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Mössbauer Spectrum of Fe^{2+} in MgO

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The appearance of a quadrupole doublet in the Mössbauer spectrum of Fe^{2+} in MgO at $T<14°K$, as observed originally by Pipkorn and Leider, is explained on the basis of crystal-field theory. The doublet is the result of the electric field gradient produced at the nucleus by the valence electrons of Fe^{2+}, combined with long electronic relaxation times and the effect of random strains in lifting the electronic degeneracy of the ground-state triplet by $\sim 10^{-2}$ cm^{-1}. Although the Jahn-Teller effect plays no essential role in the appearance of the doublet, it may change its splitting slightly and cause broadening. An Orbach-type process is proposed for the electronic relaxation that is responsible for motional narrowing of the doublet for $T>14°K$. The form predicted for the Mössbauer spectrum is also given for zero strain and for an applied magnetic field; in the latter case, in addition to a hyperfine splitting, there is a quadrupole splitting which changes sign as $\mathbf{H}$ rotates from [100] to [111].

I. INTRODUCTION

THE Mössbauer spectrum of Fe^{2+} in single crystals of MgO has been reported by Pipkorn and Leider[1] and by Frankel and Blum.[2] In these experiments, a single line was observed at temperatures above 14°K, but below 14°K a resolved quadrupole doublet was found with a peak separation of 0.27 mm/sec. Since Fe was in dilute concentration in the crystals used ($\sim$0.03 atomic % in the work of Ref. 1), and since the Fe^{2+} ions should have been at sites of undistorted cubic symmetry, Pipkorn and Leider[1] suggested that the quadrupole splitting might be due to a Jahn-Teller distortion which reoriented sufficiently rapidly above 14°K to produce a motional narrowing of the spectrum. The purpose of this paper is to show that a quadrupole doublet of approximately this splitting is to be expected at sufficiently low temperatures simply on the basis of crystal-field theory, as the result of the electric field gradient produced at the nucleus by the valence electrons of Fe^{2+}, combined with the effect of random strains in the MgO crystals and suitably long electronic relaxation times. No distortion from cubic symmetry arising from a Jahn-Teller effect is therefore required to account for these data. In fact, as will be discussed, paramagnetic resonance studies[3,4] of Fe^{2+} in MgO rule out the possibility of any static Jahn-Teller distortion for this ion. A dynamic Jahn-Teller effect consistent with the EPR data will be shown to lead to only minor changes in the predicted quadrupole doublet obtained from the static crystal field model, the principal qualitative change being a possible broadening of the doublet when the strains are random.

The paper will also consider the possible origin of the electronic relaxation mechanism that is evidently responsible for motional narrowing of the doublet at 14°K. We give also the form expected for the Mössbauer spectrum in the absence of strain, and in the presence of an external magnetic field.

In this paper we shall be content to present the principal features of the model which seems to be in at least semiquantitative agreement with the experimental data now available. A more detailed quantitative analysis of the various parameters affecting the Mössbauer and EPR spectra of Fe^{2+} in MgO will be deferred until another time.

II. CRYSTAL FIELD MODEL WITH RANDOM STRAIN

The ground electronic state of Fe^{2+} in cubic symmetry (octahedral coordination) is a spin-orbit triplet Γ_{5g} from the term ${}^5T_{2g}$.[3] Within this triplet, the interaction[5]

$$\mathcal{H}_Q=\frac{e^2Q}{2I(2I-1)}\sum_k\left[\frac{I(I+1)}{r_k^3}-\frac{3(\mathbf{r}_k\cdot\mathbf{I})^2}{r_k^5}\right] \quad (1)$$

between the electric field gradient produced at the nucleus by the valence electrons of Fe^{2+} and the nuclear quadrupole moment Q of Fe^{57m} may be represented by the operator

$$\begin{aligned}\mathcal{H}_Q'=(c_3/4)\{&[3J_z^2-J(J+1)][3I_z^2-I(I+1)]\\&+3[J_x^2-J_y^2][I_x^2-I_y^2]\}\\&+c_5\{(J_yJ_z+J_zJ_y)(I_yI_z+I_zI_y)\\&+(J_zJ_x+J_xJ_z)(I_zI_x+I_xI_z)\\&+(J_xJ_y+J_yJ_x)(I_xI_y+I_yI_x)\}. \quad (2)\end{aligned}$$

Here $\mathbf{I}$ is the nuclear spin operator ($I=\frac{3}{2}$), and $\mathbf{J}$ is the effective spin operator ($J=1$) for the triplet. The vector components in Eq. (2) are referred to the cubic axes x, y, z of the octahedron. While the general form of $\mathcal{H}_Q'$ in Eq. (2) is dictated by the cubic symmetry, we

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

[2] R. B. Frankel and N. A. Blum, Bull. Am. Phys. Soc. **12**, 24 (1967).

