crystal was doubly ionized, with no Fe^{3+} present. This is probably a gross overestimate of the Fe^{2+} concentration, since Fe^{3+} is the charge-allowed state and its APR is observed. It is known, though, that reduction to Fe^{2+} may occur in Al_2O_3 if the material is heated in vacuum to 1200°C,[11] and possibly our crystal was partially reduced during its growth or annealing. With this assumption we estimate that $[\frac{1}{4}(G_{11}-G_{12})^2+G_{16}^2]^{1/2}$ is not less than 15 cm^{-1} (unit strain)$^{-1}$.

Note added in manuscript. Since preparing the present article, we have seen a recent paper by Stevens and Walsh[12] in which the nature of the $Al_2O_3:Fe^{2+}$ ground state is suggested, and the magnitude of its spin-lattice interaction calculated. Our results are not inconsistent with their conclusions that the ground state should be a non-Kramers doublet separated by ~ 100 cm^{-1} from the lowest excited states, and that the Fe^{2+} ion is more weakly coupled to the lattice in Al_2O_3 than in a purely cubic environment such as MgO.

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Jahn-Teller Effects in the Far-Infrared, EPR, and Mössbauer Spectra of MgO:Fe^{2+}

FRANK S. HAM AND W. M. SCHWARZ*
General Electric Research and Development Center, Schenectady, New York 12301

AND

MARY C. M. O'BRIEN†
Department of Theoretical Physics, Oxford University, Oxford, England

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Measurements by Wong of the far-infrared absorption spectrum of the Fe^{2+} ion at undistorted cubic sites in MgO have revealed that the first excited spin-orbit level (evidently comprising both the Γ_{3g} and Γ_{4g} states) lies 105 cm^{-1} above the Γ_{5g} ground state, in contrast to the value $\sim$200 cm^{-1} predicted by crystal-field theory. A calculation has been made to determine if this reduced spin-orbit splitting can reasonably be attributed to a dynamic Jahn-Teller effect without leading to inconsistencies with other EPR and Mössbauer data for MgO:Fe^{2+}. It is concluded that this reduction is indeed predominantly the result of the Jahn-Teller coupling, that this reduction is consistent with the strength of Jahn-Teller coupling indicated by strain data for the Γ_{5g} level, and that significant Jahn-Teller corrections occur also in other parameters which characterize the EPR and Mössbauer spectra, such as the g factor, hyperfine field, and nuclear quadrupole coupling coefficients of the Γ_{5g} level. These Jahn-Teller corrections are calculated using the strength of the Jahn-Teller coupling to both E_g and T_{2g} vibrational modes as parameters, which are adjusted to give the observed spin-orbit reduction, and the resulting values are compared with estimates of corrections resulting from covalency. The calculations are carried out by treating the Jahn-Teller interaction by perturbation methods, and the calculation is formulated both for coupling with discrete vibrational modes and also for coupling with the continuum of lattice phonons.

I. INTRODUCTION

THE low-energy electronic states of the Fe^{2+} ion in cubic symmetry and octahedral coordination, as given by crystal-field theory,[1] result from the splitting of the $^5T_{2g}$ term by the spin-orbit interaction $\lambda\mathbf{L}\cdot\mathbf{S}$. The first excited states, a doublet Γ_{3g} and a triplet Γ_{4g}, are predicted to lie at an energy approximately $-2\lambda \simeq 200$ cm^{-1} above the ground-state triplet Γ_{5g} (the predicted separation of Γ_{3g} and Γ_{4g} being a few cm^{-1}). Wong[2] has recently measured the far-infrared absorption spectrum of Fe^{2+} in MgO, and he has found that the only absorption line in the range 10-220 cm^{-1} which can be attributed to isolated Fe^{2+} ions is a single line at 105 cm^{-1} (with a width $\sim$9 cm^{-1} at 20.3°K). If this line is attributed to one or both of the magnetic-dipole-allowed transitions $\Gamma_{5g}\rightarrow\Gamma_{3g}$ and $\Gamma_{5g}\rightarrow\Gamma_{4g}$, the excitation energy of these states is thus found to be only half of that predicted by crystal-field theory. Although one expects that effects of covalency[3] may reduce λ in the crystal by perhaps some 20% compared with the free-ion value $\lambda\simeq-100$ cm^{-1}, a 50% reduction is too large to be reasonably attributed to this cause. However, Wong's result that Fe^{2+} in MgO has an excited level very much lower in energy than expected on the basis

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* Permanent address: Physics Department, Union College, Schenectady, New York.

† Consultant at the GE Research and Development Center during the summer of 1968.

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of crystal-field theory confirms a prediction by Ham[4] made in connection with an explanation of the quadrupole splitting of the Mössbauer spectrum of Fe^{2+} in MgO which was first observed by Pipkorn and Leider.[5] Wong's value of 105 cm^{-1} for the energy of this level has been given additional quantitative confirmation from experimental determinations of the excitation energy of the level which contributes, via an Orbach process,[6] to relaxation within the Γ_{5g} ground state. Such results have recently become available from EPR (electron paramagnetic resonance) measurements of the spin-relaxation time as a function of temperature by Wilkinson, Hartman, and Castle,[7] from ultrasonic paramagnetic resonance linewidth measurements by Leisure and Bolef,[8] and from Leider and Pipkorn's application[9] of the theory of motional narrowing to their Mössbauer data.

The purpose of this paper is to explore the question whether the reduced excitation energy to the first excited state can reasonably be attributed to the effects of Jahn-Teller coupling within the $^5T_{2g}$ term of the Fe^{2+} ion. A vibronic effect of this sort in reducing the energy-level separation was suggested by Ham,[4] but no previous investigation has been made as to whether such a model is also consistent with the other data for MgO:Fe^{2+} which are available, particularly from EPR and Mössbauer studies. While a dynamic Jahn-Teller effect has been shown[10] to reduce the spin-orbit splitting of a term such as $^5T_{2g}$, there is a corresponding reduction in the orbital contribution to the Zeeman splitting of the various levels, and changes in other parameters of the system.[11] If this reduction in the orbital contribution to the g factor of the Γ_{5g} ground state were expected to be as large as the 50% reduction in the energy level separation, as is in fact suggested by an earlier calculation[10] of dynamic Jahn-Teller effects in the case of strong coupling, the expected g factor would be $\sim$3.25, and would be in clear disagreement with the experimental value 3.428 found[1,12] for MgO:Fe^{2+} (the crystal-field value is $\sim$3.5). A second question is whether the Jahn-Teller model predicts that the Γ_{3g} and Γ_{4g} levels are displaced by almost identical amounts so that they remain very nearly coincident, as is evidently required to account for Wong's observation[2] of but a single absorption line.

It is the conclusion of this paper that the observed reductions in the spin-orbit splitting and ground-state g-factor of Fe^{2+} in MgO are in large part the result of the Jahn-Teller coupling, and that a self-consistent model can be constructed on this basis which agrees with the available data.

The previous calculations[10] of the partial quenching of the spin-orbit interaction in an orbital triplet state by a dynamic Jahn-Teller effect were made for the case of a Jahn-Teller interaction strong compared with the spin-orbit interaction. If these two interactions are of comparable strength for MgO:Fe^{2+}, as Ham[4,10] has previously suggested may be the case, significant vibronic corrections to the parameters of the various levels are to be expected, but the quantitative results of the earlier theory are not applicable. In the present work we will use the opposite assumption, namely, that the Jahn-Teller interaction is weak, and we will calculate these vibronic corrections from perturbation theory. Although perturbation theory is potentially inaccurate for the strength of Jahn-Teller coupling actually indicated for MgO:Fe^{2+}, we will show from a direct numerical solution of the vibronic problem under somewhat simplified conditions, that the perturbation calculation should suffice to give a fairly accurate description of the system.

The phenomenological model for the Jahn-Teller coupling which we shall use in our calculations is one in which it is assumed that the principal coupling is with the distortions of the octahedron of six oxygen ions which are the nearest neighbors of an Fe^{2+} ion substitutionally replacing Mg^{2+} in the MgO lattice. An effective frequency of some 300 to 400 cm^{-1} (chosen to lie in the region of the peaks of the frequency distribution frunction for the lattice phonons[13] in MgO) is then assigned to each of the two modes of distortion of the oxygen octahedron which are Jahn-Teller active (a doubly degenerate mode belonging to the irreducible representation E_g of the cubic group, and a triply-degenerate mode transforming as T_{2g}). The Jahn-Teller problem is solved treating these modes as normal modes of vibration of the system. Although this model represents a considerable idealization of the actual situation, in which coupling occurs with many modes in the continuum of lattice vibrations, we believe, for reasons which we will discuss, that the vibronic effects may be interpreted and correlated in terms of such a model. The more rigorous analysis of the Jahn-Teller problem in terms of coupling with the phonon continuum is formulated in the Appendix, and this treatment is compared with a recent closely related calculation by Koloskova and Kochelaev[14] of the vibronic corrections to the ground-state g factor of MgO:Fe^{2+}.

