of a molecular-field approximation to the exchange interaction, and predictions for all relevant properties have been produced.

The theory for the static-torque anomaly can be made to agree with experiment, provided that $G_{||}M = 55$ cm^{-1}. The other parameter in the spin Hamiltonian is not determinable from the data which are available, and it would be useful in this regard if data at temperatures lower than about 0.5°K could be obtained.

The result of a comparison of the theory for ferromagnetic resonance with linewidth and lineshift measurements is encouraging. The resonance predictions depend sensitively on the exact form of the resonant susceptibility of the rare-earth ion. They thus have the potential of providing a deeper insight into this property than previous work on rare-earth-doped YIG.[17] However, it is also clear that the high-frequency behavior of the rare-earth susceptibility is still incompletely described, and it would seem that further experimental results at higher frequencies would be most valuable in resolving this point.

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Theory of Magnetically Induced Electric Field Gradients in Cubic Fe^{2+}†

U. Ganiel
Department of Physics, The Weizmann Institute of Science, Rehovoth, Israel
AND
S. Shtrikman
*Department of Electronics, The Weizmann Institute of Science, Rehovoth, Israel**

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The detection of a nonvanishing quadrupole interaction in ferrous compounds in which the Fe^{2+} ion occupies a site of cubic symmetry has been achieved in several cases, using Mössbauer spectroscopy. In some cases, the onset of this interaction has been found to be simultaneous with the appearance of magnetic ordering. A detailed theory of this effect is presented, which applies where the magnetic ordering is spontaneous (magnetic phase transitions), as well as where it is obtained by applying external magnetic fields to a paramagnetic compound. It is shown that an electric field gradient is induced by the magnetic ordering via the spin-orbit coupling. Utilizing the crystal-field approach, the magnetic ordering is described by adding a magnetic term to the Hamiltonian, using the molecular-field approximation. For cases where the magnetic term can be treated as a perturbation—which requires that it should be small compared to the spin-orbit interaction—closed expressions are obtained for the induced electric field gradient and for the magnetic hyperfine field at the site of the nucleus. The procedure required for other cases is outlined. The form of the resulting Mössbauer spectrum is discussed. It is shown that the quadrupole interaction is positive if the magnetic axis is parallel to a ⟨111⟩ direction, and that is it of equal magnitude, but negative, when the axis is parallel to a ⟨100⟩ direction. This fact may be utilized to determine the direction of the magnetic axis from Mössbauer measurements on a powder sample. Experimental evidence and possible applications of the theory are discussed.

1. INTRODUCTION

In recent years Mössbauer spectroscopy has become an important tool for investigating hyperfine interactions between nuclei and their electronic environment.[1]

The quadrupole interaction, i.e., the interaction between the quadrupole moment of the nucleus and the electric field gradient (EFG) at the site of that nucleus, has been observed to contain very interesting information on the environment of the site, as well as on the electronic structure of the ion.

In the following discussion we shall be concerned with ferrous compounds, namely compounds containing the Fe^{2+} ion.

In paramagnetic ferrous compounds, the quadrupole interaction, which causes the splitting of the Mössbauer absorption line of the Fe^{57} nucleus (ΔE_Q), can be

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[1] G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press Inc., New York, 1964).

written as[2]

$$\mathcal{H}_Q=[eQV_{zz}/4I(2I-1)][3I_z^2-I(I+1)+\eta(I_x^2-I_y^2)], \tag{1}$$

where Q is the quadrupole moment of the first-excited nuclear level, e is minus the electronic charge, I is the nuclear spin of that level, I_x, I_y, I_z are the components of the nuclear spin operator, and

$$\eta=(V_{xx}-V_{yy})/V_{zz}.$$

V_{xx}, V_{yy}, V_{zz} are the diagonal elements of the EFG tensor at the site of the nucleus. Equation 1 gives the form of the quadrupole Hamiltonian when written in a coordinate system in which the axes coincide with the principal axes of the EFG tensor. For $I=\frac{3}{2}$, the Hamiltonian (1) can be directly diagonalized, yielding

$$\Delta E_Q=\tfrac{1}{2}eV_{zz}Q[1+\eta^2/3]^{1/2}. \tag{2}$$

In (2), only V_{zz} and η depend on the environment, and are, in general, temperature-dependent. From the temperature dependence of ΔE_Q, some useful information concerning crystal-field parameters and electronic states of the Fe^{2+} ion can be deduced.[3–7]

In compounds in which the Fe^{2+} site possesses cubic symmetry, the EFG tensor vanishes, so that $\Delta E_Q=0$, and no quadrupole splitting should be observed. In several cases reported in the literature, it was found that the cubic site symmetry, as determined by x-rays or neutron diffraction at room temperature, was, in fact, confirmed by Mössbauer measurements yielding $\Delta E_Q=0$. However, when the temperature was lowered, a nonvanishing quadrupole interaction was determined from the Mössbauer experiments. One possible mechanism responsible for this phenomenon is the onset of a static Jahn–Teller distortion, which is identified also by x-ray measurements as a crystallographic phase transition lowering the symmetry. This phenomenon has been observed, for example, in $\mathrm{FeCr_2O_4}$ and in $\mathrm{FeV_2O_4}$.[8,9] One interesting feature noted in these two cases is the fact that the quadrupole splitting appears already at higher temperatures than the transition temperature as determined by the x-ray method: In $\mathrm{FeCr_2O_4}$ a well-resolved doublet is observed at 170°K (cubic to tetragonal transition seen by x rays at 135°K), and in $\mathrm{FeV_2O_4}$ a doublet is observed at 147°K (140°K determined by x ray as the transition temperature).[8] This possibly indicates the existence of local distortions, which are observed in the Mössbauer experiment, and appear prior to the cooperative effect seen in the x-ray measurement. There are, however, cases where a nonvanishing quadrupole interaction is observed as the temperature is lowered, even though the site symmetry of Fe^{2+}, as determined by x-ray measurements or by neutron diffraction, remains cubic. These cases share a common feature: the onset of the quadrupole interaction is simultaneous with the appearance of magnetic ordering. Quite a few cases of this type have been reported: Fe^{2+} in CoO,[10] Fe^{2+} in NiO, and Fe^{2+} in MnO,[11] $\mathrm{FeCr_2S_4}$ below its Curie point[12] (~180°K) and $\mathrm{KFeF_3}$ below its Néel temperature.[13,14] Until recently, $\mathrm{RbFeF_3}$, which has been studied by several groups independently,[15–17] was thought to belong to the same category. Testardi, Levinstein, and Guggenheim,[18] however, have recently reported that $\mathrm{RbFeF_3}$ becomes tetragonal in the antiferromagnetic region, and this rules out the mechanism we shall present shortly as causing the quadrupole splitting in this case.

In $\mathrm{FeCr_2S_4}$, the Fe^{2+} ion is situated at a site of tetrahedral symmetry. In all other examples mentioned above, the Fe^{2+} site has octahedral symmetry. Although a slight distortion from cubic symmetry was observed in some of the monoxides,[19] it is considered too small to produce the rather large EFG observed.[11] Moreover, no distortion of the site symmetry was found to be associated with the magnetic ordering in the case of $\mathrm{FeCr_2S_4}$, in which the sites of the Fe nuclei remain cubic down to 4.2°K.

The explanation of a nonvanishing EFG appearing simultaneously with magnetic ordering can be found in the effect of the magnetic field, which introduces a preferred direction in space. In the case of spontaneous ferro- or antiferromagnetism, the spins are ordered by the magnetic interaction, while both spins and orbital angular momentum are ordered by an external magnetic field, and a nonvanishing EFG is magnetically induced via the spin-orbit interaction. This explanation has already been suggested in a number of recent articles.[11,12,15,17] In this paper we present a detailed theory of this effect for the case of Fe^{2+} in an octahedral environment. Although all our calculations deal specifically with this case, we believe that the same ideas are applicable also for other ions in a cubic environment,

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TABLE I. Eigenvalues (E_n) and eigenfunctions (ψ_n) of the d^6 configuration within the subspace of $^5T_2$, in a cubic crystal field.

i	E_n	ψ_n
1	0	$(3/10)^{1/2}(\phi_{0,1}+\sqrt{2}\phi_{1,2}-(1/\sqrt{3})\phi_{-1,0})$
2	0	$(\frac{2}{5})^{1/2}(\phi_{0,0}+\frac{1}{2}\sqrt{3}\phi_{1,1}-\frac{1}{2}\sqrt{3}\phi_{-1,-1})$
3	0	$(3/10)^{1/2}(\phi_{0,-1}+(1/\sqrt{3})\phi_{1,0}-\sqrt{2}\phi_{-1,-2})$
4	-2λ	$(1/\sqrt{6})(\phi_{0,1}-\sqrt{2}\phi_{1,2}-\sqrt{3}\phi_{-1,0})$
5	-2λ	$(1/\sqrt{2})(\phi_{1,1}+\phi_{-1,-1})$
6	-2λ	$(1/\sqrt{6})(\phi_{0,-1}+\sqrt{3}\phi_{1,0}+\sqrt{2}\phi_{-1,-2})$
7	-2λ	$(1/\sqrt{3})(\sqrt{2}\phi_{0,-2}+\phi_{1,-1})$
8	-2λ	$(1/\sqrt{3})(-\sqrt{2}\phi_{0,2}+\phi_{-1,1})$
9	-5λ	$(1/\sqrt{15})[-2\sqrt{2}\phi_{0,1}+\phi_{1,2}-(\sqrt{6})\phi_{-1,0}]$
10	-5λ	$(1/\sqrt{5})(-\sqrt{3}\phi_{0,0}+\phi_{1,1}-\phi_{-1,-1})$
11	-5λ	$(1/\sqrt{15})[2\sqrt{2}\phi_{0,-1}-(\sqrt{6})\phi_{1,0}+\phi_{-1,-2}]$
12	-5λ	$(1/\sqrt{3})(\phi_{0,-2}-\sqrt{2}\phi_{1,-1})$
13	-5λ	$(1/\sqrt{3})(\phi_{0,2}+\sqrt{2}\phi_{-1,1})$
14	-5λ	$\phi_{1,-2}$
15	-5λ	$\phi_{-1,2}$

and similar calculations can be easily performed by changing the relevant parameters.