[3] W. Low and M. Weger, Phys. Rev. **118**, 1119, 1130 (1960); **120**, 2277 (1960).

[4] D. H. McMahon, Phys. Rev. **134**, A128 (1964).

[5] M. H. Cohen and F. Reif in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 321.

find, by evaluating the matrix elements of $\mathcal{H}_Q$ in Eq. (1) using the $3d^6$ wave functions[3] for the lowest Γ_{5g} spin-orbit level, that c_3 and c_5 are given by crystal field theory to have the value

$$-3c_3 = +4c_5 = +(\tfrac{3}{35})\langle r^{-3}\rangle(1-R)e^2Q/[I(2I-1)]. \tag{3}$$

Here $\langle r^{-3}\rangle$ is the one-electron expectation value of r^{-3}, and we have included in Eq. (3) the Sternheimer factor $(1-R)$ for the valence electrons of Fe^{2+}.[6]

In the presence of an arbitrary static strain (strain splitting small compared to spin-orbit splitting) each electronic eigenstate derived from Γ_{5g} takes the form

$$|\psi\rangle = a|\xi\rangle + b|\eta\rangle + c|\zeta\rangle, \tag{4}$$

where $|\xi\rangle$, $|\eta\rangle$, $|\zeta\rangle$ are the three Γ_{5g} states transforming respectively as yz, zx, xy, and a, b, c are *real* coefficients $[(a^2+b^2+c^2)=1]$. The diagonal matrix element of the operator (2) with respect to such a state is given by

$$\begin{aligned}\langle\psi|\mathcal{H}_Q'|\psi\rangle = &-(c_3/4)\{[3c^2-1][3I_z^2-I(I+1)]\\ &+3[a^2-b^2][I_x^2-I_y^2]\} - 2c_5\{bc(I_yI_z+I_zI_y)\\ &+ac(I_zI_x+I_xI_z)+ab(I_xI_y+I_yI_x)\},\end{aligned} \tag{5}$$

which thus gives the nuclear Hamiltonian corresponding to the electronic state (4).[7] For $I=\frac{3}{2}$, we can find the eigenvalues of Eq. (5) exactly: there are two doublets with energies given by $E=\pm(\frac{1}{2})\Delta E$, where

$$\Delta E = 3[c_3^2+(\tfrac{1}{3})(16c_5^2-9c_3^2)(a^2b^2+b^2c^2+c^2a^2)]^{1/2}. \tag{6}$$

Moreover, if c_3 and c_5 are related as in Eq. (3), we obtain from Eq. (6) a quadrupole splitting

$$\Delta E = (\tfrac{2}{70})\langle r^{-3}\rangle e^2Q(1-R), \tag{7}$$

which is independent of the choice of the (real) coefficients a, b, c in Eq. (4).

Therefore, if random strains at the site of an Fe^{2+} ion suffice to completely lift the threefold degeneracy of Γ_{5g} by energy differences larger than the energy of interaction between the valence electrons and the nuclear spin (due to quadrupole and hyperfine interactions), three nondegenerate electronic states of the form (4) result, and according to crystal-field theory each of these produces an identical quadrupole splitting ΔE for Fe^{57m} given by Eq. (7). We may expect, then, to observe a quadrupole doublet in the Mössbauer spectrum (in the absence of an external magnetic field) at temperatures sufficiently low that the relaxation time τ for electronic transitions among the three states is long compared to $\hbar/\Delta E$, if such strains are present at the site of a typical Fe^{2+} ion.

