated between the states ϕ's characterized by the effective quantum number $\vec{J}$ which in our case is 1. These are given by

$$\phi(\Gamma_5^1) = -\tfrac{1}{2}(|11\rangle - |1-1\rangle),$$

$$\phi(\Gamma_5^2) = (i/\sqrt{2})(|11\rangle + |1-1\rangle), \tag{13}$$

$$\phi(\Gamma_5^3) = |10\rangle.$$

On the right-hand side of Eqs. (13) the matrix elements of the true Hamiltonian are always with respect to the true vibronic s.o. states. Using this equivalence and the above definitions of the matrix elements we get the following relations for the effective Hamiltonian parameters:

$$g_J = -K_L(5,5) + 2K_S(5,5),$$

$$B_J = -2\mu_B\mu_N g_N \langle r^{-3} \rangle_{3d}$$
$$\times [K_L(5,5) - kK_S(5,5) + \tfrac{3}{14}K_A(5,5) - \tfrac{3}{14}K_B(5,5)],$$

$$P_3 = -\tfrac{1}{7} e^2 Q \langle r^{-3} \rangle_{3d} K_E(5,5), \tag{14}$$

and

$$P_5 = \tfrac{1}{7} e^2 Q \langle r^{-3} \rangle_{3d} K_{T_2}(5,5).$$

The evaluation of the constants of the effective Hamiltonians $\mathcal{H}_{\text{IQ}}'$, $\mathcal{H}_{NZ}'^{(2)}$ and $\mathcal{H}_{\text{IHF}}'$, on the other hand, involve second-order perturbation calculations due to the mixing of the excited Γ_{3g} and Γ_{4g} levels with the ground Γ_{5g} by the external magnetic field. For example, let us take the case of the induced quadrupole Hamiltonian which is given by

$$\mathcal{H}_{\text{IQ}}' = R_3 \sum_i (J,H)_2(\Gamma_3^i) I_2(\Gamma_3^i)$$
$$+ R_5 \sum_i (J,H)_2(\Gamma_5^i) I_2(\Gamma_5^i). \tag{15}$$

When the field is along the [001] direction, this simplifies in to

$$\mathcal{H}_{\text{IQ}}' = R_3 \sqrt{\tfrac{2}{3}} J_Z H_Z I_2(\Gamma_3^1)$$
$$+ R_5 \sqrt{\tfrac{1}{2}} [J_Y H_Z I_2(\Gamma_5^1) + J_X H_Z I_2(\Gamma_5^2)], \tag{16}$$

so that within the ground triplet $J=1$, we have

$$\langle \phi(\Gamma_5^1) | \mathcal{H}_{\text{IQ}}' | \phi(\Gamma_5^2) \rangle = -\sqrt{\tfrac{2}{3}} R_3 i H_Z I_2(\Gamma_3^1),$$
$$\langle \phi(\Gamma_5^1) | \mathcal{H}_{\text{IQ}}' | \phi(\Gamma_5^3) \rangle = \sqrt{\tfrac{1}{2}} R_5 i H_Z I_2(\Gamma_5^1). \tag{17}$$

To evaluate R_3 and R_5 we have to use the following equivalence with the second-order energies owing to the real interactions $\mathcal{H}_Z$ and $\mathcal{H}_{pq}$:

$$\langle \phi(\Gamma_5^1) | \mathcal{H}_{\text{IQ}}' | \phi(\Gamma_5^2) \rangle = -\sum_n \frac{1}{\Delta_n} \langle \psi(\Gamma_5^1) | \mathcal{H}_Z | \psi_n \rangle$$
$$\times \langle \psi_n | \mathcal{H}_{\text{Pq}} | \psi(\Gamma_5^2) \rangle, \tag{18}$$

where Δ_n is the energy separation between the ground and the excited levels. Now the right-hand side is