2. ENERGY LEVELS AND EIGENFUNCTIONS OF Fe^{2+} IN A CUBIC ENVIRONMENT

The problem of an Fe^{2+} ion in a crystalline field of cubic symmetry has been treated by Low and Weger.[20] We shall reformulate the relevant results here in order to fix the notation and obtain convenient expressions for later calculation.

The electronic configuration of Fe^{2+}, [Ar]$3d^6$, leads in the free ion to the ground term ^5D. In a cubic crystal field, ^5D splits into an orbital triplet $^5T_2$, and an orbital doublet ^5E. In the case of tetrahedral symmetry, ^5E is lower in energy, while in an octahedral site $^5T_2$ is lower. In the octahedral case, which we consider here, these two terms are separated by an amount Δ, where $\Delta \simeq 10\,000$ cm^{-1} in typical cases.[6,7,21] Since $\lambda \simeq -100$ cm^{-1} in the free ion, and some reduction is expected in the compounds, we have $|\lambda| \ll \Delta$, and mixing of ^5E states into $^5T_2$ states becomes extremely small and completely negligible for our purposes. Hence we restrict our calculations to the subspace of $^5T_2$, within which the spin-orbit interaction can be diagonalized exactly.

For convenience in further calculations, we choose two sets of orbital eigenfunctions for the T_2 triplet: one quantizing along the cubic ⟨100⟩ direction, and the other quantizing along the ⟨111⟩ direction. Writing d_m for the eigenfunction of $L^2 (L=2)$ and $L_z=m$, we choose for the ⟨100⟩ direction

$$\phi_0=(1/\sqrt{2})(d_2-d_{-2}),$$
$$\phi_1=d_1,$$
$$\phi_{-1}=d_{-1}, \tag{3}$$

and for the ⟨111⟩ direction,

$$\phi_0=d_0,$$
$$\phi_1=(\sqrt{\tfrac{2}{3}})d_2+(\sqrt{\tfrac{1}{3}})d_{-1},$$
$$\phi_{-1}=(\sqrt{\tfrac{2}{3}})d_{-2}-(\sqrt{\tfrac{1}{3}})d_1. \tag{4}$$

Note that within the subspace of T_2, both sets give

$$\langle\phi_k \mid L_z \mid \phi_r\rangle = k\delta_{kr}. \tag{5}$$

Writing $\phi_{k,\sigma}$ for the state ϕ_k with $S_z=\sigma$ $(-2\leq\sigma\leq 2)$, the eigenfunctions and eigenvalues of the Hamiltonian

$$\mathcal{H}_0=\mathcal{H}_c+\lambda(\mathbf{L}\cdot\mathbf{S}), \tag{6}$$

where $\mathcal{H}_c$ represents the contribution of the cubic crystal field (which is constant for all 15 states of $^5T_2$), are summarized in Table I. The constant contributions of $\mathcal{H}_c$ and 3λ have been substracted from all eigenvalues. Note that the eigenfunctions have exactly the same form for both sets of orbital basis functions (3) and (4).

We now proceed to examine the magnetic interaction. We shall presently describe it by a term of the form $\alpha L_z+\beta S_z$ in the Hamiltonian. For an external magnetic field H in the z direction, $\alpha=\mu_\beta H$ and $\beta=2\mu_\beta H$, μ_β being the Bohr magneton. This applies for magnetically dilute solutions of Fe^{2+} ions in a paramagnetic compound, such as MgO. On the other hand, if the environment of the Fe^{2+} ion orders magnetically, as in KFeF$_3$ or Fe^{2+} in NiO, then we shall use the molecular-field approximation, and describe the magnetic exchange interaction by an effective field acting on the spins. In that case we can write $\alpha=0$, $\beta=\mu_\beta h$, h being the molecular field, and we choose $z \parallel \mathbf{h}$.

TABLE II. Matrix elements of L_z and S_z within $^5T_2$. $\langle\psi_i \mid L_z \text{ or } S_z \mid \psi_j\rangle = \langle\psi_j \mid L_z \text{ or } S_z \mid \psi_i\rangle$, and other elements not given here vanish.

i	j	$\langle\psi_i \mid L_z \mid \psi_j\rangle$	$\langle\psi_i \mid S_z \mid \psi_j\rangle$
1	1	$\frac{1}{2}$	$\frac{3}{2}$
1	4	$-3/(2\sqrt{5})$	$-3(2\sqrt{5})$
2	5	$(3/5)^{1/2}$	$(3/5)^{1/2}$
3	3	$-\frac{1}{2}$	$-\frac{3}{2}$
3	6	$3/(2\sqrt{5})$	$3/(2\sqrt{5})$
4	4	$-\frac{1}{6}$	$\frac{5}{6}$
4	9	$-4/(3\sqrt{5})$	$-4(3\sqrt{5})$
5	10	$(2/5)^{1/2}$	$(2/5)^{1/2}$
6	6	$\frac{1}{6}$	$-\frac{5}{6}$
6	11	$-4/(3\sqrt{5})$	$-4/(3\sqrt{5})$
7	7	$\frac{1}{3}$	$-5/3$
7	12	$-\sqrt{2}/3$	$-\sqrt{2}/3$
8	8	$-\frac{1}{3}$	$5/3$
8	13	$-\sqrt{2}/3$	$-\sqrt{2}/3$
9	9	$-\frac{1}{3}$	$\frac{2}{3}$
11	11	$\frac{1}{3}$	$-\frac{2}{3}$
12	12	$\frac{2}{3}$	$-\frac{4}{3}$
13	13	$-\frac{2}{3}$	$\frac{4}{3}$
14	14	1	-2
15	15	-1	2

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[20] W. Low and M. Weger, Phys. Rev. **118**, 1119 (1960).
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The nonzero matrix elements of L_z and S_z are given in Table II in the scheme of the states ψ_n given in Table I. From these, the matrix $\alpha L_z+\beta S_z$ is immediately obtained.

3. CALCULATION OF THE INDUCED ELECTRIC FIELD GRADIENT TENSOR AND THE HYPERFINE FIELD

From here on, we shall measure all interactions in units of °K, since this simplifies various considerations where the temperature dependence is to be taken into account ($1°\text{K}\equiv 1.38\times10^{-16}$ erg). Furthermore, when dealing with magnetic fields, we shall compare them with temperature when considering the appropriate magnetic interactions, namely the product: $\mu_\beta H$. Hence we note that $1°\text{K}\equiv 14\,887$ Oe.

Our first problem is the calculation of the EFG tensor. We assume, as is justified in many cases,[3,6,7] that electronic relaxation times are much shorter than $2\hbar/\Delta E_Q$, so that the nucleus "feels" the thermal average of V_{ij} over all electronic states. Relaxation effects, which may become important at very low temperatures, are not considered here.

In our calculations we consider separately the cases:

(a) $\alpha,\beta\ll|\lambda|, T,$

(b) $T\lesssim\alpha,\beta\ll|\lambda|.$

In Fe^{2+}, $\lambda\lesssim-140°\text{K}$, which is equivalent to fields of $\sim2\times10^6$ Oe. Considering cases of internal magnetism (like $KFeF_3$), we shall deal mainly with the situation near the Néel temperature, where h is small, so that case (a) is realized. If we look at magnetically dilute solutions (Fe^{2+} ions in a cubic paramagnetic compound) we consider external magnetic fields. Even the most intense steady state fields presently available would yield $H\ll|\lambda|$, although going to low enough temperatures could mean that case (b) is realized (e.g., for $H\simeq10^5$ Oe and $T\lesssim7°\text{K}$).

A. Case (a): α, $\beta\ll|\lambda|$, T

For this case we shall perform the calculation considering the magnetic interaction $\alpha L_z+\beta S_z$ as a perturbation to the Hamiltonian (6). The EFG tensor at any temperature can be expanded in powers of the magnetic field h,[22] and h being small we shall consider only the first nonvanishing term in this expansion. From symmetry it is clear that this will be the second-order term, so that

$$\langle V_{ij}\rangle=\sum_{k,l}T_{ijkl}h_kh_l. \tag{7}$$

$\langle V_{ij}\rangle$ denotes the appropriate thermal average. The form of T_{ijkl} is found using the results of Birss,[23] as explained in Appendix A. A detailed calculation of $\langle V_{ij}\rangle$ is needed for two nonequivalent directions of $\mathbf{h}$, in order to determine it for any arbitrary direction of $\mathbf{h}$.

We now proceed to calculate $\langle V_{ij}\rangle$ for $\mathbf{h}$ in the $\langle111\rangle$ direction and for $\mathbf{h}$ in the $\langle100\rangle$ direction. $\langle V_{ij}\rangle$ appearing in (7) is a number, which is the thermal average of the expectation values the operator V_{ij} takes in all electronic eigenstates. Hence we have most generally

$$\langle V_{ij}\rangle=\mathrm{Tr}[V_{ij}\exp(-\tau\mathcal{H})]/\mathrm{Tr}[\exp(-\tau\mathcal{H})], \tag{8}$$

where $\mathcal{H}=\mathcal{H}_0+\alpha L_z+\beta S_z$, $\tau=T^{-1}$. $\mathcal{H}_0$ (6) does not commute with $\alpha L_z+\beta S_z$, so we use the well-known identity (proved in Appendix B)

$$e^{A+B}=e^A+e^A\int_0^1 e^{-XA}Be^{X(A+B)}dX, \tag{9}$$

where A and B are two noncommuting operators.