We have obtained estimates of the internal strains in typical single crystals of MgO from two studies of paramagnetic resonance line shapes, that of McMahon[4] for Fe^{2+}, and that of Feher[8] for Mn^{2+} and Fe^{3+}. From both sources we find values of the order of at least 2×10^{-5} in the various samples. Since the strain coefficients[9] for the splitting of Γ_{5g} of Fe^{2+} in MgO are $G_{11}=+800$, $G_{44}=+540$ cm^{-1}/unit strain, such internal strains are of quite sufficient magnitude to cause a splitting of Γ_{5g} large compared to the hyperfine and quadrupole interactions.[10]

The quadrupole splitting $\Delta E=0.27$ mm/sec found by Pipkorn and Leider is only about $\frac{1}{10}$ of that found[6] for Fe^{2+} in such crystals as $FeSO_4$ in which the Fe^{2+} experiences a strong noncubic crystal field. However, this is exactly the result predicted by Eq. (7), which gives for ΔE a value $\frac{1}{10}$ that obtained[6] if the ground state is an orbital singlet produced by a crystal-field splitting of $^5T_2$ which is stronger than the spin-orbit splitting.[11]

III. JAHN-TELLER EFFECTS

Paramagnetic resonance studies[3,4] of Fe^{2+} in MgO show conclusively that Jahn-Teller effects in the Γ_{5g} ground state are weak. The observed g factor is isotropic and has the value 3.428. The difference between this and the value ~3.5 given by crystal-field theory can plausibly be attributed to the effects of covalent bonding.[3] If a static Jahn-Teller distortion occurred, the low-temperature resonance spectrum should be the superposition of several anisotropic spectra with g factors near 2. One can therefore rule out the possibility of a static Jahn-Teller distortion for Fe^{2+} in MgO. A moderately strong dynamic Jahn-Teller effect,[12] while preserving an isotropic g factor, would reduce its value towards $g\sim3.0$ by dynamic quenching of the orbital part of the Zeeman interaction. However, the orbital-reduction factor associated with the orbital contribution to the g factor is approximately 0.8.[3] Thus, an upper bound of ~20% can be placed on the combined effects of covalent bonding and dynamic quenching in reducing this parameter, and as we have noted, this reduction may be largely due to covalent bonding. Even if this reduction is in part due to dynamic quenching, as the author has suggested previously,[12] the effects of Jahn-Teller coupling on the Γ_{5g} ground state are at most of very modest size.

The small effect of Jahn-Teller coupling on octa-

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

[7] The diagonal matrix element of the hyperfine interaction with respect to the state (4) is zero because the coefficients a, b, c in Eq. (4) are real.

[8] E. R. Feher, Phys. Rev. **136**, A145 (1964).

[9] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).

[10] The magnitude of the effective field at the nucleus due to the hyperfine interaction is 128 kOe for Fe^{2+} in MgO (Ref. 2).

[11] This factor of $\frac{1}{10}$ is the same factor noted by Van Vleck in Ref. 13 in explaining the evident absence of a Jahn-Teller effect in the ground state of Fe^{2+} in MgO.

[12] F. S. Ham, Phys. Rev. **138**, A1727 (1965); see in particular the discussion in connection with Eq. (2.39) and with Table II.

hedral Fe^{2+} was explained by Van Vleck[13] and Liehr,[14] who pointed out that the matrix elements of the Jahn-Teller interaction within the Γ_{5g} ground-state triplet are reduced by a factor of $\frac{1}{10}$ compared to matrix elements between the *orbital* triplet states of ${}^5T_{2g}$. This explanation assumes that the Jahn-Teller interaction is weaker than the spin-orbit interaction. There is, however, reason[12] to question this assumption; if the two interactions are of comparable strength, significant Jahn-Teller corrections to the parameters of the Γ_{5g} level are then definitely to be expected, but the theory of this complicated case has not been worked out.

A dynamic Jahn-Teller effect will affect the quadrupole splitting of the Mössbauer spectrum by changing the values of the parameters c_3 and c_5 in Eq. (2) which determine the effect of the quadrupole interaction within the ground-state Γ_{5g} triplet. Apart from this change, the calculation of the quadrupole splitting in the presence of a dynamic Jahn-Teller effect is identical with that given in Sec. II for simple crystal-field theory. However, the fractional changes in c_3 and c_5 will usually be different, so that the ratio (c_3/c_5) may now depart from the value $-\frac{4}{3}$ given by Eq. (3). Since it was this value for this ratio that led the quadrupole splitting ΔE as given by Eq. (6) to be independent of the choice of the coefficients a, b, c in Eq. (4), we see that a dynamic Jahn-Teller effect may lead to a quadrupole splitting which, unlike Eq. (7), does depend on the strain. Accordingly, if the local strains are randomly oriented, the quadrupole doublet expected in the low-temperature Mössbauer spectrum on the basis of Eq. (6) will now be broadened.