$$-(1/\Delta_1)[\langle \psi(\Gamma_5^1) | \mathcal{H}_Z(\Gamma_4^3) | \psi(\Gamma_4^2) \rangle \langle \psi(\Gamma_4^2) | \mathcal{H}_{hq}(\Gamma_3^1) | \psi(\Gamma_5^2) \rangle + \langle \psi(\Gamma_5^1) | \mathcal{H}_{hq}(\Gamma_3^1) | \psi(\Gamma_4^1) \rangle \langle \psi(\Gamma_4^1) | \mathcal{H}_Z(\Gamma_4^3) | \psi(\Gamma_5^2) \rangle]$$

$$= (2\sqrt{2}/7\sqrt{3})(i/\Delta_1)\mu_B H_Z e^2 Q \langle r^{-3} \rangle_{3d} K_E(5,4)[K_L(5,4) - 2K_S(5,4)] I_2(\Gamma_3^1). \tag{19}$$

Equating this with Eq. (17), we have

$$R_3 = \frac{2}{7} \frac{\mu_B e^2 Q \langle r^{-3} \rangle_{3d}}{\Delta_1} K_E(5,4)[-K_L(5,4) + 2K_S(5,4)]. \tag{20}$$

Similarly

$$R_5 = \tfrac{1}{7}(\mu_B e^2 Q \langle r^{-3} \rangle_{3d})\{(\Delta_1)^{-1} K_{T_2}(5,4)[-K_L(5,4) + 2K_S(5,4)] + (\Delta_2)^{-1} K_{T_2}(5,3)[-K_L(5,3) + 2K_S(5,3)]\}. \tag{21}$$

Similarly for the effective Hamiltonians $\mathcal{H}_{NZ}'^{(2)}$ and $\mathcal{H}_{ihf}'$, we derive:

$$T_0 = \tfrac{1}{3}(4\mu_B^2\mu_N g_N \langle r^{-3}\rangle_{3d})((\Delta_1)^{-1}[-K_L(5,4)+2K_S(5,4)]\{K_L(5,4)-kK_S(5,4)+\tfrac{3}{14}[K_A(5,4)-K_B(5,4)]\} \tag{22}$$

$$+2(\Delta_2)^{-1}[-K_L(5,3)+2K_S(5,3)]\{K_L(5,3)-kK_S(5,3)+\tfrac{3}{14}[K_A(5,3)-K_B(5,3)]\}),$$

$$T_3 = 8\mu_B^2\mu_N g_N \langle r^{-3}\rangle_{3d}((\Delta_1)^{-1}[-K_L(5,4)+2K_S(5,4)]\{K_L(5,4)-kK_S(5,4)+\tfrac{3}{14}[K_A(5,4)-K_B(5,4)]\}$$

$$-(\Delta_2)^{-1}[-K_L(5,3)+2K_S(5,3)]\{K_L(5,3)-kK_S(5,3)+\tfrac{3}{14}[K_A(5,3)-K_B(5,3)]\}), \tag{23}$$

and

$$T_5 = -2\mu_B^2\mu_N g_N\langle r^{-3}\rangle_{3d}(2(\Delta_1)^{-1}[-K_L(5,4)+2K_S(5,4)]\{K_L(5,4)-kK_S(5,4)+\tfrac{3}{14}[K_A(5,4)-K_B(5,4)]\}$$

$$-(\Delta_2)^{-1}[-K_L(5,3)+2K_S(5,3)]\{K_L(5,3)-kK_S(5,3)+\tfrac{3}{14}[K_A(5,3)-K_B(5,3)]\}). \tag{24}$$

The next logical step would be to evaluate the reduction factors, i.e., the matrix elements of the different electronic operators within the real vibronic s.o. states. This is, in general, a very complex problem for any arbitrary strength of $\mathcal{H}_{vib}$ and $\mathcal{H}_{s.o.}$. We shall discuss this in the following paper[17] in the background of the analysis of experimental results.