If B is small (in the usual sense of matrix elements), we can expand (9) in powers of B. To first order in B we have

$$e^{A+B}\simeq e^A+e^A\int_0^1 e^{-XA}Be^{XA}dX, \tag{10}$$

and to second order in B we obtain

$$e^{A+B}\simeq e^A+e^A\int_0^1 dXe^{-XA}Be^{XA}$$
$$+e^A\int_0^1 dXe^{-XA}Be^{XA}\int_0^1 dye^{-yXA}XBe^{yXA}. \tag{11}$$

Since we need $\langle V_{ij}\rangle$ to second order in h, we use (11), substituting $A=-\tau\mathcal{H}_0$, $B=-\tau(\alpha L_z+\beta S_z)$. Hence,

$$\exp(-\tau\mathcal{H})\simeq\exp(-\tau\mathcal{H}_0)-\exp(-\tau\mathcal{H}_0)\int_0^1 dX\,\exp(X\tau\mathcal{H}_0)\tau(\alpha L_z+\beta S_z)\,\exp(-X\tau\mathcal{H}_0)$$
$$+\exp(-\tau\mathcal{H}_0)\int_0^1 dX\,\exp(X\tau\mathcal{H}_0)\tau(\alpha L_z+\beta S_z)\,\exp(-X\tau\mathcal{H}_0)X\int_0^1 dy\,\exp(yX\tau\mathcal{H}_0)\tau(\alpha L_z+\beta S_z)\,\exp(-yX\tau\mathcal{H}_0). \tag{12}$$

The states ψ_n (Table I) are eigenstates of $\mathcal{H}_0$ (within ${}^5T_2$), so that $\mathcal{H}_0\psi_n=E_n\psi_n$. We take matrix elements of (12)

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[22] We use h here to denote any magnetic field, external or internal, so that α and β are both proportional to h.

[23] R. R. Birss, Repts. Progr. Phys. **26,** 307 (1963).

between ψ_n and $\psi_{n'}$, obtaining

$$[\exp(-\tau\mathcal{H})]_{nn'}\simeq\exp(-\tau E_n)\delta_{nn'}-\tau\exp(-\tau E_n)(\alpha L_z+\beta S_z)_{nn'}\int_0^1 dX\,\exp[X\tau(E_n-E_{n'})]$$
$$+\tau^2\exp(-\tau E_n)\sum_{n''}\left\{(\alpha L_z+\beta S_z)_{nn''}(\alpha L_z+\beta S_z)_{n''n'}\int_0^1 dX\,\exp[X\tau(E_n-E_{n''})]X\int_0^1 dy\,\exp[yX\tau(E_{n''}-E_{n'})]\right\}. \tag{13}$$

For evaluation of $\langle V_{ij}\rangle$ we need further the matrix elements of V_{ij} in the scheme of the states ψ_n. These are easily obtained, using the following simple results:

$$\langle\phi_0|V_{zz}|\phi_0\rangle=-2\langle\phi_0|V_{xx}|\phi_0\rangle=-2\langle\phi_0|V_{yy}|\phi_0\rangle=2v,$$
$$\langle\phi_1|V_{zz}|\phi_1\rangle=-2\langle\phi_1|V_{xx}|\phi_1\rangle=-2\langle\phi_1|V_{yy}|\phi_1\rangle=-v,$$
$$\langle\phi_{-1}|V_{zz}|\phi_{-1}\rangle=-2\langle\phi_{-1}|V_{xx}|\phi_{-1}\rangle=-2\langle\phi_{-1}|V_{yy}|\phi_{-1}\rangle=-v, \tag{14}$$

where

$$v=\pm(2/7)e\langle r^{-3}\rangle. \tag{15}$$

In (15), e equals minus the electronic charge, $\langle r^{-3}\rangle$ is the average of r^{-3} in the d orbitals. The plus sign should be taken for the functions ϕ_k of (3), namely for the z axis chosen parallel to the cubic $\langle 100\rangle$ direction, and the minus applies for the ϕ_i's of (4) $(z\,||\langle 111\rangle)$. Furthermore,

$$\langle\phi_k|V_{ij}|\phi_l\rangle=0,\quad\text{for}\quad k\neq l$$
$$\langle\phi_m|V_{ij}|\phi_m\rangle=0,\quad\text{for}\quad i\neq j. \tag{16}$$

Using Eqs. (14)–(16), the matrix elements of V_{ij} between the states ψ_n were calculated, and the results for V_{zz} are given in Table III.

In Appendix B we describe the calculation of $\langle V_{zz}\rangle$. The final result we obtain is

$$\langle V_{zz}\rangle=\frac{v}{T^2}\left[\frac{-(1/40)(\alpha+3\beta)^2+(7/72)(\alpha-5\beta)^2e^{2\lambda/T}-(14/15)(\alpha-2\beta)^2e^{5\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}}\right]$$
$$+\frac{v}{\lambda T}\left[\frac{(3/200)(\alpha+\beta)(29\alpha+89\beta)+(1/216)(\alpha+\beta)(31\alpha-701\beta)e^{2\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}}+\frac{(1/135)(\alpha+\beta)(-88\alpha+248\beta)e^{5\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}}\right]$$
$$+\frac{v}{\lambda^2}\left[\frac{-(153/500)(\alpha+\beta)^2+(55/108)(\alpha+\beta)^2e^{2\lambda/T}-(686/3375)(\alpha+\beta)^2e^{5\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}}\right]. \tag{17}$$

Obviously, we have also here

$$\langle V_{zz}\rangle=-2\langle V_{xx}\rangle=-2\langle V_{yy}\rangle \tag{18}$$
$$\langle V_{ij}\rangle=0\quad\text{for}\quad i\neq j.$$

The first term in (17) behaves essentially as h^2/T^2, since for $T<|\lambda|$ the contribution of the exponents is only of secondary importance $(\lambda<0)$. This term can be called a "Curie term," in analogy to the $1/T$ contribution in calculations of paramagnetic susceptibilities, as it represents thermal averaging over the values V_{zz} takes for the zero-order functions. Since, however, the magnetic perturbation affects also the eigenfunctions themselves, there are additional terms. The third term (again for $T<|\lambda|$) is nearly temperature-independent (behaving essentially as h^2/λ^2), so this is a "Van Vleck" contribution, analogous to the Van Vleck susceptibility. Since the calculation is to second order, we also have a "mixed" term, which goes essentially as $h^2/\lambda T$.

In (17), $\langle V_{zz}\rangle$ is proportional to v. Since $v>0$ for **h** parallel to the $\langle 100\rangle$ direction and $v<0$ for **h** in a $\langle 111\rangle$ direction, we find that $\langle V_{zz}\rangle$ is equal in magnitude but of opposite signs in these two cases.[24] Care should be taken in comparing the two cases: The calculation is performed choosing the z axis in each case parallel to **h**, so that in $\langle V_{zz}\rangle$ the subscript z refers to different axes.

As shown in Appendix A, we now have all the information to determine T_{ijkl}, and hence $\langle V_{ij}\rangle$ for any arbitrary direction of **h**. The details are given in Appendix C. The results we obtain are the following: Let **h** be of magnitude h and have direction cosines m, n, l with respect to the cubic axes. Choosing a new

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[24] This fact can be utilized in determining the direction of the sublattice magnetization from a Mössbauer experiment on a powder sample (Ref. 17).

coordinate system with its z axis parallel to $\mathbf{h}$, we obtain

$$
\begin{aligned}
\langle V_{xx}{}^{h}\rangle &= \tfrac{1}{2}ah^2[12m^2n^2/(1-l^2)-1],\\
\langle V_{yy}{}^{h}\rangle &= \tfrac{1}{2}ah^2[12l^2(1-l^2)-12m^2n^2l^2/(1-l^2)-1],\\
\langle V_{zz}{}^{h}\rangle &= \tfrac{1}{2}ah^2[6(m^4+n^4+l^4)-4],\\
\langle V_{xy}{}^{h}\rangle &= \langle V_{yx}{}^{h}\rangle = \tfrac{1}{2}ah^2[6mnl(m^2-n^2)/(1-l^2)],\\
\langle V_{xz}{}^{h}\rangle &= \langle V_{zx}{}^{h}\rangle = \tfrac{1}{2}ah^2[6mn(m^2-n^2)/\surd(1-l^2)],\\
\langle V_{yz}{}^{h}\rangle &= \langle V_{zy}{}^{h}\rangle = \tfrac{1}{2}ah^2[6l(m^4+n^4+l^4-l^2)/\surd(1-l^2)].
\end{aligned}
\tag{19}
$$

In (19), a is equal to the r.h.s. of Eq. (17) divided by h^2, with $v>0$. The superscript h shows that the tensor is written in a coordinate system as defined above.[25]

Within the same framework, namely, $\alpha, \beta \ll |\lambda|, T$, we now proceed to calculate the hyperfine field at the site of the nucleus, $\mathbf{H}_n$. As in the case of the EFG, we consider here only the first nonvanishing term in the expansion of $\mathbf{H}_n$ in powers of $\mathbf{h}$, which will be the first-order term. In analogy with (7), we write here

$$\langle H_n\rangle_i = \sum_j P_{ij}h_j. \tag{20}$$

For cubic symmetry, P_{ij} reduces to a scalar, namely,

$$P_{ij} = p\delta_{ij}, \tag{21}$$

and hence,

$$\langle \mathbf{H}_n\rangle = p\mathbf{h}, \tag{22}$$

which means that, within this approximation, $\mathbf{H}_n$ is parallel to $\mathbf{h}$,[26] and the proportionality factor has to be determined from one calculation for a specific case. The hyperfine field is generally given by[27]

$$
\begin{aligned}
\mathbf{H}_n = -2\mu_\beta\langle r^{-3}\rangle\mathbf{L} - 2\mu_\beta\langle r^{-3}\rangle \frac{2l+1-4S}{S(2l-1)(2l+3)(2L-1)}\\
\times[L(L+1)\mathbf{S}-\tfrac{3}{2}(\mathbf{L}\cdot\mathbf{S})\mathbf{L}-\tfrac{3}{2}\mathbf{L}(\mathbf{L}\cdot\mathbf{S})]+\bar{A}\mathbf{S}.
\end{aligned}
\tag{23}
$$