The change in c_3 and c_5 caused by the Jahn-Teller coupling is an example of the general phenomenon which shows up in other cases as the dynamic quenching of orbital operators by a dynamic Jahn-Teller effect.[12,15] However, the case of Fe^{2+} in MgO is complicated, as we have already noted, because the Jahn-Teller energy is evidently of the same order of magnitude as the separation of the spin-orbit levels, and these levels are coupled by the Jahn-Teller interaction. Accordingly, c_3 or c_5 may in this case actually be increased by the Jahn-Teller coupling. A perturbation calculation suggests, however, that the changes in c_3 and c_5 from their crystal-field value of Eq. (3) (as modified by covalent bonding through a change of $\langle r^{-3}\rangle$) are less than some 10% so long as the Jahn-Teller energy[16] E_{JT} is less than the spin-orbit parameter λ.

Thus, a dynamic Jahn-Teller effect will change c_3 and c_5 from their values given by crystal field theory, but for Fe^{2+} in MgO we do not expect such changes to be large.

It should be remarked that a dynamic Jahn-Teller effect does not lift the degeneracy of the Γ_{5g} ground state of the Fe^{2+} ion (this state must now be viewed as an eigenstate of the Hamiltonian of overall cubic symmetry describing the coupled system of electrons and phonons). Therefore, a dynamic Jahn-Teller effect can in no sense substitute for the random strains (due to other impurity ions or crystal defects) which represent true departures from cubic symmetry for a given Fe^{2+} ion and are required to lift the degeneracy of Γ_{5g} as described in Sec. II so that the quadrupole doublet described by Eqs. (6) or (7) may be observed.

IV. RELAXATION MECHANISMS

On the basis of our proposed model, the disappearance of the quadrupole doublet above 14°K must be attributed to motional narrowing resulting from rapid electronic transitions among the three strain-split states of each Fe^{2+} ion ($\tau \ll \hbar/\Delta E$ for $T > 14°\mathrm{K}$). If the strain splitting is much less than kT, the average of Eq. (5) over the three states is zero, and the quadrupole doublet will be replaced by a single line above 14°K, as observed. Even though the quadrupole splitting ΔE given by Eq. (7) is the same for each of the three states, the orientation of the electric field gradient at the nucleus depends on the state. When reorientation occurs rapidly with respect to the quadrupole precession time, as a result of rapid electronic transitions among the states, the nucleus sees an effectively isotropic field if the three states are equally probable, and the quadrupole splitting vanishes. If this explanation is correct, the electronic relaxation time τ in Γ_{5g} must be $\sim\hbar/\Delta E = 5\times10^{-8}$ sec at $T = 14°\mathrm{K}$.

So far as we are aware, the relaxation time of Fe^{2+} in MgO has not been measured at temperatures $\sim$14°K, so that we have no experimental value for τ with which to compare this estimate from the Mössbauer data. On theoretical grounds, however, we believe this value is reasonable. To demonstrate this, we have calculated the transition probability P per unit time for phonon-induced transitions between two of the Γ_{5g} states, say $\zeta \rightarrow \xi$. Since direct processes[17] are very much too slow to account for the observed relaxation, because of the small separation ($\sim 10^{-2}$ cm^{-1}) of the strain-split levels, we must consider Raman processes, and Orbach processes[17] involving the higher spin-orbit levels of Fe^{2+}.

It appears that Raman processes are unable to account for this value of τ, unless the long-wave approximation used to calculate P can possibly lead to an underestimation of P by a factor of $\sim 10^3$. There are several Raman processes because of the various intermediate states available, but a representative value is given by the process in which the intermediate state is

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[13] J. H. Van Vleck, Physica **26**, 544 (1960); Disc. Faraday Soc. **26**, 98 (1958).

[14] A. D. Liehr, Bell System Tech. J. **39**, 1617 (1960).

[15] W. C. Scott and M. D. Sturge, Phys. Rev. **146**, 262 (1966).

[16] For the precise definition of E_{JT} in the various cases, see Ref. (12).