III. THEORETICAL EXPRESSIONS FOR THE MÖSSBAUER TRANSITIONS IN Fe^{2+} IN OCTAHEDRAL SYMMETRY

The effective Hamiltonian for the $\tilde{J}=1$ ground level of the Fe^{2+} ion given by Eq. (7) is described in the crystal axis system. To study the Mössbauer spectra with different orientations of the Zeeman field, it is convenient to transform this

Hamiltonian to a coordinate axis system whose Z axis is given by the Zeeman-field direction. Using the rotation-group matrix elements $D_1^{m,m'}$ between the two sets of axes we can write

$$J_2(\Gamma_\alpha^i) = \sum_\mu D_2^{\Gamma_\alpha^i,\mu} J_2^\mu$$

$$I_2(\Gamma_\alpha^i) = \sum_{\mu'} D_2^{\Gamma_\alpha^i,\mu'} I_2^{\mu'}, \quad \text{etc.}, \tag{25}$$

where the left-hand side operators are in the crystal axis system and those on the right-hand side are in the field axis system. As the Zeeman field quantizes J along the field direction, we shall have $\mu=\mu'=0$. Thus in the field axis system the effective Hamiltonian of Eq. (7) would be transformed as follows:

$$\mathcal{H}_{eff} = \mu_B g_J J_Z H + B_J J_Z I_Z + J_2^0 I_2^0 \left(P_3 \sum_i D_2^{\Gamma\frac{i}{3},0} D_2^{\Gamma\frac{i}{3},0} + P_5 \sum_i D_2^{\Gamma\frac{i}{5},0} D_2^{\Gamma\frac{i}{5},0} \right)$$

$$+(J,H)_2^0 I_2^0 \left(R_3 \sum_i D_2^{\Gamma\frac{i}{3},0} D_2^{\Gamma\frac{i}{3},0} + R_5 \sum_i D_2^{\Gamma\frac{i}{5},0} D_2^{\Gamma\frac{i}{5},0} \right)$$

$$+T_0 I_Z H + (I,H)_2^0 J_2^0 \left(T_3 \sum_i D_2^{\Gamma\frac{i}{3},0} D_2^{\Gamma\frac{i}{3},0} + T_5 \sum_i D_2^{\Gamma\frac{i}{5},0} D_2^{\Gamma\frac{i}{5},0} \right) - \mu_N g_N I_Z H. \tag{26}$$

In terms of the direction cosines l, m, and n of the field $\vec{H}$ with respect to the crystal axes, we have

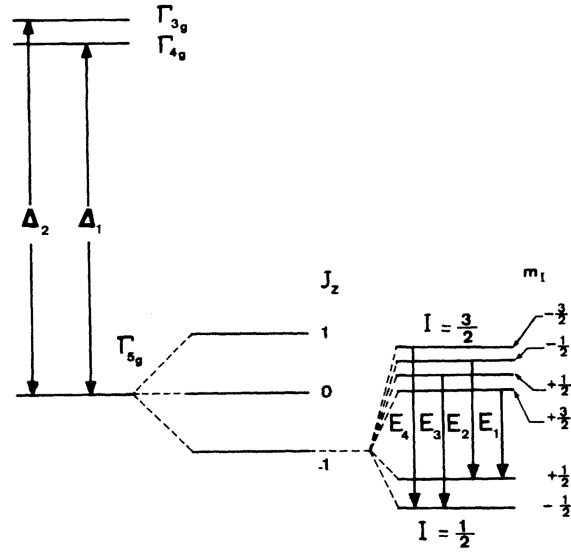$$\sum_i D_2^{\Gamma\frac{i}{3},0} D_2^{\Gamma\frac{i}{3},0} = 1 - 3(l^2 m^2 + m^2 n^2 + n^2 l^2)$$

and

$$\sum_i D_2^{\Gamma\frac{i}{5},0} D_2^{\Gamma\frac{i}{5},0} = 3(l^2 m^2 + m^2 n^2 + n^2 l^2). \tag{27}$$