The first term is the orbital contribution to the hyperfine field, the second is the dipolar term, and the third is the Fermi contact interaction, which is written here in a simplified form, $\bar{A}$ being a constant depending on the ion one is dealing with. Choosing the z axis parallel to $\mathbf{h}$, we note that $\mathbf{H}_n$ has only a z component. Inserting all values for the case of Fe^{2+}, we obtain

$$
\begin{aligned}
\langle H_n\rangle = -2\mu_\beta\langle r^{-3}\rangle\{\langle L_z\rangle-(1/42)[6\langle S_z\rangle-\langle\tfrac{3}{2}(\mathbf{L}\cdot\mathbf{S})L_z\\
+\tfrac{3}{2}L_z(\mathbf{L}\cdot\mathbf{S})\rangle]\}+\bar{A}\langle S_z\rangle.
\end{aligned}
\tag{24}
$$

In (24) we take, as before, appropriate thermal averages. We need $\langle L_z\rangle$, $\langle S_z\rangle$, and $\langle\tfrac{3}{2}(\mathbf{L}\cdot\mathbf{S})L_z+\tfrac{3}{2}L_z(\mathbf{L}\cdot\mathbf{S})\rangle$. Denoting any of these three operators by O, we want to calculate

$$\langle O\rangle = \{\mathrm{Tr}[O\exp(-\tau\mathcal{H})]\}/\mathrm{Tr}[\exp(-\tau\mathcal{H})] \tag{25}$$

to first order in h, so we use (10), obtaining

$$
\begin{aligned}
\mathrm{Tr}[O\exp(-\tau\mathcal{H})] \simeq \sum_n \exp(-\tau E_n)O_{nn} - \tau\sum_{n,n'}\exp(-\tau E_n)(\alpha L_z+\beta S_z)_{nn'}O_{n'n}\delta(E_n,E_{n'})\\
+\sum_{n,n'}[1-\delta(E_n,E_{n'})](\alpha L_z+\beta S_z)_{nn'}O_{n'n}\frac{\exp(-\tau E_n)-\exp(-\tau E_{n'})}{E_n-E_{n'}}.
\end{aligned}
\tag{26}
$$

The matrix elements needed for the evaluation of (26) are given in Tables II and IV. Using these, we find that, as expected, in the r.h.s. of (26), zero-order terms in h vanish, and hence we need the denominator in (25) only to zero order. The results we obtain are

$$
\begin{aligned}
\langle L_z\rangle = -T^{-1}\frac{\tfrac{1}{2}(\alpha+3\beta)+(5/18)(\alpha-5\beta)e^{2\lambda/T}+(28/9)(\alpha-2\beta)e^{5\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}}\\
+\lambda^{-1}\frac{\tfrac{3}{2}(\alpha+\beta)-(25/54)(\alpha+\beta)e^{2\lambda/T}-(28/27)e^{5\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}},
\end{aligned}
\tag{27a}
$$

$$
\begin{aligned}
\langle S_z\rangle = -T^{-1}\frac{\tfrac{3}{2}(\alpha+3\beta)-25/18)(\alpha-5\beta)e^{2\lambda/T}-(56/9)(\alpha-2\beta)e^{5\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}}\\
+\lambda^{-1}\frac{\tfrac{3}{2}(\alpha+\beta)-(25/54)(\alpha+\beta)e^{2\lambda/T}-(28/27)e^{5\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}},
\end{aligned}
\tag{27b}
$$

$$
\begin{aligned}
\langle\tfrac{3}{2}(\mathbf{L}\cdot\mathbf{S})L_z+\tfrac{3}{2}L_z(\mathbf{L}\cdot\mathbf{S})\rangle = -T^{-1}\frac{\tfrac{9}{2}(\alpha+3\beta)+(5/6)(\alpha-5\beta)e^{2\lambda/T}-(56/3)(\alpha-2\beta)e^{5\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}}\\
+\lambda^{-1}\frac{9(\alpha+\beta)-(25/9)(\alpha+\beta)e^{2\lambda/T}+(14/9)(\alpha+\beta)e^{5\lambda/T}}{3+5e^{2\lambda/T}+7e^{5\lambda/T}}.
\end{aligned}
\tag{27c}
$$

---

[25] In this form, the result is useful for calculation of the nuclear energy levels, which are needed later on (Sec. 4).

[26] This is, however, not necessarily true in the general case.

[27] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, New York, 1964), pp. 325–8.

TABLE III. Matrix elements $\langle\psi_i \mid V_{zz} \mid \psi_j\rangle$ within ${}^5T_2$, in units of v [Eq. (15)]. $\langle\psi_i \mid V_{zz} \mid \psi_j\rangle = \langle\psi_j \mid V_{zz} \mid \psi_i\rangle$, and other elements not given here vanish.

i	j	$\langle\psi_i \mid V_{zz} \mid \psi_j\rangle$
1	1	$-\frac{1}{10}$
1	4	$3/\sqrt{20}$
1	9	$-6/5$
2	2	$1/5$
2	10	$-3\sqrt{6/5}$
3	3	$-\frac{1}{10}$
3	6	$3/\sqrt{20}$
3	11	$6/5$
4	4	$-\frac{1}{2}$
4	9	$-2/\sqrt{5}$
5	5	-1
6	6	$-\frac{1}{2}$
6	11	$2/\sqrt{5}$
7	7	1
7	12	$\sqrt{2}$
8	8	1
8	13	$-\sqrt{2}$
9	9	$\frac{3}{5}$
10	10	$\frac{4}{5}$
11	11	$\frac{3}{5}$
14	14	-1
15	15	-1

These results, when substituted into (24), give $\langle H_n\rangle$. The final expression for $\langle H_n\rangle$ can be separated into two contributions: One which behaves essentially (for $T<|\lambda|$) as h/T can again be called the "Curie term," whereas the other, which is essentially temperature-independent (again for $T<|\lambda|$) is the "Van Vleck" term.

Care should be taken in using the results expressed in (17), (19), and (27), since these will only apply as long as the approximations involved hold. The main point to note is $|h| \ll T$, since $|h| \ll |\lambda|$ is true in most cases for Fe^{2+}. On the other hand, as will be discussed later, this requirement is often realized in practice, so the theory can be applied in cases which are experimentally possible.

TABLE IV. Matrix elements of $\frac{3}{2}L_z(\mathbf{L}\cdot\mathbf{S})+\frac{3}{2}(\mathbf{L}\cdot\mathbf{S})L_z$ within ${}^5T_2$. $\langle\psi_i \| \psi_j\rangle = \langle\psi_j \| \psi_i\rangle$, and other elements not given here vanish.

i	j	$\langle\psi_i \mid (\frac{3}{2})(\mathbf{L}\cdot\mathbf{S})L_z + (\frac{3}{2})L_z(\mathbf{L}\cdot\mathbf{S}) \mid \psi_j\rangle$
1	1	$\frac{9}{2}$
1	4	$-9/\sqrt{5}$
2	5	$6\sqrt{\frac{3}{5}}$
3	3	$-\frac{9}{2}$
3	6	$9/\sqrt{5}$
4	4	$-\frac{1}{2}$
4	9	$2/\sqrt{5}$
5	10	$-3/\sqrt{10}$
6	6	$\frac{1}{2}$
6	11	$2/\sqrt{5}$
7	7	1
7	12	$1/\sqrt{2}$
8	8	-1
8	13	$1/\sqrt{2}$
9	9	2
11	11	-2
12	12	-4
13	13	4
14	14	-6
15	15	6

B. Case (b): $T \lesssim \alpha$, $\beta \ll |\lambda|$

This situation can be realized in magnetically dilute solutions, where the Fe^{2+} ion occupies a cubic site, and an external magnetic field is applied. Another possibility could be a case of internal magnetism, with a low enough transition temperature[28] so that even when $|h| \gtrsim T$, we still have $|h| \ll \lambda$.

We first calculate the EFG tensor. Here we shall confine our attention to cases where $\mathbf{h}$ is either in a $\langle 111\rangle$ or in the $\langle 100\rangle$ direction, since then we know by symmetry that the major axis of the EFG tensor will be parallel to $\mathbf{h}$, and $\eta=0$, so that all we need is $\langle V_{zz}\rangle$. In this case we cannot use approximations like (10) or (11), since B will not be small ($h/T \gtrsim 1$). On the other hand, since $T \ll |\lambda|$, we neglect contributions from all the states except for the lowest triplet (Table I) in the thermal averaging, since the higher states will be practically unoccupied. Since $h \ll |\lambda|$, we neglect terms of order $(h/\lambda)^2$, but not terms like $h^2/\lambda T$, and certainly no term of any order in h/T will be neglected.[29] Hence we need energy levels up to second order in h and eigenfunctions only up to first order in h, as given in Table V. Using these and Table III, we calculate the expectation values $\langle\bar{\psi}_i \mid V_{zz} \mid \bar{\psi}_i\rangle$ for $i=1, 2, 3$ up to first order in h/λ. Thermal averaging using (8) within the lowest triplet will give $\langle V_{zz}\rangle$. We shall give the explicit result only for the case of an external field $\mathbf{H}$, in which case: $\alpha=H$, $\beta=2H$. In this case we obtain

TABLE V. Energy levels ($\bar{E}_i$) to second order in the magnetic perturbation $\alpha L_z+\beta S_z$, and eigenfunctions ($\bar{\psi}_i$) to first order in the perturbation, for the lowest triplet of ${}^5T_2$. The $\bar{\psi}_i$ are defined in Table I.

i	$\bar{E}_i$	$\bar{\psi}_i$
1	$\frac{1}{2}\alpha+\frac{3}{2}\beta+(9/40)(\alpha+\beta)^2/\lambda$	$\psi_1-3/(4\sqrt{5})[(\alpha+\beta)/\lambda]\psi_4$
2	$(3/10)(\alpha+\beta)^2/\lambda$	$\psi_2-\frac{1}{2}(\sqrt{\frac{3}{5}})[(\alpha+\beta)/\lambda]\psi_5$
3	$-\frac{1}{2}\alpha-\frac{3}{2}\beta+(9/40)(\alpha+\beta)^2/\lambda$	$\psi_3+3/(4\sqrt{5})[(\alpha+\beta)/\lambda]\psi_6$

$$\langle V_{zz}\rangle = (Z_0^{-1})(v/10)\{2-(27/5)(H^2/\lambda T) - [2-(81/20)(H^2/\lambda T)]\cosh(7H/2T) + 27(H/\lambda)\sinh(7H/2T)\}, \quad (28)$$

---

[28] In our choice of units, the saturation value of h in cases of internal magnetism is normally of the order of the transition temperature.