The relative roles of covalency and Jahn-Teller

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effects in reducing the spin-orbit splitting and in contributing to the various reduction factors are assessed in Sec. IV C. Effects of covalency are not considered explicitly in the analysis of Secs. II and III, where to simplify the presentation it is assumed that the only modifications of the predictions of crystal-field theory are those resulting from the Jahn-Teller coupling.

II. JAHN-TELLER SHIFTS OF ENERGY LEVELS

The lowest term of the $\mathrm{Fe}^{2+}(3d^6)$ ion in octahedral coordination is given[1] by crystal-field theory to be ${}^5T_{2g}$, an orbital T_{2g} triplet[15] with spin $S=2$ derived from the free ion term ${}^5D$. The orbital doublet ${}^5E_g$ also derived from ${}^5D$ is higher in energy than ${}^5T_{2g}$ by $\Delta\simeq 10Dq$, where Dq is the one-electron cubic-field parameter, and $\Delta\simeq 10{,}850\ \mathrm{cm}^{-1}$ [16] for $\mathrm{MgO:Fe}^{2+}$. At a site of cubic symmetry the spin-orbit splitting of ${}^5T_{2g}$ given by crystal-field theory may be described conveniently by the Hamiltonian[17]

$$\mathcal{H}_{\mathrm{so}}=\zeta(\mathfrak{L}\cdot\mathbf{S})+\mu(\mathfrak{L}\cdot\mathbf{S})^2 +\rho(\mathcal{L}_x{}^2S_x{}^2+\mathcal{L}_y{}^2S_y{}^2+\mathcal{L}_z{}^2S_z{}^2)\,, \tag{2.1}$$

where ζ, μ, and ρ are given to the accuracy of second-order perturbation theory taking account only of spin-orbit interaction between ${}^5T_{2g}$ and ${}^5E_g$ by[18]

$$\begin{aligned}\zeta&=-\lambda-2\lambda^2/\Delta\,,\\ \mu&=-2\lambda^2/\Delta\,,\\ \rho&=+6\lambda^2/\Delta.\end{aligned}\tag{2.2}$$

Here λ is the parameter characterizing the spin-orbit interaction $\lambda(\mathbf{L}\cdot\mathbf{S})$ for the states derived from ${}^5D$, where $\hbar\mathbf{L}$ and $\hbar\mathbf{S}$ are the electronic orbital and spin angular momenta, respectively, and we have $\lambda\simeq -100\ \mathrm{cm}^{-1}$ for the Fe^{2+} free ion. In Eq. (2.1) the effective orbital angular momentum operator $\mathfrak{L}$ has components $(\mathcal{L}_x,\mathcal{L}_y,\mathcal{L}_z)$ defined[19] so that their only nonzero matrix elements are those between the real orbital states $|T_{2g}\xi\rangle$, $|T_{2g}\eta\rangle$, $|T_{2g}\zeta\rangle$ of ${}^5T_{2g}$ given by

$$\mathcal{L}_x=\begin{bmatrix}0&0&0\\0&0&-i\\0&i&0\end{bmatrix}\,,\quad \mathcal{L}_y=\begin{bmatrix}0&0&i\\0&0&0\\-i&0&0\end{bmatrix}\,,$$

$$\mathcal{L}_z=\begin{bmatrix}0&-i&0\\i&0&0\\0&0&0\end{bmatrix}\,. \tag{2.3}$$

Defining an effective total angular momentum operator $\mathbf{J}$ by

$$\mathbf{J}=\mathfrak{L}+\mathbf{S}\,, \tag{2.4}$$

we find for ${}^5T_{2g}$ that $\mathbf{J}$ has eigenvalues $J'=1$, 2, and 3, since $S=2$ and $\mathfrak{L}=1$. If we ignore the matrix elements of the last term of Eq. (2.1) between levels belonging to different J', on the assumption that $|\zeta|\gg|\rho|$, we obtain for the relative energies[1,20,21] of the spin-orbit eigenstates of $\mathcal{H}_{\mathrm{so}}$ for ${}^5T_{2g}$ the following:

$$\begin{aligned}
J'=1:&\quad E(\Gamma_{5g})=-3\zeta+9\mu+(27/5)\rho\,,\\
J'=2:&\quad E(\Gamma_{3g})=-\zeta+\mu+2\rho\,,\\
&\quad E(\Gamma_{4g})=-\zeta+\mu+3\rho\,,\\
J'=3:&\quad E(\Gamma_{1g})=+2\zeta+4\mu+2\rho\,,\\
&\quad E(\Gamma_{4g})=+2\zeta+4\mu+4\rho\,,\\
&\quad E(\Gamma_{5g})=+2\zeta+4\mu+(28/5)\rho.
\end{aligned}\tag{2.5}$$

The Jahn-Teller coupling of the electronic states of ${}^5T_{2g}$ with a doubly degenerate vibrational mode Q_θ, Q_ϵ belonging to E_g and a triply degenerate mode Q_ξ, Q_η, Q_ζ belonging to T_{2g} is described by the interaction Hamiltonian[22,23]

$$\mathcal{H}_{JT}=V_E(Q_\theta\mathcal{E}_\theta+Q_\epsilon\mathcal{E}_\epsilon) +V_T(Q_\xi\mathcal{T}_\xi+Q_\eta\mathcal{T}_\eta+Q_\zeta\mathcal{T}_\zeta)\,. \tag{2.6}$$

The electronic orbital operators $\mathcal{E}_\theta$, $\mathcal{E}_\epsilon$ belonging to E_g and the T_{2g} operators $\mathcal{T}_\xi$, $\mathcal{T}_\eta$, $\mathcal{T}_\zeta$ may be given in terms of the orbital operators $\mathcal{L}_x$, $\mathcal{L}_y$, $\mathcal{L}_z$ of Eq. (2.3) as

$$\begin{aligned}
\mathcal{E}_\theta&=\mathcal{L}_z{}^2-\tfrac{1}{2}(\mathcal{L}_x{}^2+\mathcal{L}_y{}^2)=\tfrac{3}{2}\mathcal{L}_z{}^2-\mathcal{I}\,,\\
\mathcal{E}_\epsilon&=(\tfrac{1}{2}\surd 3)(\mathcal{L}_x{}^2-\mathcal{L}_y{}^2)\,,\\
\mathcal{T}_\xi&=(\mathcal{L}_y\mathcal{L}_z+\mathcal{L}_z\mathcal{L}_y)\,,\\
\mathcal{T}_\eta&=(\mathcal{L}_z\mathcal{L}_x+\mathcal{L}_x\mathcal{L}_z)\,,\\
\mathcal{T}_\zeta&=(\mathcal{L}_x\mathcal{L}_y+\mathcal{L}_y\mathcal{L}_x)\,,
\end{aligned}\tag{2.7}$$

where $\mathcal{I}$ denotes the unit matrix. Alternatively they may be represented equivalently in terms of their matrix elements among the orbital states $|T_{2g}\xi\rangle$, $|T_{2g}\eta\rangle$,

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[15] We use interchangeably the notation of Mulliken A_{1g}, A_{2g}, E_g, T_{1g}, T_{2g} [R. S. Mulliken, Phys. Rev. **43**, 279 (1933)] and that of Bethe Γ_{1g}, Γ_{2g}, Γ_{3g}, Γ_{4g}, Γ_{5g} [H. A. Bethe, Ann. Physik **3**, 133 (1929)] to denote the even irreducible representations of the symmetry group O_h of the cube. We use the former in particular to label orbital states, the latter for spin-orbit states. The labels ξ, η, and ζ are used to designate the three partners ($|T_{2g}\xi\rangle$, $|T_{2g}\eta\rangle$, $|T_{2g}\zeta\rangle$; $|\Gamma_{5g}\xi\rangle$, $|\Gamma_{5g}\eta\rangle$, $|\Gamma_{5g}\zeta\rangle$; Q_ξ, Q_η, Q_ζ; P_ξ, P_η, P_ζ; $\mathcal{T}_\xi$, $\mathcal{T}_\eta$, $\mathcal{T}_\zeta$; etc). which belong to $T_{2g}(\Gamma_{5g})$ and transform respectively as yz, zx, xy, where x, y, and z denotes Cartesian coordinates with respect to the fourfold axes of the cube. Labels θ and ϵ denote partners belonging to $E_g(\Gamma_{3g})$ and transforming respectively as $z^2-\frac{1}{2}(x^2+y^2)$ and $\frac{1}{2}\surd 3(x^2-y^2)$, while x, y, and z denote partners belonging to $T_{1g}(\Gamma_{4g})$ and transforming as L_x, L_y, L_z.