Also we have

$$J_2^0 = (1/\sqrt{6})[3J_Z^2 - J(J+1)], \quad \text{etc.} \tag{28}$$

So that, putting $\delta = 3(l^2 m^2 + m^2 n^2 + n^2 l^2)$, we get

$$\mathcal{H}_{eff} = \mu_B g_J J_Z H + B_J J_Z I_Z + \tfrac{1}{6}(3J_Z^2 - 2)[3I_Z^2 - I(I+1)][P_3(1-\delta)+P_5\delta]$$

$$+\tfrac{1}{3}(J_Z H)[3I_Z^2 - I(I+1)][R_3(1-\delta)+R_5\delta] + T_0 I_Z H + \tfrac{1}{3}(3J_Z^2 - 2)I_Z H[T_3(1-\delta)+T_5\delta] - \mu_N g_N I_Z H. \tag{29}$$

FIG. 2. Schematic diagram of the Mössbauer transitions associated with the $J_Z = -1$ level of the lowest vibronic s.o. level of the Fe^{2+} ion in octahedral symmetry.

The Zeeman field splits the $\vec{J} = 1$ triplet into three singlets of which $J_Z = -1$ is the ground one (Fig. 2) and at temperatures $\sim 4.2\,°K$, only this level would be populated. The effective nuclear Hamiltonian within this $J_Z = -1$ level can be written down from the above equation as

$$\mathcal{H}_N = -\mu_B g H - B I_z + \tfrac{1}{6}[3I_z^2 - I(I+1)][P_3(1-\delta) + P_5\delta]$$
$$- \tfrac{1}{3}H[3I_z^2 - I(I+1)][R_3(1-\delta) + R_5\delta]$$
$$+ T_0 I_z H + \tfrac{1}{3}I_z H[T_3(1-\delta) + T_5\delta] - \mu_N g_N I_z H .$$

(30)

In this equation B, T_0, T_3, and T_5 are proportional to $\mu_N g_N$ as given by Eq. (14) and (22)–(24). Thus defining the magnetic field at the nucleus

$$H_N = H_{hf} + H$$

(31)

and putting

$$B = \mu_N g_N b , \quad T_0 = \mu_N g_N t_0 ,$$
$$T_3 = \mu_N g_N t_3 , \quad and \quad T_5 = \mu_N g_N t_5 ,$$

(32)

we get

$$\mathcal{H}_N = -\mu_B g H_0 - \mu_N g_N (H_{hf} + H) I_z$$
$$+ \tfrac{1}{6}[3I_z^2 - I(I+1)][P_3(1-\delta) + P_5\delta]$$
$$+ \tfrac{1}{3}[3I_z^2 - I(I+1)][R_3(1-\delta) + R_5\delta]H ,$$

(33)

where

$$H_{hf} = b - t_0 H - \tfrac{1}{3}[t_3(1-\delta) + t_5\delta]H .$$

(34)

Denoting the four nuclear transitions

$$|\tfrac{3}{2}, \tfrac{3}{2}\rangle \rightarrow |\tfrac{1}{2}, \tfrac{1}{2}\rangle , \quad |\tfrac{3}{2}, -\tfrac{1}{2}\rangle \rightarrow |\tfrac{1}{2}, \tfrac{1}{2}\rangle ,$$
$$|\tfrac{3}{2}, \tfrac{1}{2}\rangle \rightarrow |\tfrac{1}{2}, \tfrac{1}{2}\rangle , \quad and \quad |\tfrac{3}{2}, -\tfrac{3}{2}\rangle \rightarrow |\tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

that would be observed in a Mössbauer spectroscopic setup with the external magnetic field aligned in the direction of propagation of the γ rays by E_1, E_2, E_3, and E_4, respectively; the quadrupole splitting will be given by

$$\Delta E_Q = (E_1 + E_4) - (E_2 + E_3)$$
$$= 2[P_3(1-\delta) + P_5\delta] - 4[R_3(1-\delta) + R_5\delta]H .$$

(35)

The hyperfine field which has been defined by Eq. (34) will be given by

$$H_{hf} = (E_4 - E_1)/\mu_N(3g_N' - g_N) - H ,$$

(36)

where g_N' and g_N correspond to the excited $(I = \tfrac{3}{2})$ and the ground $(I = \tfrac{1}{2})$ nuclear levels.