[29] Contrary to case a, where contributions of orders h^2/λ^2, $h^2/\lambda T$, and h^2/T^2 were comparable, in case (b):

$$h^2/\lambda^2 \ll |h^2/\lambda T| \ll h^2/T^2,$$

so terms of order h^2/λ^2 may be neglected.

where

$$Z_0=[2-(81/20)(H^2/\lambda T)]\cosh(7H/2T)$$
$$+1-(27/10)(H^2/\lambda T). \quad (29)$$

This result is invariant under reversal of **H**, as it should. Furthermore, we find again that $\langle V_{zz}\rangle$ has the same magnitude but opposite signs for **H** parallel to a $\langle 111\rangle$ direction and for **H** parallel to the $\langle 100\rangle$ direction. This is, in fact, independent of the approximation we use as long as we restrict the calculation to within $^5T_2$, since it results from Eqs. (14) and (15).

For very low temperatures, such that only the ground state is occupied $(T\ll H)$, we obtain

$$\langle V_{zz}\rangle(T\rightarrow 0)=(v/10)(-1+27H/\lambda), \quad (30)$$

so that a saturation value larger than $v/10$ should be expected for the magnitude of $\langle V_{zz}\rangle$ (note that $\lambda<0$).

The hyperfine field is calculated in a similar fashion, for **h** parallel to either a $\langle 111\rangle$ or to the $\langle 100\rangle$ direction, since by symmetry $\mathbf{H}_n$ is then parallel to **h**. We need $\langle L_z\rangle$, $\langle S_y\rangle$, and $\langle\frac{3}{2}L_z(\mathbf{L\cdot S})+\frac{3}{2}(\mathbf{L\cdot S})L_z\rangle$ to be substituted into (24), where thermal averages are taken only within the lowest triplet. Using Tables V, II, and IV, we obtain the required results, which we give here for the case of an external field **H**:

$$\langle L_z\rangle=(Z_0^{-1})\{[-1+(81/40)(H^2/\lambda T)]\sinh(7H)2T)$$
$$+(9H/5\lambda)[(\tfrac{3}{2})\cosh(7H/2T)-1]\}, \quad (31a)$$

$$\langle S_z\rangle=(Z_0^{-1})\{3[-1+(81/40)(H^2/\lambda T)]\sinh(7H/2T)$$
$$+(9H/5\lambda)[(\tfrac{3}{2})\cosh(7H/2T)-1]\}, \quad (31b)$$

$$\langle\tfrac{3}{2}L_z(\mathbf{L\cdot S})+\tfrac{3}{2}(\mathbf{L\cdot S})L_z\rangle$$
$$=(Z_0^{-1})\{9[-1+(81/40)(H^2/\lambda T)]\sinh(7H/2T)$$
$$+(54H/5\lambda[(\tfrac{3}{2})\cosh(7H/2T)-1]\}, \quad (31c)$$

where Z_0 is defined in (29).

C. General Case

Cases (a) and (b) which are treated above lend themselves to a fairly general treatment, so the results can be expressed analytically. By the general case we mean a situation where the approximations used above are not justified, so an exact diagonalization of the ionic Hamiltonian is required. In this case we have to take

$$\mathcal{H}=\mathcal{H}_c+\lambda(\mathbf{L\cdot S})+(\alpha\mathbf{L}+\beta\mathbf{S})\cdot\mathbf{t}, \quad (32)$$

where **t** is a unit vector parallel to the effective magnetic field **h** (internal or external). Working only within $^5T_2$ is still justified, but if $|\lambda|\gg|h|$ is not true, neither case (a) nor (b) is realized. In practice, this can occur only for cases of internal magnetism, in which the transition temperature (T_c) is not low compared to $|\lambda|$,[28] and we deal with a range of temperatures not too close to the transition point. A typical example is Fe^{2+} in NiO (with a Néel temperature of 523°K), which has been treated by Siegwarth.[11]

In order to obtain the results for the general case, $\mathcal{H}$ must be diagonalized by machine calculations. Once the eigenvalues and eigenstates are known, the expectation values of V_{ij}, **L**, **S**, and $\{\frac{3}{2}\mathbf{L}(\mathbf{L\cdot S})+\frac{3}{2}(\mathbf{L\cdot S})\mathbf{L}\}$ can be found, and with (23) the hyperfine field is calculated.

It is worth noting that also here, in the general case, $\langle V_{ij}\rangle$ will be equal in magnitude but of opposite signs in the two special cases where **h** is in a $\langle 111\rangle$ direction and in the $\langle 100\rangle$ direction. This is easily understood since we can then diagonalize $\lambda(\mathbf{L\cdot S})+(\alpha\mathbf{L}+\beta\mathbf{S})\cdot\mathbf{t}$ starting from the matrices written in the scheme of the states ψ_n (Table I). When written in this manner, the matrices are exactly the same in both cases, so the eigenstates will also have exactly the same form. $\langle V_{ij}\rangle$, which will be obtained, will therefore be the same in both cases, being proportional to v (15). Since v changes sign in going from $\mathbf{h}\,||\langle 111\rangle$ to $\mathbf{h}\,||\langle 100\rangle$, so will $\langle V_{ij}\rangle$. From symmetry, it is clear that in these two cases, the major axis of the EFG tensor will be parallel to **h**, and $\eta=0$. Furthermore, it is clear that in these two cases $\mathbf{H}_n\,||\,\mathbf{h}$. These facts will simplify the consideration of the Mössbauer spectrum for these two cases.

In all the cases treated above, we have explicitly assumed one mechanism to be responsible for the induced EFG. The possibility of magnetostriction, which can accompany a magnetic transition and distort the crystal, is neglected. However, as long as such strictions are not revealed by x-ray measurements, it seems reasonable to assume their effect to be negligible in comparison to the main mechanism, described above.

4. MÖSSBAUER SPECTRA OF Fe^{2+} IN A CUBIC ENVIRONMENT

Having calculated in Sec. 3 the induced EFG and the hyperfine field at the Fe nucleus, we now consider the Mössbauer spectrum in the presence of a magnetic interaction. For the case of internal magnetic ordering, the Hamiltonian of the excited $(I=\frac{3}{2})$ nuclear state will be of the form[30]

$$\mathcal{H}_e=\mathcal{H}_M+\mathcal{H}_Q$$
$$=-\tfrac{2}{3}\mu_e\langle H_n\rangle I_{z'}+[eQ\langle V_{zz}\rangle/4I(2I-1)]$$
$$\times[3I_z^2-I(I+1)+\eta(I_x^2-I_y^2)]. \quad (33)$$

μ_e is the magnetic moment of the excited nuclear state. Note that z refers here to the major axis of the EFG tensor, and z' to the direction of $\langle\mathbf{H}_n\rangle$. In the ground

---

[30] In this expression the assumption we made about electronic relaxation times (Sec. 3) is explicitly implied in using $\langle V_{zz}\rangle$ and $\langle H_n\rangle$.

state ($I=\frac{1}{2}$) there is no quadrupole interaction, so

$$\mathcal{H}_g=-2\mu_g\langle H_n\rangle I_{z'}, \tag{34}$$

μ_g being the magnetic moment of the nuclear ground state.

If an external field **H** causes the magnetic interaction, one should substitute $\mathbf{H}+\langle\mathbf{H}_n\rangle$ for $\langle H_n\rangle$ in (33) and (34); but since normally $|\mathbf{H}|\ll|\langle\mathbf{H}_n\rangle|$, we shall not bother to include it in our expressions.

The form of the Mössbauer spectrum for the different possibilities arising from (33) has already been discussed by many authors.[31] We shall use these well-known results for the different cases described in Sec. 3.

A. Case (a): α, $\beta\ll|\lambda|$, T

For this case we have shown above that $\langle\mathbf{H}_n\rangle\|\mathbf{h}$. If **h** is in a $\langle 111\rangle$ or the $\langle 100\rangle$ direction, $\langle V_{ij}\rangle$ has its major axis parallel to **h**, so $\langle V_{zz}\rangle=\langle V_{zz}{}^h\rangle$ (19), and $z'\equiv z$.

The nuclear energy levels of the excited and ground states are then obtained[32]:

$$(E_e)_{I_z}=-\tfrac{2}{3}\mu_e\langle H_n\rangle I_z+(-1)^{|I_z|}+\tfrac{1}{2}e\langle V_{zz}{}^h\rangle Q/4, \tag{35a}$$

$$(E_g)_{I_z}=-2\mu_g\langle H_n\rangle I_z. \tag{35b}$$

In the case in which **h** is not parallel to any of these two directions,[33] the problem is still simple as long as α, $\beta\ll|\lambda|$, T, since $\langle H_n\rangle$ is of first order in h while $\langle V_{ij}\rangle$ is of second order. Hence, in (33) we expect $\mathcal{H}_Q\ll\mathcal{H}_M$, so $\mathcal{H}_Q$ can be treated as a perturbation on $\mathcal{H}_M$, and we take only its diagonal elements between the eigenstates of $\mathcal{H}_M$. In this case we obtain for $(E_e)_{I_z}$ the same expression as (35a).