[17] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

also a state of Γ_{5g}. We obtain for this process the value

$$P\sim\frac{6(kT)^5G_{44}{}^2(4G_{44}{}^2+9G_{11}{}^2)}{25\pi^3\rho^2\hbar^7v_T{}^{10}}\left[1+\frac{2}{3}\left(\frac{v_T}{v_L}\right)^5\right]^2, \quad (8)$$

where $\rho(=3.58\ \text{g/cm}^3)$ is the density of MgO, and v_T and v_L are the velocities of propagation of transverse and longitudinal acoustic waves, respectively. From values[9] of the strain coefficients, using $v_T=6.5\times10^5$ cm/sec and $v_L=9.1\times10^5$ cm/sec obtained from the elastic constants[18] of MgO, we obtain from Eq. (8) the result $\tau\sim(1/3P)\sim1\times10^{-4}$ sec at $T=14°$K. This value is much too long to account for the motional narrowing.

A more likely process is the Orbach process through the next higher spin-orbit level of Fe^{2+} (the Γ_{3g} and Γ_{4g} states which are given by crystal-field theory to lie an energy $\Delta\sim2\,|\,\lambda\,|$ above Γ_{5g}, where λ is the spin-orbit parameter). We calculate for this process that at low temperatures P is given approximately by

$$P\sim\frac{2G_{44}{}^2\Delta^3}{\pi\rho\hbar^4v_T{}^5}\left[1+\frac{2}{3}\left(\frac{v_T}{v_L}\right)^5\right]\exp(-\Delta/kT), \quad (9)$$

where we have again used the long-wave approximation to relate the phonon matrix elements to the known strain parameters for Γ_{5g}. Evaluating Eq. (9) using the free ion value $|\,\lambda\,|=100\ \text{cm}^{-1}$, we obtain $\tau\sim(1/3P)\sim 3\times10^{-4}$ sec at $T=14°$K, a value also much too long to account for the motional narrowing. However, whereas P calculated for the Raman processes varies only moderately[19] with Δ, the value of P obtained from Eq. (9) depends very strongly on Δ at low temperatures because of the factor $\exp(-\Delta/kT)$. If we use Eq. (9) to determine the value of Δ that would give $(1/3P)\sim 5\times10^{-8}$ sec at 14°K, we obtain $\Delta=95\ \text{cm}^{-1}$. Such a reduced energy separation from Γ_{5g} to Γ_{3g} and/or Γ_{4g} is not unreasonable: Covalent bonding can be expected to reduce λ by up to perhaps 30% relative to free ion values; moreover, the coupling of the Γ_{3g} and Γ_{4g} levels to strains is predicted by theory to be five times stronger than that of Γ_{5g}, and an estimate of the Jahn-Teller displacement of the Γ_{3g}, Γ_{4g}, and Γ_{5g} levels shows that the first two may very well be depressed by 50–100 cm^{-1} relative to Γ_{5g}.

V. MÖSSBAUER SPECTRUM IN ZERO STRAIN

If strains were negligible, there would still be a splitting of the Mössbauer spectrum in the low-temperature region where the relaxation time is long, even in the absence of a magnetic field. This case may be of no experimental interest, since to study it we should need MgO crystals of much greater perfection than those used in the work to date. However, we give the results for this case in order to give emphasis to the vital role played by the strains in the model offered in Sec. II to account for the quadrupole doublet found experimentally.

The nuclear state of $Fe^{57m}(I=\frac{3}{2})$ belongs to the irreducible representation[20] Γ_8 of the rotation group of the cube. Since $\Gamma_5\times\Gamma_8=\Gamma_6+\Gamma_7+2\Gamma_8$, we obtain in perfect cubic symmetry four energy levels of the coupled electron-nuclear system corresponding to the excited Mössbauer state. To evaluate these energy levels we must now add the hyperfine interaction $B_1\mathbf{I}\cdot\mathbf{J}$ to $\mathcal{H}_Q'$ in Eq. (2). The exact eigenvalues of the resulting Hamiltonian are the following:

$$\Gamma_6:\quad E=-(\tfrac{3}{2})c_3+3c_5+(\tfrac{3}{2})B_1,$$

$$\Gamma_7:\quad E=+(\tfrac{3}{2})c_3+3c_5-(\tfrac{5}{2})B_1,$$

$$\Gamma_8:\quad E=-(\tfrac{3}{2})c_5+(\tfrac{1}{4})B_1\pm\{(\tfrac{9}{4})[c_3{}^2+c_5{}^2]+(\tfrac{25}{16})B_1{}^2 +3B_1[c_3+(\tfrac{3}{4})c_5]\}^{1/2}. \quad (10)$$