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$|T_{2g}\zeta\rangle$ as follows:

$$\mathcal{E}_\theta=\begin{bmatrix} +\frac{1}{2} & 0 & 0 \\ 0 & +\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad \mathcal{E}_\epsilon=\begin{bmatrix} -\frac{1}{2}\sqrt{3} & 0 & 0 \\ 0 & +\frac{1}{2}\sqrt{3} & 0 \\ 0 & 0 & 0 \end{bmatrix}, \tag{2.8a}$$

$$\mathcal{T}_\xi=\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix}, \quad \mathcal{T}_\eta=\begin{bmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix},$$

$$\mathcal{T}_\zeta=\begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{2.8b}$$

The coupling coefficients V_E and V_T in Eq. (2.6) determine the strength of the Jahn-Teller coupling. If μ_E, μ_T, and ω_E, ω_T denote, respectively, the effective mass and angular frequency for the E_g and T_{2g} modes, we may define what we call the Jahn-Teller energy E_{JT} for each type of mode by

$$\begin{aligned}(E_{JT})_E&=V_E^2/2\mu_E\omega_E^2,\\ (E_{JT})_T&=2V_T^2/3\mu_T\omega_T^2.\end{aligned} \tag{2.9a}$$

This is the amount by which the energy of the lowest electronic state is lowered, as a result of the Jahn-Teller coupling (2.6), with account taken also of the corresponding elastic energy

$$\mathcal{H}_{\text{el}}=\tfrac{1}{2}\mu_E\omega_E^2(Q_\theta^2+Q_\epsilon^2)\mathcal{I} +\tfrac{1}{2}\mu_T\omega_T^2(Q_\xi^2+Q_\eta^2+Q_\zeta^2)\mathcal{I}, \tag{2.10}$$

when one goes from the symmetrical configuration $Q_\alpha=0$ to one of the configurations of minimum energy that one finds by considering each type of mode (E_g or T_{2g}) separately and by ignoring the spin-orbit interaction (2.1). The definitions (2.9) thus agree with those given previously for an orbital triplet.[10] In the present problem, because of the spin-orbit splitting of $^5T_{2g}$, $(E_{JT})_E$ and $(E_{JT})_T$ do not correspond to the displacement of any energy level, but they nevertheless provide a useful measure of the strength of the Jahn-Teller interaction with each type of mode.

Formulation of the vibronic problem is now completed by including the terms in the vibrational Hamiltonian corresponding to the kinetic energy associated with the Q's. These are given by

$$\mathcal{H}_K=(1/2\mu_E)(P_\theta^2+P_\epsilon^2)\mathcal{I} +(1/2\mu_T)(P_\xi^2+P_\eta^2+P_\zeta^2)\mathcal{I}, \tag{2.11}$$

where P_α is the momentum conjugate to Q_α. The Hamiltonian which we must solve for the vibronic states derived from the electronic term $^5T_{2g}$ is then obtained by combining Eqs. (2.1), (2.6), (2.10), and (2.11):

$$\mathcal{H}=\mathcal{H}_{\text{so}}+\mathcal{H}_{JT}+\mathcal{H}_{\text{el}}+\mathcal{H}_K. \tag{2.12}$$

Since $\mathcal{H}$ is invariant under transformations belonging to the symmetry group O_h, for simultaneous transformation of both the electronic and vibrational operators, the eigenstates of $\mathcal{H}$ may be classified by the irreducible representation of O_h to which they belong, and the degeneracy of vibronic levels belonging to two- or three-dimensional irreducible representations of O_h is not disturbed by the Jahn-Teller coupling. The coupling does, however, change the energy of levels such as those of Eq. (2.5), from that which one obtains when Jahn-Teller coupling is zero, and it is the relative shift of these levels which we now wish to calculate.

When the Jahn-Teller coupling is weak, that is, when $(E_{JT})_E$ and $(E_{JT})_T$ as given by Eq. (2.9) are small compared with the vibrational quanta $\hbar\omega_E$ and $\hbar\omega_T$, we may treat $\mathcal{H}_{JT}$ by perturbation theory to calculate the Jahn-Teller shift in the vibronic energy levels. The spin-orbit energy levels (2.5) then represent the states of the unperturbed Hamiltonian

$$\mathcal{H}_0=\mathcal{H}_{\text{so}}+\mathcal{H}_{\text{el}}+\mathcal{H}_K \tag{2.13}$$

in which each vibrational oscillator is in its ground state (we omit the common zero-point vibrational energy $\hbar\omega_E+\frac{3}{2}\hbar\omega_T$). Since $\mathcal{H}_{JT}$ is linear in the Q's, to the accuracy of second-order perturbation theory we need consider only the interaction via $\mathcal{H}_{JT}$ between these states and states of identical symmetry among the vibronic states with one vibrational quantum excited. These latter states can be constructed explicitly, using tables of coupling coefficients[24] for the group O_h, from the electronic wavefunctions appropriate to the levels (2.5) and the vibrational wavefunctions corresponding to one excited quantum. Each such state lies at an energy $\hbar\omega_E$ or $\hbar\omega_T$ (depending on which type of mode is excited) above the corresponding level in Eq. (2.5). The perturbation calculation, using $\mathcal{H}_{JT}$, of the energy shift of the levels (2.5) is then straightforward. We obtain for the Γ_{5g} ($J'=1$) ground state and the first excited states Γ_{3g}, Γ_{4g} ($J'=2$) the following results [where to simplify the expressions we have omitted from the energy denominators the small terms in ρ and μ (which are proportional to $\lambda^2/\Delta\simeq 1$ cm^{-1} for MgO:Fe^{2+}) in the energy level separations from Eq. (2.5)]:

$$\Delta E(\Gamma_{5g})=-(E_{JT})_E F_1(\zeta,\omega_E)-\tfrac{3}{2}(E_{JT})_T F_1(\zeta,\omega_T), \tag{2.14a}$$

$$\Delta E(\Gamma_{3g})=-(E_{JT})_E F_2(\zeta,\omega_E)-\tfrac{3}{2}(E_{JT})_T F_3(\zeta,\omega_T), \tag{2.14b}$$

$$\Delta E(\Gamma_{4g})=-(E_{JT})_E F_3(\zeta,\omega_E)-\tfrac{3}{2}(E_{JT})_T F_4(\zeta,\omega_T), \tag{2.14c}$$

where the functions $F_n(\zeta,\omega)$ are defined to be

$$F_1(\zeta,\omega)=\frac{1}{100}+\frac{21}{25}\frac{\hbar\omega}{\hbar\omega+5\zeta}+\frac{3}{20}\frac{\hbar\omega}{\hbar\omega+2\zeta}, \tag{2.15a}$$

$$F_2(\zeta,\omega)=\frac{1}{2}+\frac{1}{2}\frac{\hbar\omega}{\hbar\omega+3\zeta}, \tag{2.15b}$$

$$F_3(\zeta,\omega)=\frac{1}{4}+\frac{3}{5}\frac{\hbar\omega}{\hbar\omega+3\zeta}+\frac{3}{20}\frac{\hbar\omega}{\hbar\omega-2\zeta}, \tag{2.15c}$$

$$F_4(\zeta,\omega)=\frac{5}{12}+\frac{8}{15}\frac{\hbar\omega}{\hbar\omega+3\zeta}+\frac{1}{20}\frac{\hbar\omega}{\hbar\omega-2\zeta}. \tag{2.15d}$$

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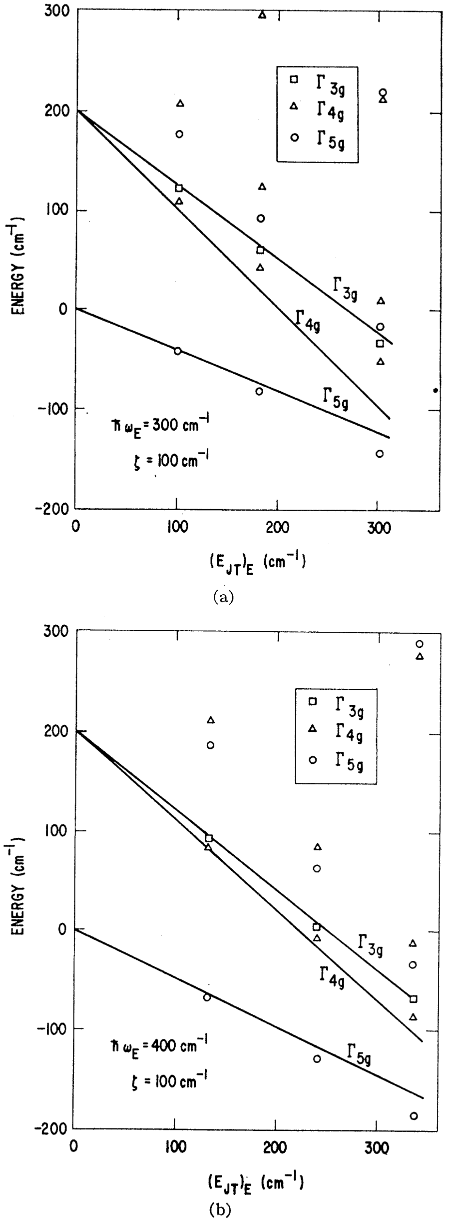
[24] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (Technology Press, Cambridge, Massachusetts, 1963).