Let us denote the positions (energies) of the Mössbauer absorption lines by Δ_i, taking the zero at the energy of the γ transition when the hyperfine and quadrupole interactions are absent.[34] In both cases with which we deal here, there will be six absorption lines, yielding[32]

$$\begin{aligned}
\Delta_1&=-\tfrac{3}{2}g_1-\tfrac{1}{2}g_0+(eQ/4)\langle V_{zz}{}^h\rangle,\\
\Delta_2&=-\tfrac{1}{2}g_1-\tfrac{1}{2}g_0-(eQ/4)\langle V_{zz}{}^h\rangle,\\
\Delta_3&=\tfrac{1}{2}g_1-\tfrac{1}{2}g_0-(eQ/4)\langle V_{zz}{}^h\rangle,\\
\Delta_4&=-\tfrac{1}{2}g_1+\tfrac{1}{2}g_0-(eQ/4)\langle V_{zz}{}^h\rangle,\\
\Delta_5&=\tfrac{1}{2}g_1+\tfrac{1}{2}g_0-(eQ/4)\langle V_{zz}{}^h\rangle,\\
\Delta_6&=\tfrac{3}{2}g_1+\tfrac{1}{2}g_0+(eQ/4)\langle V_{zz}{}^h\rangle,
\end{aligned} \tag{36}$$

where

$$g_1=|\tfrac{2}{3}\mu_e\langle H_n\rangle|,\quad g_0=|2\mu_g\langle H_n\rangle|.$$

Here we have to deal separately with cases of internal magnetic ordering and with cases where the magnetic field is external. In the first case, **h** has a definite direction relative to the cubic axes, defined by its direction cosines m, n, l. Hence, all the Fe^{2+} ions "see" the same **h**, and g_1, g_0, and $\langle V_{zz}{}^h\rangle$ are the same for all the Fe nuclei, so that in a powder sample, as well as in a single crystal, the spectral lines will be sharp as in a usual Mössbauer experiment. The same is true for the second case, provided one works with a single crystal. If, however, one works with a powder sample, then the external field **H** has different m, n, l at the different Fe^{2+} ions, so we need an appropriate average over directions. The situation is reminiscent of the problem of nuclear magnetic resonance (NMR) experiments in solids, in the "high field" case, where the directions of the major axes of the EFG vary within the powder, so that a broadening and a marked change in the line shape of the NMR lines results.[35] In our case, $\langle\mathbf{H}_n\rangle\|\mathbf{H}$, so g_1 and g_0 are the same for all the Fe nuclei. $\langle V_{zz}{}^h\rangle$, however, varies. We can write

$$\Delta_i=\Delta_i{}^0+\delta_i, \tag{37a}$$

where $\Delta_i{}^0$ is the part of Δ_i containing only g_1 and g_0 (36), and $\delta_i=\pm(eQ/4)\langle V_{zz}{}^h\rangle$, which has to be averaged. We calculate the first moments of Δ_i using (19):

$$\begin{aligned}
\langle\Delta_i-\Delta_i{}^0\rangle_{\mathrm{Av}}=\bar{\delta}_i&=\pm\tfrac{1}{4}(eQ)(\tfrac{1}{2}ah^2)\int\frac{d\Omega}{4\pi}[6(m^4+n^4+l^4)-4]\\
&=\pm(eQ/4)(\tfrac{1}{2}ah^2)(-2/5),
\end{aligned} \tag{37b}$$

where the + sign applies for $i=1$, 6, and the minus sign for $i=2$, 3, 4, 5. This result should be compared with the case of a single crystal, where for $\mathbf{H}\|\langle 111\rangle$ we have

$$\delta_i=\pm(eQ/4)(\tfrac{1}{2}ah^2)(+2), \tag{38a}$$

and for $\mathbf{H}\|\langle 111\rangle$

$$\delta_i=\pm(eQ/4)(\tfrac{1}{2}ah^2)(-2). \tag{38b}$$

We find that in comparison to the maximum effect of the quadrupole interaction, powder measurements lead to a reduction by a factor of five. Furthermore, the lines will be broadened, and the line shapes will be distorted compared to the symmetric absorption spectrum which is usually obtained in a Mössbauer experiment.

B. Case (b): $T\lesssim\alpha$, $\beta\ll|\lambda|$, and the General Case

In the cases for which (28) and (31) apply, namely, $\mathbf{H}\|\langle 111\rangle$ or $\mathbf{H}\|\langle 100\rangle$, the former results are still of some use. In these cases we observe that, by symmetry, $\langle\mathbf{H}_n\rangle\|\mathbf{H}$, and the major axis of $\langle V_{ij}\rangle$ is parallel to **H**, $\eta=0$, and Eq. (36) still applies, giving the positions of the Mössbauer absorption lines. The results of a powder experiment in an external field are not included in the previous argument, since there the direction of **H** is

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[31] See, e.g., Ref. 1, Chap. 7.

[32] Ref. 1, p. 81.

[33] So that z' is not identical with z in Eq. (33).

[34] The isomer shift is already included in the choice of the zero point for the Δ_i.

[35] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. VII.

not unique throughout the material, as discussed for case (a).

The case of $\mathbf{h}$ in a general direction, as well as the general case, where no approximations apply, can be solved in the following manner: first $\langle V_{ij} \rangle$ and $\langle \mathbf{H}_n \rangle$ have to be calculated using the eigenstates of the ionic Hamiltonian (32). Then the Hamiltonian of the nuclear excited state (33) has to be diagonalized. Note that here z' is not identical with z, so the eigenstates obtained will not be eigenstates of I_z or $I_{z'}$. Once the four energy levels and eigenstates of $\mathcal{H}_e$ are known, and the two energy levels and eigenstates of $\mathcal{H}_g$ are calculated, the positions of the Mössbauer absorption lines are determined by the allowed nuclear γ-transition energies between them. This procedure, although straightforward in principle, calls for machine calculation, so that each case has to be treated separately with the relevant parameters of the problem, and no general expressions of the kind we have obtained in case (a) can be written down.

5. EXPERIMENTAL EVIDENCE AND CONCLUSIONS

On the experimental side, there have recently been a number of investigations which lend support to the theory described in the previous sections. Most of the results belong to the category of internal magnetic ordering.

The case of Fe^{2+} in NiO investigated by Siegwarth,[11] falls into the category of the "general case" (Secs. 3 and 4), since the transition temperature is 523°K, so for the temperature range investigated, $|h| \gtrsim T, |\lambda|$.

The case of $RbFeF_3$, which is an ideal (cubic) perovskite at room temperature and down to 102°K, has been until recently explained in terms of the above mechanism (Ganiel *et al.*,[17] Wertheim *et al.*[15]). However, careful x-ray measurements by Testardi *et al.*[18] revealed that this compound becomes tetragonal simultaneously with the magnetic transition, the ratio c/a increasing continuously as the temperature is lowered from 102° to 86°K, where a second transition takes place. This rules out our mechanism as an explanation for the appearance of a nonvanishing EFG, since the measured quadrupole splitting is *positive*, so that on the basis of the present theory one would expect a distortion (if any) which favors a $\langle 111 \rangle$ direction.

A favorable case for the application of the present theory is the case of $KFeF_3$, which is a cubic perovskite at room temperature.[36] As expected, the Mössbauer spectrum above the Néel temperature consists of a single peak. Magnetic measurements show that this compound becomes antiferromagnetic, where different authors find slightly different values for T_N.[37] Recent susceptibility measurements by Hirakawa[38] show the antiferromagnetic transition to occur at 122°K, and no spontaneous magnetization has been detected down to about 40°K. Fatehally *et al.*,[13] as well as Ganiel *et al.*[14] have found the onset of a quadrupole interaction to occur simultaneously with the magnetic hyperfine interaction. It should be noted that, since $T_N = 121°K$, and the region which fits the theory of the previous sections ranges down to 40°K, we already encounter a situation where $|h| \gtrsim |\lambda|, T$, so the procedure for the "general case" (Sec. 4) has to be applied.

The actual comparison of the experimental results with theory, however, presents certain difficulties. If we use, for this case, $\alpha = 0$, $\beta = h$, there arises the question of the sharp temperature dependence of h, which is not well known *a priori*.[39] Another problem is the value of vQ [v as defined in (15)], to which the quadrupole splitting is proportional. Estimates of Q ranging from 0.1 to 0.4 b can be found in the literature.[40] Furthermore, the quantity $v = (2/7)e\langle r^{-3} \rangle$ should be corrected for the effect of the electronic core as well as for covalency effects.[3] We therefore feel that it is preferable to rely on the abundance of data concerning the quadrupole splitting in paramagnetic ferrous compounds, in which the Fe^{2+} ion occupies a site of distorted octahedral symmetry. At low temperatures, the quadrupole splitting (in cases where the orbital ground state is a singlet) saturates typically at 3–4 mm/sec, so it is rather safe to take $evQ = 3.5$ mm/sec. For the calculation of $\mathbf{H}_n$ by (24), $\bar{A}$ and $\langle r^{-3} \rangle$ are needed. For $\langle r^{-3} \rangle$, a value of 4.4 a.u. has been used in this connection,[13,17] although higher estimates are found in the literature.[41] $\bar{A}$ can be estimated from the hyperfine field in FeF_3,[42] since in Fe^{3+} we expect the orbital and dipolar contributions to vanish (^6S term). This yields $\bar{A} \simeq 250$ kOe. A somewhat higher estimate ($\bar{A} = 275$ kOe) has been given for the free ion.[43] Although the quantities mentioned above seem to be known to within 10–15%, the situation is complicated by the fact that the orbital term and the contact term are of comparable magnitude, but their contributions to $\langle H_n \rangle$ are of opposite signs. Hence, a rather small change in each of them can change $\langle H_n \rangle$ considerably, and a good estimation of the dipolar contribution is essential.