The nuclear ground state $(I=\frac{1}{2})$ is Γ_6, and since $\Gamma_5\times\Gamma_6=\Gamma_7+\Gamma_8$ there are two levels of this state, in which the only interaction is the hyperfine interaction $B_0\mathbf{J}\cdot\mathbf{I}$:

$$\Gamma_7:\quad E=-B_0,$$

$$\Gamma_8:\quad E=+(\tfrac{1}{2})B_0. \quad (11)$$

Since magnetic-dipole selection rules allow all transitions between the levels of Eq. (10) and those of Eq. (11) except $\Gamma_6\rightarrow\Gamma_7$, the Mössbauer spectrum for the perfect cubic symmetry may therefore show seven distinct lines at low temperatures if all the lines can be resolved.

VI. MÖSSBAUER SPECTRUM IN A MAGNETIC FIELD

Frankel and Blum[2] have found that by applying an external magnetic field, a hyperfine pattern in the Mössbauer spectrum may be developed. At 4.2°K this hyperfine structure began to appear for fields ~250 Oe and was fully developed at ~750 Oe. These results are consistent with the model of Sec. II, as we will now show.

When a magnetic field $\mathbf{H}$ is applied to the model of Sec. II, with H large enough so that the Zeeman splitting of Γ_{5g} is larger than the strain splitting, the electronic eigenstates are then the eigenstates of J_ζ with $J_\zeta'=0, \pm1$ (where $\hat{\zeta}$ is in the direction of $\mathbf{H}$) instead of being determined by the strain. The nuclear Hamiltonian for Fe^{57m} corresponding to each electronic state

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[18] A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. **122**, 1469 (1961).

[19] The value of P obtained from Eq. (8) of course does not depend at all on the energy of the excited spin-orbit levels, but contributions from other Raman processes in which the intermediate state is an excited level vary approximately as the inverse square of the energy difference.

[20] Our notation for the irreducible representations of the group O agrees with that of G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (The M.I.T. Press, Cambridge, Massachusetts, 1963), p. 88.

is then given by the part of Eq. (2) which is diagonal with respect to J_ζ', to which must be added the hyperfine and nuclear Zeeman terms. Thus, instead of $\langle\psi\,|\,\mathcal{H}_Q'\,|\,\psi\rangle$ from Eq. (5), we now have

$$\begin{aligned}\langle J_\zeta'\,|\,\mathcal{H}'\,|\,J_\zeta'\rangle &= B_1 I_\zeta J_\zeta' - g_1\beta_N I_\zeta H \\ &+[(\tfrac{3}{2})(J_\zeta')^2-1][\![(c_3/4)\{[3\zeta_z^2-1][3I_z^2-I(I+1)] \\ &+3[\zeta_x^2-\zeta_y^2][I_x^2-I_y^2]\}+2c_5\{\zeta_y\zeta_z(I_yI_z+I_zI_y) \\ &+\zeta_x\zeta_z(I_zI_x+I_xI_z)+\zeta_x\zeta_y(I_xI_y+I_yI_x)\}]\!], \qquad (12)\end{aligned}$$

while in the Mössbauer ground state we have

$$\langle J_\zeta'\,|\,\mathcal{H}'\,|\,J_\zeta'\rangle = B_0 I_\zeta J_\zeta' - g_0\beta_N I_\zeta H. \qquad (13)$$

Here g_1, g_0 are the nuclear g factors for the excited and ground states, respectively, β_N is the nuclear magneton, and ζ_x, ζ_y, ζ_z denote the direction cosines of **H** with respect to the cubic axes. From Eqs. (12) and (13) it is clear that the Mössbauer spectrum should now show both hyperfine and quadrupole splittings.