In Table I, we give the expressions of ΔE_Q and H_{hf} for two orientations of the magnetic field $\vec{H}$, one along the [100] and the other along the [111] crystal axes. The main points to be noted are:

(i) The E_Q vs H graphs for the two different orientations of the field would be linear below a certain value of the field which would depend on the strength of the Jahn-Teller coupling within the system being studied. The extrapolated value of ΔE_Q at $H \rightarrow 0$ would give the pure quadrupole splitting expected within the $J_Z = -1$ state of the unmixed Γ_{5g} triplet of Fe^{2+}. For $\vec{H} \parallel [100]$ and $\vec{H} \parallel [111]$ these values are given by $2P_3$ and $2P_5$, respectively. The gradients of the linear parts of the ΔE_Q vs H graphs are given by $4R_3$ and $4R_5$, respectively, for the two orientations of H.

Using Eqs. (14), (20), and (23), the ratio of $\Delta E_Q|_{[100]}$ and $\Delta E_Q|_{[111]}$ for any value of H can be written down as

$$\frac{\Delta E_Q|_{[100]}}{\Delta E_Q|_{[111]}} = \frac{-K_E(5,5) - (4/\Delta_1)\mu_B H K_E(5,4)[-K_L(5,4) + 2K_S(5,4)]}{K_{T_2}(5,5) - (4/\Delta_1)\mu_B H K_{T_2}(5,4)[-K_L(5,4) + 2K_S(5,4)]} ,$$

where assumptions have been made that the Γ_{4g} and Γ_{3g} levels are degenerate, i.e., $\Delta_1 = \Delta_2$ and the reduction factors between the Γ_{5g} and Γ_{3g} levels [Eq. (10)] are equal to these calculated be-

tween the Γ_{5g} and Γ_{4g} levels [Eq. (11)]. The above ratio tends to the expression given by Ham, Schwartz, and O'Brien[5] for $MgO:Fe^{2+}$ where the field-dependent part is not important.

TABLE I. Theoretical expressions for the quadrupole splitting and hyperfine field for different orientations of the Zeeman field.

Magnetic field H oriented along	Quadrupole splitting ΔE_Q	Hyperfine field H_{hf} isotropic part	anisotropic part
[100] axis	$2P_3 - 4R_3H$	$b - t_0H$	$-\frac{1}{3}t_3H$
[111] axis	$2P_5 - 4R_5H$	$b - t_0H$	$-\frac{1}{3}t_5H$

(ii) Similarly from the H_{hf} vs H graphs, if one remains in the linearly field-dependent region, one can get the extrapolated value of H_{hf} at $H \to 0$ which would give the value of the hyperfine coupling constant b. From the gradients of the two curves we would get an estimate of $(t_0 + \frac{1}{3}t_3)$ and $(t_0 + \frac{1}{3}t_5)$, respectively. Any significant anisotropy in H_{hf} can be attributed to the difference in t_3 and t_5.

Thus from a study of the Mössbauer spectra with different magnitudes and orientations of the Zeeman field, precise determinations of the parameters of P_3, P_5, R_3, R_5, etc., are possible. From P_3 and P_5 we would obtain the Ham reduction factors $K_E(5, 5)$ and $K_{T_2}(5, 5)$. From R_3, R_5, t_0, t_3, and t_5 we should be able to get an idea of the relative values of the Ham reduction factors between the Γ_{5g} and Γ_{3g} and Γ_{4g} states. This will be discussed in more details in the following paper in connection with the analysis of the experimental results.