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[36] A. Okazaki, Y. Suemune, and T. Fuchikami, J. Phys. Soc. Japan **14**, 1823 (1959).

[37] R. L. Martin *et al.*, Chem. Ind. (London) **3**, 38 (1956): $T_N = 115°K$; K. Hirakawa *et al.*, J. Phys. Soc. Japan **15**, 2063 (1960): $T_N = 113°K$; A. Okazaki *et al.* (Ref. 36): $T_N = 121°K$; Ganiel *et al.* (Ref. 14): $T_N = (121 \pm 1)°K$.

[38] K. Hirakawa (private communication).

[39] This is contrary to the case of Fe^{2+} in NiO, where $T_N = 523°K$. Siegwarth (see Ref. 11) dealt with temperatures below 295°K, where he could safely assume h to have reached its saturation value, and treat it as an adjustable parameter, independent of temperature.

[40] A. H. Muir, K. J. Ando, and H. M. Coogan, *Mössbauer Effect Data Index* (John Wiley & Sons, Inc., New York, 1966), p. 24; see also A. J. Nozik and M. Kaplan, Phys. Rev. **159**, 273 (1967); and A. H. Muir, Jr., H. Wiedersich, and J. O. Artman, in Proceedings of the Asilomar Conference on Hyperfine Interactions, 1967 (to be published).

[41] A. J. Freeman and R. E. Watson, Phys. Rev. **121**, 2566 (1963) ($\langle r^{-3} \rangle = 4.8$ a.u.).

[42] D. N. A. Buchanan and G. K. Wertheim [Bull. Am. Phys. Soc. **7**, 227 (1962)] give the value $H_n = 622$ kOe for Fe^{3+} in FeF_3.

[43] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

Fatehally *et al.*[13] have performed a fit of this kind, which shows the correct behavior of ΔE_Q and $\langle H_n \rangle$ versus temperature, although the quantitative agreement for $\langle H_n \rangle$ is not very good, which is not surprising in the light of the previous remarks.

An important feature, already mentioned above, which is of importance in the case of $KFeF_3$, is the fact that for $\mathbf{h} \,||\, \langle 111 \rangle$ the quadrupole splitting is positive, whereas for $\mathbf{h} \,||\, \langle 100 \rangle$ it is of the same magnitude, but negative. From symmetry considerations, one expects the magnetic axis to be parallel to either of these two directions in the case of cubic symmetry, at least near the transition point, so that in some cases a determination of the magnetic axis is possible from a Mössbauer experiment on a powder sample. A similar argument for Fe^{2+} in a tetrahedral site has been given by Eibschutz *et al.*[12] In $KFeF_3$ $\langle V_{zz} \rangle > 0$, so we believe the sublattice magnetization to be parallel to a $\langle 111 \rangle$ direction. This can be checked, in principle, by calculating the magnetocrystalline anisotropy. A calculation of this kind, assuming single ion anisotropy, has been performed for the case of $FeCr_2S_4$,[12] and the result conformed with the result anticipated by the analysis of the Mössbauer experiment. A similar calculation for the octahedral case would, however, demand incorporating the ^5E orbital states, since within $^5T_2$ the energy is isotropic with respect to the magnetic direction. (This is easily understood if one remembers the equivalence between T_2 and a triplet of p orbitals). On the experimental side, neutron diffraction experiments on a powder cannot determine the magnetic axis in a cubic compound. Hence a single-crystal experiment, using either neutron diffraction or magnetization measurements is needed in order to confirm the result which is obtained in the Mössbauer experiment on a powder sample.

Regarding the possibility of inducing the EFG by an external magnetic field, the relevant systems should be magnetically dilute solutions of Fe^{2+} ions in a cubic paramagnetic compound. Here a single-crystal experiment is highly favored, since in a powder experiment the lines will broaden and the effect will be smaller by about a factor of 5, so the possibility of its observation becomes negligible.

In a single crystal, using high external fields (H) and working at low temperatures (4°K) we estimate the following results, using (28), (29), and (31) and the values quoted above for A, $\langle r^{-3} \rangle$ and evQ: for $H = 5 \times 10^4$ Oe: $\Delta E_Q = \pm (eQ/2) \langle V_{zz} \rangle = 0.2$ mm/sec, $\langle H_n \rangle = -140$ kOe; for $H = 10^5$ Oe: $\Delta E_Q = 0.27$ mm/sec, $\langle H_n \rangle = -140$ kOe. These results are calculated for $\mathbf{H} \,||\, \langle 111 \rangle (\Delta E_Q > 0)$ or $\mathbf{H} \,||\, \langle 100 \rangle (\Delta E_Q < 0)$. The negative sign of $\langle H_n \rangle$ indicates that $\langle \mathbf{H}_n \rangle$ will be of opposite direction to the external field $\mathbf{H}$. It is interesting to note that $\langle H_n \rangle$ saturates at high fields, so that at 50 and 100 kOe we obtain the same result. Chappert *et al.*[44] report a saturation value of -120 kOe for $\mathbf{H}_n$ in the case of Fe^{2+} in MgO. The slight discrepancy can easily be attributed to the values of the parameters used in the calculation. It should be noted, however, that the full magnetic hyperfine splitting of the spectrum of Fe^{2+} in MgO was found to exist already for $H \sim 800$ Oe.[44] This phenomenon cannot be explained within the framework of the present theory, and is probably due to slow paramagnetic relaxation effects.[44] In this case, namely, Fe^{2+} in MgO, a quadrupole splitting has been observed even in the absence of an external magnetic field, at temperatures below 14°K.[44,45] This has been explained by Ham[46] as being caused by the combined effect of random strains which lift the degeneracy of the lowest spin-orbit triplet (T_{5g}), together with long electronic relaxation times between the levels of this triplet. In this paper we have considered only the case of an ideal crystal, namely, the case where no random strains are present, and furthermore, relaxation phenomena which may become pronounced at low temperatures (where electronic relaxation times become longer than $h/\Delta E_Q$) have not been considered.

On the other hand, when a large enough external magnetic field is applied, the electronic eigenstates are again determined by the Hamiltonian (32) and our calculation should give the correct result at low temperatures, where $g\mu_\beta H \gg kT$, g being the g factor of the lowest triplet. Leider and Pipkorn,[45] and Chappert, Frankel, and Blum[47] have independently found for Fe^{2+} in MgO, applying a field $H = 50$ kOe at $T = 4.2$°K, that $\Delta E_Q > 0$ for $\mathbf{H} \,||\, \langle 111 \rangle$, and $\Delta E_Q < 0$ for $\mathbf{H} \,||\, \langle 100 \rangle$, ΔE_Q being of equal magnitude in both cases: $|\Delta E_Q| \simeq 0.17$ mm/sec. Both the signs and the magnitude are in excellent agreement with our calculations.

Finally, we would like to point out that the effect of magnetic ordering on the electric quadrupole interactions should, in principle, be observed in other cases, too. Although the results obtained above are specific to the case of Fe^{2+}, the same principles can be applied in other cases. Ghatikar[48] has recently dealt with Zeeman field-dependent quadrupolar interactions in some rare-earth ions. Although in that case the dependence is of different origin than that which we have discussed in the present paper, it still adds interest to the general idea of mutual dependence between magnetic and electric hyperfine interactions, for which the Mössbauer effect is a very important tool of investigation.

APPENDIX A

We show here how the independent components of the tensor T_{ijkl} are determined. We have full cubic symmetry, so the symmetry class is $m3m$ (Birss,[22]

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[44] J. Chappert, R. B. Frankel, and N. A. Blum, Phys. Letters **25A**, 149 (1967).

[45] D. N. Pipkorn and H. R. Leider, Bull. Am. Phys. Soc. **11**, 49 (1966); and H. R. Leider and D. N. Pipkorn, Phys. Rev. **165**, 494 (1968).

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

[47] J. Chappert (private communication).

[48] M. N. Ghatikar, Proc. Phys. Soc. (London) **87**, 727 (1966).

Table II). T_{ijkl} is a polar tensor of rank 4. Writing the components as: $T_{ijkl}=ijkl$ we have, in principle, 4 independent components. If x, y, z are the cubic axes, then:

$$\begin{aligned} xxxx&=yyyy=zzzz=a,\\ xxyy&=yyxx=xxzz=zzxx=yyzz=zzyy=b,\\ xyxy&=yxyx=xzxz=zxzx=yzyz=zyzy=c,\\ xyyx&=yxxy=xzzx=zxxz=yzzy=zyyz=d. \end{aligned} \tag{A1}$$

Since $\nabla^2 V=0$, we have: $\sum_i V_{ii}=0$, and this leads to

$$b=-\tfrac{1}{2}a. \tag{A2}$$

Furthermore, since V_{ij} is quadratic in the components of $\mathbf{h}$, we immediately have

$$d=c. \tag{A3}$$

T_{ijkl} is therefore completely determined by calculating V_{ij} for two specific cases in which $\mathbf{h}$ is in two nonequivalent directions.

APPENDIX B

We start by proving Eq. (9). Let A and B be two noncommuting operators. Then, θ being a parameter,

$$\begin{aligned} d\{e^{-\theta A}e^{\theta(A+B)}\}/d\theta&=-Ae^{-\theta A}e^{\theta(A+B)}+e^{-\theta A}(A+B)e^{\theta(A+B)}\\ &=e^{-\theta A}Be^{\theta(A+B)}. \end{aligned}$$

Integrating, we have

$$e^{-\theta A}e^{\theta(A+B)}=1+\int_0^\theta e^{-XA}Be^{X(A+B)}dX.$$

Substituting $\theta=1$, and multiplying by e^A gives Eq. (9).