To evaluate the dependence of the quadrupole splittings on the orientation of **H**, for the Mössbauer spectra corresponding to the electronic states $J_\zeta=\pm1$, we make the approximation that the Zeeman splitting of the nuclear levels (including that due to the internal field[10] arising from the hyperfine interaction), is large compared to the quadrupole splitting. Keeping therefore only those parts of the quadrupole terms in Eq. (12) which are diagonal with respect to I_ζ, we then obtain for the quadrupole splitting {here we define $\Delta E \equiv (\tfrac{1}{2})[E(I_\zeta=+\tfrac{3}{2})+E(-\tfrac{3}{2})-E(+\tfrac{1}{2})-E(-\tfrac{1}{2})]$}

$$\Delta E = (\tfrac{3}{2})[c_3+(4c_5-3c_3)(\zeta_x^2\zeta_y^2+\zeta_y^2\zeta_z^2+\zeta_z^2\zeta_x^2)]. \qquad (14)$$

For **H** along [100] or [111], Eq. (14) is exact, so that ΔE is given for these two directions by $+(\tfrac{3}{2})c_3$ and $+2c_5$, respectively; according to Eq. (3) these values have the same magnitude [one-half that given by Eq. (7)] for the crystal-field model, but opposite signs.

For the state with $J_\zeta'=0$ there is no hyperfine field at the nucleus. Therefore, as long as H is small enough so that $g_1\beta_N IH$ is smaller than the linewidth, this spectrum appears for arbitrary orientation of **H** as a quadrupole doublet with a splitting identical to that obtained by substituting ζ_x, ζ_y, ζ_z for a, b, c in Eq. (6).

VII. DISCUSSION

We have shown that a quadrupole doublet is to be expected on the basis of simple crystal-field theory, at suitably low temperatures, in the Mössbauer spectrum of octahedral Fe^{2+} if random strains in the crystal are of sufficient magnitude, even though the Fe^{2+} site symmetry is completely cubic. We propose therefore that this model explains at least semiquantitatively the quadrupole doublet observed by Pipkorn and Leider[1] and by Frankel and Blum[2] for Fe^{2+} in MgO at temperatures below 14°K. Jahn-Teller effects play no essential role in the appearance of this doublet, although a dynamic Jahn-Teller effect may cause small changes in the parameters c_3 and c_5, which determine the splitting of the doublet, and may contribute to its broadening.

There is however a quantitative discrepancy between the observed doublet splitting[1] of 0.27 mm/sec (1.0×10^{-4} cm^{-1}) and that calculated on the basis of crystal-field theory from Eq. (7) using the currently accepted value for the Fe^{57m} quadrupole moment Q. Taking the value $Q\sim+0.29$ b obtained by Ingalls,[6] and reducing Freeman and Watson's estimate[6,21] of $\langle r^{-3}\rangle(1-R)=3.3$ atomic units (a.u.) for the Fe^{2+} free ion by ~20% to take into approximate account the combined effect of covalent bonding and dynamical quenching, we obtain from Eq. (7) the value $\Delta E\sim0.44$ mm/sec (1.7×10^{-4} cm^{-1}). To eliminate this discrepancy by revising our estimate of the effect on ΔE of covalent bonding and dynamic quenching would require a larger change than seems plausible. Accordingly, if the proposed model is the correct one to give a quantitative description of the present experimental results, this discrepancy may be evidence that Ingalls' value for Q is somewhat too high.

To account for the motional narrowing of the Mössbauer line which occurs at 14°K, we suggest that the Orbach process described in Sec. IV is responsible for the electronic relaxation that produces this narrowing. The fact that this narrowing occurs over a narrow temperature range[1,2] is at least qualitatively consistent with the strong dependence of Eq. (9) on temperature through the exponential factor. However, for the Orbach process to account for the relaxation, it is evidently essential that one or more excited spin-orbit levels of Fe^{2+} be substantially lower than predicted by crystal-field theory, quite possibly as a result of the Jahn-Teller coupling. It should be possible to establish whether or not this is true from the far infrared absorption of Fe^{2+} in MgO, since the transitions $\Gamma_{5g}\rightarrow\Gamma_{4g}$ and $\Gamma_{5g}\rightarrow\Gamma_{3g}$ are both magnetic-dipole allowed.

We have estimated from resonance data that typical strains $>2\times10^{-5}$ occur in the MgO crystals, so that the strain splittings of the ground-state triplet are $\gtrsim10^{-2}$ cm^{-1}. Since the magnitudes of the hyperfine and quadrupole interactions are at least an order of magnitude smaller [$3\,|\,c_3\,|=1.0\times10^{-4}$ cm^{-1}, $3\,|\,B_1\,|\sim1.0\times10^{-3}$ cm^{-1} for Fe^{2+} in MgO from the data of Refs. (1) and (2)], this value of the strain splitting is amply sufficient to prevent observation of the zero-strain Mössbauer spectrum described in Sec. V. We may also obtain the order of magnitude of the strain splitting from the value of the applied magnetic field H_1 at which the hyperfine structure begins to appear in the Mössbauer spectrum. Using $H_1\sim250$ Oe from the work of Frankel and Blum[2]

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[21] A. J. Freeman and R. E. Watson, Phys. Rev. **131**, 2566 (1963).

we obtain $gBH_1 \sim 4\times10^{-2}$ cm^{-1}, so that these two estimates of the strain splitting agree.