To test the accuracy of the energy displacements as given by Eq. (2.14) when E_{JT} is comparable to the spin-orbit splitting and also not small compared with the vibrational quanta, we have calculated the energy levels of $\mathcal{H}$ in Eq. (2.12) by direct numerical diagonalization of the energy matrix for the case in which the Jahn-Teller coupling is with the E_g modes alone [i.e., $V_T=0$ in Eq. (2.6), so that we have $(E_{JT})_T=0$; the small terms in μ and ρ in $\mathcal{H}_{so}$ in Eq. (2.1) were also omitted in the calculation]. In making this calculation for the three sets of states Γ_{3g}, Γ_{4g}, and Γ_{5g}, all the eigenstates of $\mathcal{H}_0$ in Eq. (2.13) having the given symmetry were included which had fewer than four vibrational quanta excited. This gave us a 20×20 energy matrix for the Γ_{4g} and Γ_{5g} states, and 10×10 for Γ_{3g}.[25] The results are shown in Fig. 1 for two choices of the vibrational quantum, 300 and 400 cm^{-1}. In Fig. 1, the straight lines represent the perturbation results of Eq. (2.14) for the lowest state of each symmetry type, while the points indicate all the eigenvalues, obtained from the diagonalization, which lie in the energy range of the figure. The expressions obtained from the second-order perturbation calculation are seen to give the energy displacements of these lowest levels quite accurately out to $(E_{JT})_E\sim200$ cm^{-1} and to somewhat poorer accuracy beyond this point. The level given least accurately is Γ_{4g} in the case of $\hbar\omega_E=300$ cm^{-1}; the perturbation results in this case exaggerate the energy shift because the second Γ_{4g} level lies at $+300$ cm^{-1} for $(E_{JT})_E=0$, only 100 cm^{-1} above the level in question, so that the corresponding energy denominator in Eq. (2.14c) is smaller than for the other levels.[26] We may note that the perturbation results exaggerate somewhat the splitting between the Γ_{3g} and Γ_{4g} levels. We note also the presence of additional levels of symmetry Γ_{4g} and Γ_{5g} only slightly above the lowest Γ_{3g} and Γ_{4g} levels. These levels originate in the lowest vibronic levels at $(E_{JT})_E=0$ which have one vibrational quantum excited.[26] Although we have not calculated the displacement of these levels in our perturbation calculations, we will discuss these later in connection with the fact that no such levels are observed in Wong's far-infrared absorption spectrum.[2]

In view of the fairly good accuracy of the perturbation results in giving the energy level shifts in this simplified situation, and the similar results of the next section for the reduction factors in the Γ_{5g} ground state, we will assume in the subsequent parts of this paper that the perturbation results provide a satisfactory basis for our estimate of the importance of Jahn-Teller effects for MgO:Fe^{2+} and of the mutual consistency of these effects. This assumption is of course subject to subsequent verification that the estimates of $(E_{JT})_E$



(a)

(b)

FIG. 1. Shift in the spin-orbit energy levels of the $^5T_{2g}$ term of the Fe^{2+} ion in cubic symmetry, as a result of Jahn-Teller coupling to one doubly degenerate E_g vibrational mode. The abscissa is the Jahn-Teller energy defined in Eq. (2.9a) of the text. The straight lines represent the lowest Γ_{3g}, Γ_{4g}, and Γ_{5g} levels as given by Eq. (2.14), from a second-order perturbation treatment of the Jahn-Teller interaction, while the points indicate the levels found by direct numerical diagonalization of the energy matrix. The calculations were made for a spin-orbit parameter [Eq. (2.2)] $\zeta=+100$ cm^{-1} and a mode energy $\hbar\omega_E$ of (a) 300 cm^{-1} and (b) 400 cm^{-1}. Second-order spin-orbit splitting of the levels is neglected.

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[25] As a measure of the accuracy of omitting from the energy matrix terms with $n>3$, where n is the number of vibrational quanta excited, we extended the Γ_{3g} calculation to include all terms with $n\leq5$, for the case $\hbar\omega=300$ cm^{-1}, $(E_{JT})_E=182$ cm^{-1} [see Fig. 1(a)]. The correction to the lowest Γ_{3g} eigenvalue [the only one lying in the energy range of Fig. (1a)] was -1.6 cm^{-1}.

[26] Since $\Gamma_{3g}\times\Gamma_{5g}=\Gamma_{4g}+\Gamma_{5g}$, the vibronic states Γ_{4g} and Γ_{5g} which result from the lowest electronic Γ_{5g} spin-orbit state with the excitation of one $E_g(\Gamma_{3g})$ vibrational quantum lie an energy $\hbar\omega_E$ above this lowest Γ_{5g} level when the Jahn-Teller coupling is zero. In Fig. 1(a) these Γ_{4g}, Γ_{5g} levels lie, therefore, at $+300$ cm^{-1} for $(E_{JT})_E=0$, while in Fig. 1(b) they lie at $+400$ cm^{-1}.

and $\frac{3}{2}(E_{\mathrm{JT}})_T$ which we thereby obtain do not substantially exceed the values $\sim 200\ \mathrm{cm}^{-1}$ (for $\hbar\omega \simeq 300$–$400\ \mathrm{cm}^{-1}$) for which we infer that the perturbation results are reasonably accurate.

III. REDUCTION FACTORS IN Γ_{5g} GROUND STATE

The electronic operators $\boldsymbol{\mathfrak{L}}$, $\mathbf{S}$, $\mathcal{E}_\theta$, $\mathcal{E}_\epsilon$, $\mathcal{T}_\xi$, $\mathcal{T}_\eta$, $\mathcal{T}_\zeta$ have matrix elements within the Γ_{5g} vibronic ground state $|\Gamma_{5g}\xi\rangle$, $|\Gamma_{5g}\eta\rangle$, $|\Gamma_{5g}\zeta\rangle$ which determine the splitting of this triplet state by various perturbations. Although the relative values of these matrix elements are fixed by symmetry for a given set of operators belonging as partners to an irreducible representation of O_h (such as $\mathcal{E}_\theta$ and $\mathcal{E}_\epsilon$ or the components of $\boldsymbol{\mathfrak{L}}$), a common factor in all the matrix elements of each set depends upon the detailed nature of the state, and is affected by the Jahn-Teller coupling. These "reduction factors" are defined[27] by the following representative matrix elements:

$$\begin{aligned}
K_L &= i\langle\Gamma_{5g}\xi|\mathcal{L}_z|\Gamma_{5g}\eta\rangle\,,\\
K_S &= i\langle\Gamma_{5g}\xi|S_z|\Gamma_{5g}\eta\rangle\,,\\
K_E &= -\langle\Gamma_{5g}\zeta|\mathcal{E}_\theta|\Gamma_{5g}\zeta\rangle\,,\\
K_T &= -\langle\Gamma_{5g}\xi|\mathcal{T}_\zeta|\Gamma_{5g}\eta\rangle\,,\\
K_A &= i\langle\Gamma_{5g}\xi|(\boldsymbol{\mathfrak{L}}\cdot\mathbf{S})\mathcal{L}_z+\mathcal{L}_z(\boldsymbol{\mathfrak{L}}\cdot\mathbf{S})|\Gamma_{5g}\eta\rangle\,,\\
K_B &= i\langle\Gamma_{5g}\xi|\mathcal{L}_z{}^2S_z|\Gamma_{5g}\eta\rangle\,,
\end{aligned}\tag{3.1}$$

where in addition to the more important reduction factors K_L, K_S, K_E, and K_T we have included two, K_A and K_B, appropriate to more complicated operators that appear in the theory of the hyperfine interaction and in the second-order corrections to the g factor.

To evaluate the reduction factors (3.1) to the accuracy of terms proportional to the square of the Jahn-Teller coupling coefficients V_E and V_T, we may use second-order perturbation theory to obtain the perturbed wave functions, then evaluate the matrix elements using these wave functions. This calculation yields the following results:

$$\begin{aligned}
K_L &= -\tfrac{1}{2}+x_EG_1(\zeta,\omega_E)+x_TG_1(\zeta,\omega_T)\,,\\
K_S &= +\tfrac{3}{2}+x_EG_2(\zeta,\omega_E)+x_TG_2(\zeta,\omega_T)\,,\\
K_E &= +\tfrac{1}{10}+x_EG_3(\zeta,\omega_E)+x_TG_4(\zeta,\omega_T)\,,\\
K_T &= +\tfrac{1}{10}+x_EG_4(\zeta,\omega_E)+x_TG_5(\zeta,\omega_T)\,,\\
K_A &= +3+x_EG_6(\zeta,\omega_E)+x_TG_6(\zeta,\omega_T)\,,\\
K_B &= +(6/5)+x_EG_7(\zeta,\omega_E)+x_TG_8(\zeta,\omega_T)\,,
\end{aligned}\tag{3.2}$$