IV. DISCUSSION

The quadrupole splitting in the limit $H \to 0$ that we have discussed in the previous sections corresponds to the interaction between the $J_z = -1$ electronic level and the nuclear quadrupole moment. On the other hand, the quadrupole splitting that is observed in these cubic systems at low temperatures in the absence of any external magnetic field has been shown to be due to the strain-field splitting[2,6,14,15] of the Γ_{5g} ground level. In this case, each strain split level contributes individually to the quadrupole splitting and the net effect is the sum total of all the three. A comparison between $\Delta E_Q|_{H=0}$, i.e., E_Q in the absence of any external

field and $\Delta E_Q|_{H \to 0}$, i.e., ΔE_Q extrapolated to $H \to 0$ in the presence of the Zeeman field, might give some information about the magnitude of the strain field.

The Ham reduction factors $K_E(5, 5)$, $K_E(5, 4)$, etc., in Eqs. (9)–(11) are defined between vibronic (s.o.) states and these could be, in principle, related to the orbital reduction factors K_E, K_{T_2}, K_{T_1}, etc., by specific model calculations for any particular system. In the next paper, we shall discuss the limiting values of these factors for the case of strong Jahn-Teller coupling under certain approximations. In general, however, numerical procedure would be necessary to explain these reduction parameters.

We have developed the above analysis for the case of the triplet orbital of Fe^{2+} ion. It would be interesting to extend it to the case of the Fe^{2+} ion in eight-fold cubic symmetry like CaF_2 or in tetrahedral symmetry like[16] ZnS, where the orbital doublet (E) is lowest. The spin-orbit level splitting of this doublet is caused by higher-order spin-orbit effects involving the excited vibronic levels and the excited triplet (T_2), thus leading to small s.o. level separations. The pure quadrupole interaction would be zero for the ground vibronic (s.o.) (Γ_1), and it would be interesting to see if the induced quadrupole interaction due to the mixing of the excited levels with the ground one is important in these systems.

The case of Kramers ions in cubic systems like CaO:Fe^+, YSb:Dy^{3+}, etc., would be similar, where the pure quadrupole interaction for the ground s.o. level would be zero; but the induced effect might be brought into play by a suitable choice of temperature and external magnetic field.

[1]B. Bleaney, *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967).

[2]F. S. Ham, Phys. Rev. 160, 328 (1967).

[3]U. Ganiel and S. Shtrikman, Phys. Rev. 167, 258 (1968).

[4]M. N. Ghatikar, Proc. Phys. Soc. Lond. 87, 727 (1966).

[5]F. S. Ham, W. M. Schwarz, and M. C. M. O'Brien, Phys. Rev. 185, 548 (1969).

[6]H. R. Leider and D. N. Pipkorn, Phys. Rev. 165, 494 (1968).

[7]T. Ray, J. R. Regnard, J. M. Laurent, and A. Ribeyron, Solid State Commun. 13, 1959 (1973); R. Weber and V. Dürr (private communication); E. L. Wilkinson, Phys. Rev. B 6, 2517 (1972); J. R. Regnard, J. Chappert, and A. Ribeyron, Solid State Commun. 15, 1539 (1974).

[8]W. Low and M. Weger, Phys. Rev. <u>118</u>, 1119 (1960).

[9]T. Ray, D. K. Ray, and M. J. L. Sangster, Solid State Commun. (to be published).

[10]T. Ray and J. R. Regnard, Phys. Rev. B <u>9</u>, 2110 (1974).

[11]B. Bleaney and K. W. H. Stevens, Rep. Prog. Phys. <u>16</u>, 109 (1953).

[12]T. Ray, Proc. R. Soc. A <u>277</u>, 76 (1964).

[13]F. S. Ham, Phys. Rev. A <u>138</u>, 1727 (1965).

[14]R. B. Frankel, J. Chappert, J. R. Regnard, A. Misetich, and C. R. Abeledo, Phys. Rev. B <u>5</u>, 2469 (1972).

[15]J. R. Regnard, Solid State Commun. <u>12</u>, 207 (1973).

[16]J. T. Vallier, G. A. Slack, and C. C. Bradley, Phys. Rev. B <u>2</u>, 4406 (1970).

[17]J. R. Regnard and T. Ray, following paper, Phys. Rev. B <u>14</u>, 1805 (1976).