We now proceed to calculate $\langle V_{zz}\rangle$ from (8), using (13). In the integrals appearing at the r.h.s. of (13), we separate terms in which $E_n=E_{n'}$ from those where $E_n\neq E_{n'}$. After integrating and rearranging terms we have

$$\begin{aligned} [\exp(-\tau\mathcal{H})]_{nn'}={}&\exp(-\tau E_n)\delta_{nn'}-\tau\exp(-\tau E_n)(\alpha L_z+\beta S_z)_{nn'}\delta(E_n,E_{n'})\\ &+[1-\delta(E_n,E_{n'})](\alpha L_z+\beta S_z)_{nn'}[\exp(-\tau E_n)-\exp(-\tau E_{n'})]/(E_n-E_{n'})\\ &+\tfrac{1}{2}\tau^2\exp(-\tau E_n)\sum_{n''}\delta(E_{n'},E_{n''})\delta(E_n,E_{n''})(\alpha L_z+\beta S_z)_{nn''}(\alpha L_z+\beta S_z)_{n''n'}\\ &+\tau\sum_{n''}\{\delta(E_{n'},E_{n''})[1-\delta(E_n,E_{n''})][\exp(-\tau E_{n''})/(E_n-E_{n''})]\\ &+\delta(E_n,E_{n'})[1-\delta(E_{n'},E_{n''})][\exp(-\tau E_n)/(E_{n''}-E_{n'})]-\delta(E_n,E_{n''})\\ &\times[1-\delta(E_{n'},E_{n''})][\exp(-\tau E_n)/(E_{n''}-E_{n'})]\}(\alpha L_z+\beta S_z)_{nn''}(\alpha L_z+\beta S_z)_{n''n'}\\ &+\sum_{n''}\{\delta(E_{n'},E_{n''})[1-\delta(E_n,E_{n''})][\exp(-\tau E_n)-\exp(-\tau E_{n''})]/(E_n-E_{n''})^2\\ &+[1-\delta(E_{n'},E_{n''})][1-\delta(E_n,E_{n'})][\exp(-\tau E_n)-\exp(-\tau E_{n'})]/[(E_n-E_{n'})(E_{n'}-E_{n''})]\\ &+[1-\delta(E_{n'},E_{n''})][1-\delta(E_n,E_{n''})][\exp(-\tau E_n)-\exp(-\tau E_{n''})]/[(E_n-E_{n''})(E_{n''}-E_{n'})]\}\\ &\times(\alpha L_z+\beta S_z)_{nn''}(\alpha L_z+\beta S_z)_{n''n'}, \end{aligned} \tag{B1}$$

where

$$\begin{aligned} \delta(a,b)&=0, \quad \text{for} \quad a\neq b\\ &=1, \quad \text{for} \quad a=b. \end{aligned}$$

Since α and β are proportional to h, the first term is of order zero in h, the next two terms are of first order in h, and all other terms are of second order.

We are interested in

$$\langle V_{zz}\rangle=\mathrm{Tr}[\exp(-\tau\mathcal{H})V_{zz}]/\mathrm{Tr}[\exp(-\tau\mathcal{H})] \tag{B2}$$

to second order in h. Calculating

$$\mathrm{Tr}[\exp(-\tau\mathcal{H})V_{zz}]=\sum_{n,n'}[\exp(-\tau\mathcal{H})]_{nn'}(V_{zz})_{n'n}, \tag{B3}$$

we find, as expected, that zero- and first-order contributions in h vanish, so that only second-order terms in h remain, and in the denominator of (B2) we need only zero-order terms. Taking the form of the matrices $\mathcal{H}_0$,

$\alpha L_z+\beta S_z$, and V_{zz} into account, we obtain

$$\begin{aligned}\mathrm{Tr}[\exp(-\tau\mathcal{H})V_{zz}]=&\tfrac{1}{2}\tau^2\sum_n \exp(-\tau E_n)(\alpha L_z+\beta S_z)_{nn}{}^2(V_{zz})_{nn}\\ &+\tau\sum_{n,n'}\{(1-\delta_{nn'})(\alpha L_z+\beta S_z)_{nn'}{}^2(V_{zz})_{nn}[\exp(-\tau E_n)/(E_{n'}-E_n)]\\ &-(1-\delta_{nn'})(\alpha L_z+\beta S_z)_{nn'}(\alpha L_z+\beta S_z)_{n'n'}(V_{zz})_{n'n}[2\exp(-\tau E_{n'})/(E_{n'}-E_n)]\}\\ &+\sum_{n,n'}\{\sum_{n''}\{(1-\delta_{nn'})(1-\delta_{n'n''})[(\alpha L_z+\beta S_z)_{nn''}(\alpha L_z+\beta S_z)_{n''n'}(V_{zz})_{n'n}\\ &+(\alpha L_z+\beta S_z)_{nn'}(\alpha L_z+\beta S_z)_{n'n''}(V_{zz})_{n''n}][\exp(-\tau E_n)-\exp(-\tau E_{n'})]/[(E_n-E_{n'})(E_{n'}-E_{n''})]\}\\ &+(1-\delta_{nn'})(\alpha L_z+\beta S_z)_{nn'}(\alpha L_z+\beta S_z)_{n'n'}(V_{zz})_{n'n}[\exp(-\tau E_n)-\exp(-\tau E_{n'})]/(E_n-E_{n'})^2]\}.\end{aligned}\tag{B4}$$

This result, divided by

$$\sum_n \exp(-\tau E_n)=3+5e^{2\lambda/T}+e^{5\lambda/T},\tag{B5}$$

gives $\langle V_{zz}\rangle$ to second order in h. Substituting the values of the matrix elements and performing the summations, we obtain Eq. (17).

APPENDIX C

As shown in Appendix A, only two independent components of T_{ijkl} remain to be determined: a and c. If we denote the r.h.s. of Eq. (17), divided by h^2 (with $v>0$) by γ, then for **h** parallel to a $\langle 100\rangle$ direction we have

$$\langle V_{zz}{}^h\rangle=\gamma h^2,$$

and for **h** parallel to a $\langle 111\rangle$ direction we obtain

$$\langle V_{zz}{}^h\rangle=-\gamma h^2.$$

For the first case $\mathbf{h}=h(1,0,0)$. Using (7) and (A1) we have

$$ah^2=\gamma h^2,$$

so that

$$\gamma=a.\tag{C1}$$

For the second case: $\mathbf{h}=(h/\sqrt{3})(1,1,1)$, so we obtain ($x$, y, z denoting the cubic axes)

$$\langle V_{xx}\rangle=\langle V_{yy}\rangle=\langle V_{zz}\rangle=0,$$

$$\langle V_{xy}\rangle=\langle V_{yx}\rangle=\langle V_{xz}\rangle=\langle V_{zx}\rangle=\langle V_{yz}\rangle=\langle V_{zy}\rangle=\tfrac{2}{3}ch^2.$$

In order to evaluate c, we diagonalize $\langle V_{ij}\rangle$, so that it is written in a coordinate system where the z axis is parallel to **h**. This performed, we obtain

$$\langle V_{zz}{}^h\rangle=-2\langle V_{xx}{}^h\rangle=-2\langle V_{yy}{}^h\rangle=\tfrac{4}{3}ch^2;$$

hence,

$$(\tfrac{4}{3})ch^2=-\gamma h^2=-ah^2,$$

$$c=-\tfrac{3}{4}a.\tag{C2}$$

(C1) and (C2) determine T_{ijkl} completely.

Let **h** be in an arbitrary direction, so that $\mathbf{h}=h(m,n,l)$ where m, n, l are the direction cosines of **h**. Then, using (7), $\langle V_{ij}\rangle$ in the cubic coordinate system is given by

$$\begin{aligned}&\langle V_{xx}\rangle=\tfrac{1}{2}ah^2(3m^2-1),\\ &\langle V_{yy}\rangle=\tfrac{1}{2}ah^2(3n^2-1),\\ &\langle V_{zz}\rangle=\tfrac{1}{2}ah^2(3l^2-1),\\ &\langle V_{xy}\rangle=\langle V_{yx}\rangle=-\tfrac{3}{2}ah^2mn,\\ &\langle V_{xz}\rangle=\langle V_{zx}\rangle=-\tfrac{3}{2}ah^2ml,\\ &\langle V_{yz}\rangle=\langle V_{zy}\rangle=-\tfrac{3}{2}ah^2nl.\end{aligned}\tag{C3}$$

For the determination of the nuclear energy levels, which are needed later, we want $\langle V_{ij}{}^h\rangle$, namely the components of $\langle V_{ij}\rangle$, in a coordinate system in which the z axis is parallel to **h**. This is obtained by performing an orthogonal transformation, using standard transformation techniques. A transformation matrix T is found, which transforms the right handed triad of unit vectors of the cubic system into the three new unit vectors. T is given by

$$\begin{aligned}&T_{xx}=n/(1-l^2)^{1/2},\\ &T_{xy}=-m/(1-l^2)^{1/2},\\ &T_{xz}=0;\\ &T_{yx}=ml/(1-l^2)^{1/2},\\ &T_{yy}=nl/(1-l^2)^{1/2},\\ &T_{yz}=-(1-l^2)^{1/2};\\ &T_{zx}=m,\\ &T_{zy}=n,\\ &T_{zz}=l.\end{aligned}$$

$\langle V_{ij}{}^h\rangle$ is then obtained from

$$\langle V_{ij}{}^h\rangle=\sum_{r,s}T_{ir}T_{js}V_{rs},\text{ and hence Eq. (19).}$$