where

$$\begin{aligned}
x_E &= (E_{\mathrm{JT}})_E/\hbar\omega_E\,,\\
x_T &= \tfrac{3}{2}(E_{\mathrm{JT}})_T/\hbar\omega_T\,,
\end{aligned}\tag{3.3}$$

and

$$\begin{aligned}
G_1(\zeta,\omega) &= +3/400+(49/50)u_{55}+(7/80)u_{22}\\
&\qquad -(13/40)u_{25}-(9/40)v_{25}\,,\\
G_2(\zeta,\omega) &= -9/400-(7/50)u_{55}-(13/80)u_{22}\\
&\qquad +(13/40)u_{25}+(9/40)v_{25}\,,\\
G_3(\zeta,\omega) &= +(33/250)u_{55}+(3/50)u_{22}-(24/125)u_{25}\\
&\qquad +(54/125)v_{25}\,,\\
G_4(\zeta,\omega) &= -3/2000+(27/250)u_{55}+(9/400)u_{22}\\
&\qquad -(279/1000)u_{25}-(27/1000)v_{25}\,,\\
G_5(\zeta,\omega) &= -1/2000+(31/250)u_{55}+(19/400)u_{22}\\
&\qquad -(221/1000)u_{25}+(279/1000)v_{25}\,,\\
G_6(\zeta,\omega) &= -9/200-(7/25)u_{55}-(19/40)u_{22}\\
&\qquad -(1/10)u_{25}+(9/10)v_{25}\,,\\
G_7(\zeta,\omega) &= -9/500-(8/125)u_{55}-(13/100)u_{22}\\
&\qquad +(53/250)u_{25}+(99/250)v_{25}\,,\\
G_8(\zeta,\omega) &= -9/500-(18/125)u_{55}-(9/50)u_{22}\\
&\qquad +(21/500)u_{25}+(93/500)v_{25}\,,
\end{aligned}\tag{3.4}$$

$$\begin{aligned}
u_{22} &= (\hbar\omega)^2/(\hbar\omega+2\zeta)^2\,,\\
u_{55} &= (\hbar\omega)^2/(\hbar\omega+5\zeta)^2\,,\\
u_{25} &= (\hbar\omega)^2/(\hbar\omega+2\zeta)(\hbar\omega+5\zeta)\,,\\
v_{25} &= \zeta\hbar\omega/(\hbar\omega+2\zeta)(\hbar\omega+5\zeta)\,.
\end{aligned}\tag{3.5}$$

The reduction factors K_L, K_S, K_E, and K_T given by Eq. (3.2) are plotted in Fig. 2 for the case of Jahn-Teller coupling with the E_g modes alone, for $\hbar\omega = 300\ \mathrm{cm}^{-1}$. Almost identical results are obtained for $\hbar\omega = 400\ \mathrm{cm}^{-1}$. Also plotted in Fig. 2 for comparison are the reduction factors evaluated from the eigenstates obtained in the direct matrix diagonalization described in Sec. II. These values are indicated by the crosses in Fig. 2 and are seen to agree fairly well with the second-order perturbation results; the agreement is found to be even better for $\hbar\omega = 400\ \mathrm{cm}^{-1}$ (not shown). We see that the magnitude of K_L, the reduction factor for the orbital angular momentum, is reduced by some 20% for $(E_{\mathrm{JT}})_E \sim 300\ \mathrm{cm}^{-1}$ relative to its crystal-field value. For K_T the corresponding reduction is $\sim$40%, while K_E is enhanced by $\sim$40% by the Jahn-Teller coupling with the E_g mode [for Jahn-Teller coupling with a

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[27] The reduction factors K_L, K_E, and K_T as defined by Eq. (3.1) give the ratio of the matrix element of the appropriate orbital operator in the Γ_{5g} ground state to the corresponding matrix element of the same operator among the electronic orbital triplet states $|T_{2g}\xi\rangle$, $|T_{2g}\eta\rangle$, $|T_{2g}\zeta\rangle$, [see Eqs. (2.3) and (2.8)]. These reduction factors (together with K_S, K_A, and K_B) differ from unity not only because of vibronic effects but also as a result of the mixing of orbital and spin wave functions in Γ_{5g} as a result of the spin-orbit interaction. They should, therefore, not be confused with the "orbital reduction factors" often used to represent the reduction in matrix elements of orbital operators among *orbital* states because of covalent and vibronic effects. In the case treated in this paper, we have to treat each spin-orbit level separately and cannot define "orbital reduction factors" common to all the spin-orbit levels, because the spin-orbit and Jahn-Teller interactions are of similar magnitude.

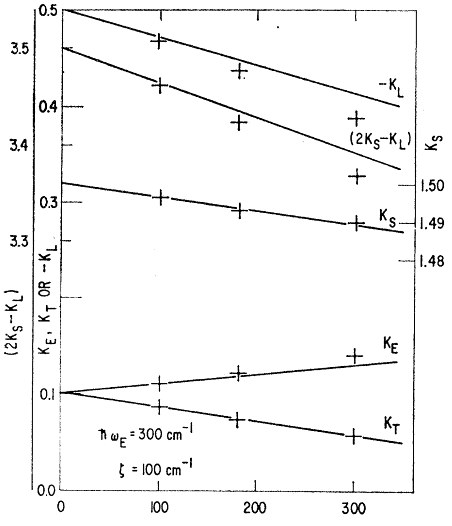

FIG. 2. Reduction factors K_L, K_S, K_E, and K_T for the Γ_{5g} spin-orbit ground state of the Fe^{2+} ion in cubic symmetry, as a function of the Jahn-Teller energy $(E_{JT})_E$. Coupling is with a single E_g mode for the case shown in Fig. 1(a). The straight lines give the second-order perturbation results given by Eq. (3.2), while the crosses give the values calculated from the vibronic wave functions obtained from the direct numerical diagonalization of the energy matrix. Also shown is the combination $2K_S-K_L$ which gives the ground-state g factor if covalent effects and higher order corrections are neglected.

T_{2g} mode alone K_T is found from Eq. (3.2) and Table II to be slightly enhanced, while K_E is reduced]. The reduction factor K_S for the spin is however only very slightly diminished by the Jahn-Teller coupling from its crystal-field value $\frac{3}{2}$. We have also plotted in Fig. 2 the quantity $2K_S-K_L$ which gives the g factor for the Γ_{5g} state (neglecting covalent effects) apart from the corrections due to the spin-orbit coupling between $^5T_{2g}$ and ^5E_g. The reduction in $2K_S-K_L$ from its crystal-field value 3.5 is mostly the result of the partial quenching of the orbital angular momentum.

IV. APPLICATION TO MgO:Fe^{2+}

We cannot expect that the highly simplified theoretical model of the Jahn-Teller coupling used in Secs. II and III can give a precisely accurate representation of the effects of coupling an isolated Fe^{2+} ion to all the phonons of the MgO lattice. On the other hand, to treat this coupling by the more rigorous procedure of the Appendix would require detailed knowledge of the coupling coefficients for phonons in all branches of the phonon spectrum, as functions of phonon frequency. We do not now have such information, and such an analysis in any case would be extremely complicated. We shall be satisfied for the present time, therefore, to show on the basis of the simplified model that the vibronic effects are important and that they can be made consistent with the salient experimental facts if reasonable values are used for the various parameters of the model. Since these conclusions are found to hold over a range of values of these parameters, we believe that they are qualitatively correct despite the possible oversimplifications of the model. However, these estimates of vibronic effects can certainly be made quantitatively more precise as more detailed models are used and additional experimental evidence becomes available.

A. Reduction of Spin-Orbit Splitting

The separation of the lowest excited states Γ_{3g} and Γ_{4g} from the ground state Γ_{5g} is given by crystal-field theory according to Eqs. (2.2) and (2.5) by

$$E(\Gamma_{3g})-E(\Gamma_{5g}) = -2\lambda-(42/5)(\lambda^2/\Delta)$$
$$\text{and} \qquad \qquad (4.1)$$
$$E(\Gamma_{4g})-E(\Gamma_{5g}) = -2\lambda-(12/5)(\lambda^2/\Delta).$$

Omitting all consideration of covalent bonding for the present, and taking the values $\lambda = -100\text{ cm}^{-1}$, $\Delta = 10\,850\text{ cm}^{-1}$, we find for these excitation energies as predicted by crystal-field theory the values 192 and 198 cm^{-1}, respectively, with Γ_{4g} above Γ_{3g}. Wong's result[2] that the only line in the far infrared absorption spectrum of isolated Fe^{2+} ions in MgO within the range 10–220 cm^{-1} is a single line at 105 cm^{-1} (linewidth $\sim 9\text{ cm}^{-1}$ at 20.3°K) suggests that these two levels actually have excitation energies of only 105 cm^{-1} and that they coincide to within a few cm.$^{-1}$ Taking both of these levels therefore to lie 105 cm^{-1} above Γ_{5g}, we find that Γ_{3g} and Γ_{4g} are in fact displaced relative to Γ_{5g} by approximately -87 and -93 cm^{-1}, respectively, compared with the predictions of crystal-field theory.