A more exacting test of our proposed model would be provided by a precise determination of the quadrupole splitting in the presence of an applied magnetic field. As we found in Sec. VI, when **H** is along [100] the splitting of the $J_\zeta=\pm1$ spectrum equals $+(\frac{3}{2})c_3$, while for **H** along [111] it equals $+2c_5$, so that these parameters, including their signs, may be determined independently. Since c_3 is given by the crystal-field model to be negative and c_5 positive (for Q positive[22]), the sign of the splitting should change as **H** is rotated from [100] to [111]. Any departure in the ratio c_3/c_5 from that given by Eq. (3) would give a measure of the importance of departures from the crystal-field model, such as those that may arise from Jahn-Teller effects.

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Nuclear Magnetic Resonance and Nonexponential Spin-Lattice Relaxation in Ferroelectric Ammonium Fluoroberyllate*

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Nuclear spin-lattice relaxation times T_1 and relaxation times along the rf field ($T_{1\rho}$) have been measured for H^1 and F^{19} in $(NH_4)_2BeF_4$. Below 250°K the relaxation is due to reorientation of NH_4^+ ions; proton T_1 versus T has two minima due to two inequivalent NH_4^+ ions in the unit cell. Above the transition temperature T_c (176°K) and below 130°K, the logarithm of the correlation time τ_c is a linear function of T^{-1} with normal values of pre-exponential factors. Immediately below T_c, the time τ_c is anomalously short, as found previously in $(NH_4)_2SO_4$. Above 250°K, both proton and F^{19} relaxation become nonexponential and may be characterized by the same pair of relaxation times T_1' and T_1''. The shorter component (T_1') is ascribed to H-F dipolar interactions, and the longer component (T_1'') to H-F, H-H, and Be-F dipolar interactions. On deuteration, only the longer component remains; also, T_1' and T_1'' depend only on the rate of reorientation of BeF_4 tetrahedra. Deuteron-resonance results indicate that the dipole moment per NH_4^+ ion in $(NH_4)_2BeF_4$ is about half that in $(NH_4)_2SO_4$, in agreement with spontaneous-polarization measurements. The phase transition in $(NH_4)_2BeF_4$ is not as abrupt as in $(NH_4)_2SO_4$, and may be described by a weaker dependence of the interaction parameter on the spontaneous polarization.

I. INTRODUCTION

The crystal structures of ammonium fluoroberyllate and ammonium sulfate are very similar, and both are known to be ferroelectric; but many differences between those two crystals have also been found.[1,2] By precise x-ray studies, it was found that the crystal symmetries are different in both their room- and low-temperature phases. The axes of polarization in the ferroelectric phases are not in the same crystallographic direction. The phase transition in $(NH_4)_2SO_4$ is first-order and very abrupt, while the transition in $(NH_4)_2BeF_4$ is more gradual.

In view of the similarities and also the differences of these two crystals, both the deuteron magnetic resonance and nuclear magnetic relaxation of H^1 and F^{19} in $(NH_4)_2BeF_4$ have been studied in some detail. The natures of the ferroelectricity and molecular motions will be compared with previous results[3] on $(NH_4)_2SO_4$ deduced from magnetic resonance studies. In addition, molecular motions of BeF_4 ions can be deduced from F^{19} nuclear resonance studies; whereas, similar studies on sulfate ions would be very difficult. By measuring both spin-lattice relaxation time T_1 and the relaxation time $T_{1\rho}$ in the rotating coordinate system, it is possible to observe the molecular motions over wide ranges of correlation times.

In the present work, it was also found experimentally that the nuclear spin-lattice relaxation becomes markedly nonexponential over certain temperature ranges; the relaxation processes have been studied and interpreted in some detail in Sec. IIIB. Although deviations from exponential behavior have been observed and predicted[4] for certain systems, the deviations are very

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