In Table I we give values for $(E_{JT})_E$ and $\frac{3}{2}(E_{JT})_T$ which are consistent with energy level shifts

$$\Delta[E(\Gamma_{3g})-E(\Gamma_{5g})] = -87\text{ cm}^{-1},$$
$$\Delta[E(\Gamma_{4g})-E(\Gamma_{5g})] = -93\text{ cm}^{-1},$$

as a result of the Jahn-Teller coupling, for various

TABLE I. Jahn-Teller energies for MgO:Fe^{2+} and corresponding reduction factors for the Γ_{5g} ground state, for various choices of the effective mode frequencies ω_E and ω_T.[a]

$\hbar\omega_E(\text{cm}^{-1})$ $\hbar\omega_T(\text{cm}^{-1})$	303 303	345 345	400 400	303 400	400 303
$(E_{JT})_E(\text{cm}^{-1})$	91	110	132	71	158
$\frac{3}{2}(E_{JT})_T(\text{cm}^{-1})$	99	108	115	155	68
x_E	0.299	0.318	0.331	0.233	0.396
x_T	0.326	0.314	0.287	0.387	0.225
K_L	-0.445	-0.434	-0.422	-0.430	-0.430
K_S	$+1.493$	$+1.494$	$+1.494$	$+1.494$	$+1.494$
$2K_S-K_L$	$+3.432$	$+3.421$	$+3.410$	$+3.418$	$+3.418$
K_E	$+0.094$	$+0.094$	$+0.093$	$+0.085$	$+0.101$
K_T	$+0.089$	$+0.085$	$+0.082$	$+0.090$	$+0.079$
K_A	$+2.867$	$+2.848$	$+2.830$	$+2.844$	$+2.844$
K_B	$+1.175$	$+1.173$	$+1.172$	$+1.162$	$+1.183$

[a] The values of $(E_{JT})_E$ and $\frac{3}{2}(E_{JT})_T$ given for each choice of ω_E, ω_T are those which according to Eq. (2.14) give $\Delta[E(\Gamma_{3g})-E(\Gamma_{5g})] = -87\text{ cm}^{-1}$, $\Delta[E(\Gamma_{4g})-E(\Gamma_{5g})] = -93\text{ cm}^{-1}$, where ζ is taken to be $+100\text{ cm}^{-1}$. These values and the corresponding values of the reduction factors given by Eq. (3.2) are obtained from the values of F_n and G_n tabulated in Table II. The parameters x_E and x_T are defined in Eq. (3.3).

TABLE II. Values of $F_n(\zeta,\omega)$ and $G_n(\zeta,\omega)$, as defined by Eqs. (2.15) and (3.4), for selected values of the ratio $\zeta/\hbar\omega$.

$\zeta/\hbar\omega$	F_1	F_2	F_3	F_4	G_1	G_2
0.25	0.4833	0.7857	0.8929	0.8214	+0.1270	−0.0094
0.27	0.4648	0.7762	0.9076	0.8200	+0.1153	−0.0098
0.29	0.4478	0.7674	0.9280	0.8209	+0.1050	−0.0101
0.31	0.4320	0.7591	0.9556	0.8246	+0.0960	−0.0104
0.33	0.4173	0.7513	0.9927	0.8317	+0.0880	−0.0106

$\zeta/\hbar\omega$	G_3	G_4	G_5	G_6	G_7	G_8
0.25	+0.0278	−0.0556	+0.0003	−0.2744	+0.0037	−0.1002
0.27	+0.0284	−0.0523	+0.0017	−0.2565	+0.0037	−0.0945
0.29	+0.0288	−0.0493	+0.0030	−0.2403	+0.0037	−0.0893
0.31	+0.0291	−0.0465	+0.0041	−0.2257	+0.0037	−0.0846
0.33	+0.0293	−0.0440	+0.0051	−0.2125	+0.0036	−0.0803

choices of the frequencies ω_E and ω_T of the E_g and T_{2g} modes. These results for the Jahn-Teller energies, together with the corresponding values for the reduction factors also given in Table I, were calculated from Eqs. (2.14) and (3.2) using the values tabulated in Table II for the functions $F_n(\zeta,\omega)$ and $G_n(\zeta,\omega)$ that enter these equations. It was assumed that the values used for ω_E and ω_T should be taken from the region of the principal peaks in the frequency distribution of the lattice phonon spectrum[13] of MgO. It is clear from Tables I and II that whatever the choice of ω_E and ω_T within this range, it is possible to fit the inferred energy shifts of Γ_{3g} and Γ_{4g} by using values of $(E_{JT})_E$ and $\frac{3}{2}(E_{JT})_T$ in the vicinity of 100–150 cm^{-1}. This conclusion will remain true if Γ_{3g} and Γ_{4g} are taken to lie a few cm^{-1} apart instead of being assumed degenerate, if the separation of these levels as given by crystal-field theory is somewhat different from that given in Eq. (4.1) as a result of spin-spin interaction or spin-orbit interaction to other levels, or if the correct value for λ departs slightly from the value -100 cm^{-1}. Moreover, according to the conclusions of Secs. II and III, such values for the Jahn-Teller energies are consistent with our assumption that perturbation theory suffices for a reasonably accurate description of the effects of the Jahn-Teller coupling.

B. *g* Factor of Γ_{5g} Ground State

The effect of the Zeeman interaction

$$\mathcal{H}_H=\beta(\mathbf{L}\cdot\mathbf{H})+g_s{}^0\beta(\mathbf{S}\cdot\mathbf{H})\,, \tag{4.2}$$

with $\beta=e\hbar/2mc$, $g_s{}^0=2.0023$, and $\mathbf{H}$ the magnetic field, on the ${}^5T_{2g}$ term as given by crystal-field theory may be expressed[17] as

$$\begin{aligned}\mathcal{H}_H({}^5T_{2g})=&(g_s{}^0-8\lambda/\Delta)\beta\mathbf{S}\cdot\mathbf{H}-k\beta\mathfrak{L}\cdot\mathbf{H}\\&-(2\lambda/\Delta)\beta[(\mathfrak{L}\cdot\mathbf{S})(\mathfrak{L}\cdot\mathbf{H})+(\mathfrak{L}\cdot\mathbf{H})(\mathfrak{L}\cdot\mathbf{S})]\\&+(12\lambda/\Delta)\beta(\mathcal{L}_x{}^2S_xH_x+\mathcal{L}_y{}^2S_yH_y+\mathcal{L}_z{}^2S_zH_z)\end{aligned} \tag{4.3}$$

to the accuracy of second-order perturbation theory, where we have introduced a parameter k (Sec. IV C) to represent the covalent modification of the orbital term. Taking account of the Jahn-Teller coupling as well as of the spin-orbit splitting, we may, however, describe the Zeeman splitting of the Γ_{5g} ground state in the usual simple form,

$$\mathcal{H}_H(\Gamma_{5g})=g\beta(\mathfrak{J}\cdot\mathbf{H}) \tag{4.4}$$

with a g factor given by

$$g=[g_s{}^0-8\lambda/\Delta]K_S-kK_L-(2\lambda/\Delta)K_A+(12\lambda/\Delta)K_B\,. \tag{4.5}$$

The effective angular momentum $\mathfrak{J}$ in Eq. (4.4) is defined with respect to the Γ_{5g} vibronic ground state $|\Gamma_{5g}\xi\rangle$, $|\Gamma_{5g}\eta\rangle$, $|\Gamma_{5g}\zeta\rangle$ in precise analogy with the definition of $\mathfrak{L}$ in Eq. (2.3) with respect to the orbital T_{2g} state [i.e., $\langle\Gamma_{5g}\xi|\mathcal{J}_z|\Gamma_{5g}\eta\rangle=-i$, etc.]. The expression for g in Eq. (4.5) is then obtained by equating corresponding matrix elements of Eqs. (4.3) and (4.4), using the reduction factors defined in Eq. (3.1).

The experimental value[1,12] of g for MgO:Fe^{2+} is 3.428. Using the values of the reduction factors given in Table I, we obtain for $(-8K_S-2K_A+12K_B)(\lambda/\Delta)$ in Eq. (4.5) a value close to its crystal-field value $-(18/5)(\lambda/\Delta)\simeq+0.03$. Adding this value to those for $(2K_S-K_L)$ given in Table I (neglecting covalent effects for the present and therefore taking $k=1$), we therefore obtain values for g in Eq. (4.5) which are all *larger* by 0.01 to 0.03 than the experimental value. In none of the cases of Table I, therefore, is the g factor reduced to a value smaller than the experimental value by Jahn-Teller coupling sufficiently strong to account for the reduced spin-orbit splitting. This result settles the question raised in the Introduction whether the proportional reduction in the orbital contribution to the g factor would not be predicted to be roughly the same as that of the spin-orbit splitting, a prediction suggested by experience[10] with the case with Jahn-Teller coupling strong compared with spin-orbit interaction. There is therefore no conflict between the experimental value for g and the supposition that the reduction of the spin-orbit splitting is due primarily to the Jahn-Teller coupling.

C. Effects of Covalency

Although our primary concern in this paper is to demonstrate the self-consistency of a model for Fe^{2+} in MgO in which a large part of the reduction in the spin-orbit splitting and in the ground-state g factor is the result of the Jahn-Teller coupling, we want also to estimate what part of these reductions may reasonably be attributed to the effects of covalent bonding noted originally by Stevens[28] and Owen.[3] Within the ${}^5T_{2g}$ term, the spin-orbit parameter λ in Eq. (2.2) and the orbital reduction factor k in Eq. (4.3)[29] reflect the properties of the t_{2g} electron orbitals on the Fe^{2+} as modified by the formation of π bonds with the $2p$ orbitals of the surrounding octahedron of oxygen

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[28] K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

[29] In this paper, we will ignore covalent corrections to the small second-order terms in λ^2/Δ and λ/Δ in Eqs. (2.2) and (4.3).

ligands.[30] As shown first by Stevens,[28] we have (in the notation of Owen and Thornley[31])

$$k=k_{\pi\pi}=1-\tfrac{1}{2}N_{\pi}^{2}\alpha_{\pi}^{2}\,, \tag{4.6}$$

where N_π and α_π are the normalization factor and admixture coefficient, respectively, in the one-electron antibonding t_{2g} orbital. In terms of the parameter[31] $f_\pi \equiv \frac{1}{4}N_\pi{}^2\alpha_\pi{}^2$ which gives the fraction of unpaired electron spin transferred to a π orbital on the ligand as a result of the covalent bonding, we may write Eq. (4.6) alternatively as

$$k=k_{\pi\pi}=1-2f_{\pi}\,. \tag{4.7}$$

For λ we have

$$\lambda=-\tfrac{1}{4}\zeta_{\pi\pi}=-\tfrac{1}{4}N_{\pi}^{2}(\zeta_{d}+\tfrac{1}{2}\alpha_{\pi}^{2}\zeta_{p})\,, \tag{4.8}$$

where $\zeta_{\pi\pi}$ is the one-electron spin-orbit parameter[31] for the t_{2g} antibonding orbital, and ζ_d and ζ_p are the spin-orbit parameters for a $3d$ orbital on the Fe^{2+} and for a $2p$ orbital on the oxygen, respectively.

For Fe^{2+} in MgO we have as yet no independent measurements of f_π such as have been obtained for many other complexes from the transferred hyperfine interaction with the ligand (such measurements for $MgO:Fe^{2+}$ would, of course, require a crystal doped with O^{17}). However, Hall *et al.*[32] have obtained in this way a value $f_\pi \simeq 2.5\%$ for Fe^{2+} in NaF, a complex having a g factor (3.420) quite close to that of Fe^{2+} in MgO. If, despite the differences between F and O, we take such a value as representative, we would then have $k\simeq 0.95$. In Eq. (4.8) for λ, if we again take $\frac{1}{2}\alpha_\pi{}^2 \simeq 2f_\pi \simeq 5\%$, we see that the contribution of the oxygen spin-orbit coupling *increases* slightly that of the Fe^{2+} ($\zeta_d \simeq +400$ cm^{-1} for the free ion), and that this sum is then reduced by the factor $N_\pi{}^2$, which is probably not much smaller than 0.9. Although these estimates are not very precise in the absence of detailed calculations for $MgO:Fe^{2+}$, they do indicate that covalent bonding is not likely to reduce λ for this complex by more than $\sim 10\%$ from its free ion value.

The observed reduction of nearly 50% in the spin-orbit splitting between the lowest states of $MgO:Fe^{2+}$ is thus much too large to be reasonably attributed to the effect of covalent bonding alone. If, as we propose, this reduction is in large part due to the Jahn-Teller coupling, we see thus from the results of Table I that a large part of the reduction in g from its crystal-field value 3.53 to its experimental value 3.428 must also be due to the Jahn-Teller coupling. Indeed, from the results of Sec. IV B we see that a value $k\simeq 0.95$ in Eq. (4.5) is more or less what is needed to bring the calculated results of Table I into agreement with the experimental g factor.

D. Hyperfine Interaction

The hyperfine interaction[19] is given by

$$\mathcal{H}_I=2\gamma\beta\beta_N\sum_k\left[\frac{(\mathbf{l}_k-\mathbf{s}_k)\cdot\mathbf{I}}{r_k{}^3}+3\frac{(\mathbf{r}_k\cdot\mathbf{s}_k)(\mathbf{r}_k\cdot\mathbf{I})}{r_k{}^5}+\frac{8\pi}{3}\delta(\mathbf{r}_k)(\mathbf{s}_k\cdot\mathbf{I})\right], \tag{4.9}$$

where γ is the nuclear g factor, β_N the nuclear magneton, $\hbar\mathbf{I}$ the nuclear angular momentum, and $\hbar\mathbf{l}_k$, $\hbar\mathbf{s}_k$, and $\mathbf{r}_k$ the orbital angular momentum, spin, and position of the kth electron. Within the ${}^5T_{2g}$ term of Fe^{2+} (for which we are thus concerned only with the 2% naturally abundant isotope Fe^{57}), $\mathcal{H}_I$ is equivalent to

$$\begin{aligned}\mathcal{H}_I({}^5T_{2g})=A\mathbf{S}\cdot\mathbf{I}+2\gamma\beta\beta_N\{&-\langle r^{-3}\rangle_{LI}\mathfrak{L}\cdot\mathbf{I}+[(3/28)\\ &\times\langle r^{-3}\rangle_{SD}-(2\lambda/\Delta)\langle r^{-3}\rangle_{LI}][(\mathfrak{L}\cdot\mathbf{S})\,(\mathfrak{L}\cdot\mathbf{I})+(\mathfrak{L}\cdot\mathbf{I})(\mathfrak{L}\cdot\mathbf{S})]\\ &+[-(3/7)\langle r^{-3}\rangle_{SD}+(12\lambda/\Delta)\langle r^{-3}\rangle_{LI}][\mathfrak{L}_x{}^2S_xI_x\\ &+\mathfrak{L}_y{}^2S_yI_y+\mathfrak{L}_z{}^2S_zI_z]+[(1/7)\langle r^{-3}\rangle_{SD}\\ &-(8\lambda/\Delta)\langle r^{-3}\rangle_{LI}](\mathbf{S}\cdot\mathbf{I})\}\,.\end{aligned} \tag{4.10}$$

Here the term $A(\mathbf{S}\cdot\mathbf{I})$ represents the contact hyperfine interaction resulting from the exchange polarization of the inner shells by the $3d$ electrons, while $\langle r^{-3}\rangle_{LI}$ and $\langle r^{-3}\rangle_{SD}$ denote the effective one-electron averages of r^{-3} for a $3d$ electron for the orbital and spin-dipolar interactions, respectively. As discussed particularly by Freeman and Watson[33,34] $\langle r^{-3}\rangle_{LI}$, $\langle r^{-3}\rangle_{SD}$, and the effective average $\langle r^{-3}\rangle_{Q}$ appropriate to the quadrupole interaction will not be the same, as would be predicted by conventional restricted Hartree-Fock theory, because of the corrections that result from the exchange polarization of the inner shells. In writing Eq. (4.10), we have included the second-order perturbation corrections resulting from the combined coupling of the orbital interaction in Eq. (4.9) and the spin-orbit interaction, but we have omitted the smaller such corrections from the spin-dipolar interaction.

Within the Γ_{5g} vibronic ground state, Eq. (4.10) is in turn equivalent to

$$\mathcal{H}_I(\Gamma_{5g})=B(\mathfrak{J}\cdot\mathbf{I})\,, \tag{4.11}$$

in analogy to Eq. (4.4), with B given by

$$\begin{aligned}B=AK_S+2\gamma\beta\beta_N\{&-K_L\langle r^{-3}\rangle_{LI}+(1/28)\langle r^{-3}\rangle_{SD}\\ &\times(4K_S+3K_A-12K_B)+(\lambda/\Delta)\langle r^{-3}\rangle_{LI}\\ &\times(-8K_S-2K_A+12K_B)\}\,,\end{aligned} \tag{4.12}$$

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[30] The only one-electron matrix elements that contribute to λ and k for the ${}^5T_{2g}$ term are those that involve the t_{2g} antibonding orbitals. The e_g orbitals on the Fe^{2+} form σ bonds with the ligands, but although these contribute to the transferred spin density[32] on the ligands, they do not affect the values of λ or k.

[31] J. Owen and J. H. M. Thornley, Rept. Progr. Phys. **29**, 675 (1966).

[32] T. P. P. Hall, W. Hayes, R. W. H. Stevenson, and J. Wilkens, J. Chem. Phys. **39**, 35 (1963).

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

[34] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. II A, p. 167.

and we have again used the reduction factors defined in Eq. (3.1).

The effective hyperfine field $\mathbf{H}_{\text{eff}}$ at the Fe^{2+} nucleus has been measured for MgO:Fe^{2+} by Chappert, Frankel, and Blum,[35] and also by Leider and Pipkorn,[9] from the Zeeman splitting of the Fe^{57} Mössbauer spectrum in an applied magnetic field. Their result, under conditions corresponding to having only the electronic state with $\mathcal{J}_\zeta=-1$ occupied (where ζ denotes the direction of the applied field $\mathbf{H}$), is that $\mathbf{H}_{\text{eff}}$ is antiparallel to $\mathbf{H}$ and has the magnitude 120 kOe. From the relation

$$H_{\text{eff}}=-B\langle\mathcal{J}_\zeta\rangle/\gamma\beta_N \qquad (4.13)$$

and the value[36] $\gamma=+0.1805$, we thus obtain the experimental value of B in Eq. (4.11),

$$B=-5.5\times10^{-4}\ \text{cm}^{-1}, \qquad (4.14)$$

for the nuclear ground state of Fe^{57}.

A comparison of the value (4.14) with the prediction of Eq. (4.12) is not a conclusive test of the theory because we have no independent measurements of A or $\langle r^{-3}\rangle_{\text{LI}}$, while theoretical calculation of these quantities is somewhat uncertain.[34] We do, however, have a measurement of A [the coefficient in the hyperfine interaction $A\mathbf{S}\cdot\mathbf{I}$] for the Fe^{3+} ion in MgO from the work of Locher and Geschwind.[36] This value $A=-10.066\times10^{-4}$ cm^{-1} corresponds to an effective hyperfine field per electron $H_c/2S$ of -110 kOe (which compares with a value[37] $A=-81.0\times10^{-4}$ cm^{-1} or $H_c/2S=-115$ kOe for the isoelectronic ion Mn^{2+} in MgO). The systematics [34,38,39] of the variation of the exchange-polarized hyperfine field for different charge states of the same atom in the same environment suggest that $H_c/2S$ should be increased by some 10% in going from Fe^{3+} to Fe^{2+}. Accordingly, we take for an estimate for $H_c/2S$ (and thus for $+A/2\gamma\beta_N$) for MgO:Fe^{2+} the value -120 kOe. Giving K_S its crystal-field value $+\frac{3}{2}$ (or equivalently the value $\sim+1.494$ from Table I) we obtain for the contribution to H_{eff} in Eq. (4.13) from the first term AK_S in Eq. (4.12) the value -360 kOe. For the small spin-dipolar and second-order contributions to Eq. (4.12) we find from Table I that the vibronic effects reduce the quantities $(1/28)\times(4K_S+3K_A-12K_B)$ and $(\lambda/\Delta)(-8K_S-2K_A+12K_B)$ only slightly from their crystal-field values of $+(3/140)$ and $-(18/5)(\lambda/\Delta)$, respectively. Taking for the sum of these quantities a value $\sim+0.045$ and taking both $\langle r^{-3}\rangle_{SD}$ and $\langle r^{-3}\rangle_{LI}$ equal to ~4.5 atomic units[33,34] in these small terms, we obtain for the combined contributions of these terms to H_{eff} a value $\sim+25$ kOe. Combining this with the contribution -360 kOe from AK_S and the experimental value -120 kOe for H_{eff}, we deduce for the remaining term in Eq. (4.12) an orbital contribution to H_{eff} of $+215$ kOe, or

$$-K_L\langle r^{-3}\rangle_{LI}\cong1.72\ \text{a.u.} \qquad (4.15)$$

Finally, taking $K_L\simeq-0.43$ from Table I, we thus obtain from Eq. (4.15) the estimate

$$\langle r^{-3}\rangle_{LI}\cong4.0\ \text{a.u.} \qquad (4.16)$$

This compares well with Freeman and Watson's theoretical value[33,34] $\langle r^{-3}\rangle_{LI}=4.59$ a.u. obtained from an unrestricted Hartree-Fock (UHF) calculation for the free Fe^{2+} ion. The theoretical value is of course uncertain because of the unresolved uncertainties[34] in UHF theory, and the calculated value was obtained by Freeman and Watson by taking into account the "radial" antishielding, but not the "angular" antishielding which may also be important.[33,34] We may note that our deduced value (4.16) included no corrections for covalent effects, so that part of the difference between Eq. (4.16) and Freeman and Watson's value may be simply due to the reduction of $\langle r^{-3}\rangle$ in the crystal as the result of covalent bonding.

This analysis[40] of the hyperfine data is thus seen to be consistent with our proposed model of Jahn-Teller effects in MgO:Fe^{2+}.

E. Quadrupole Interaction

The quadrupole interaction,[19]

$$\mathcal{H}_Q=\frac{e^2Q}{2I(2I-1)}\sum_k\left[\frac{I(I+1)}{r_k^3}-\frac{3(\mathbf{r}_k\cdot\mathbf{I})^2}{r_k^5}\right], \qquad (4.17)$$

is equivalent within the $^5T_{2g}$ term of Fe^{2+} to

$$\begin{aligned}\mathcal{H}_Q(^5T_{2g})=&-(1/7)[e^2Q/2I(2I-1)]\langle r^{-3}\rangle_Q\\&\times\{2\mathcal{E}_\theta[3I_z^2-I(I+1)]+2\sqrt{3}\mathcal{E}_\epsilon[I_x^2-I_y^2]\\&-3\mathcal{T}_\xi(I_yI_z+I_zI_y)-3\mathcal{T}_\eta(I_zI_x+I_xI_z)\\&-3\mathcal{T}_\zeta(I_xI_y+I_yI_x)\},\end{aligned} \qquad (4.18)$$

where we have used the orbital operators defined in Eqs. (2.7) and (2.8). We are now concerned of course with the excited Mössbauer level Fe^{57m} $(I=\frac{3}{2})$, since the quadrupole moment Q vanishes in the Fe^{57} nuclear ground state $(I=\frac{1}{2})$. Within the Γ_{5g} vibronic ground state, Eq. (4.18) may be represented[4] by

$$\begin{aligned}\mathcal{H}_Q(\Gamma_{5g})=&(\tfrac{1}{4}c_3)\{3\mathcal{J}_z^2-\mathcal{J}(\mathcal{J}+1)][3I_z^2-I(I+1)]\\&+3[\mathcal{J}_x^2-\mathcal{J}_y^2][I_x^2-I_y^2]\}+c_5\{(\mathcal{J}_y\mathcal{J}_z+\mathcal{J}_z\mathcal{J}_y)\\&\times(I_yI_z+I_zI_y)+(\mathcal{J}_z\mathcal{J}_x+\mathcal{J}_x\mathcal{J}_z)(I_zI_x+I_xI_z)\\&+(\mathcal{J}_x\mathcal{J}_y+\mathcal{J}_y\mathcal{J}_x)(I_xI_y+I_yI_x)\},\end{aligned} \qquad (4.19)$$

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[35] J. Chappert, R. B. Frankel, and N. A. Blum, Phys. Letters **25A**, 149 (1967); J. Chappert, R. B. Frankel, A. Misetich, and N. A. Blum, Phys. Rev. **179**, 578 (1969).

[36] P. R. Locher and S. Geschwind, Phys. Rev. **139**, A991 (1965).

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

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

[39] S. Geschwind, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967), p. 225.

[40] A slightly different analysis, based on crystal-field theory modified by including an orbital reduction factor, was given by Chappert *et al.*[35] for their data on the hyperfine fields of Fe^{2+} and also Fe^{1+} in MgO. Their analysis of the several contributions to the hyperfine field is essentially consistent with the one described here, although there are differences in detail.

where, using the reduction factors K_E and K_T from Eq. (3.1), we have

$$\begin{aligned} c_3 &= -(2/7)K_E\langle r^{-3}\rangle_Q e^2Q/[I(2I-1)], \\ c_5 &= +(3/14)K_T\langle r^{-3}\rangle_Q e^2Q/[I(2I-1)]. \end{aligned} \tag{4.20}$$

It has been shown by several authors[4,41] that in an applied magnetic field (or an internal field) the Mössbauer spectrum of an Fe^{57} ion in a site of perfect cubic symmetry exhibits not only a Zeeman splitting, but also a quadrupole splitting, and that the latter depends on the orientation ζ of **H**. For **H** along the [100] and [111] crystal directions, in particular, we find that the quadrupole splitting[42] ΔE_Q for the electronic states $\mathcal{J}_\zeta = \pm 1$ (we assume slow electronic relaxation) is given by $\mathcal{H}_Q$ in Eq. (4.19) to be

$$\Delta E_Q[100] = +\tfrac{3}{2}c_3$$
and
$$\Delta E_Q[111] = +2c_5. \tag{4.21}$$

According to Eq. (4.20), these values for ΔE_Q have opposite signs, but they would have equal magnitude if K_E and K_T were equal [crystal-field theory gives both K_E and K_T the value $+\frac{1}{10}$]. Following Ham's prediction[4] that such a sign reversal in the quadrupole splitting should occur in the Mössbauer spectrum of $MgO{:}Fe^{2+}$ when **H** is rotated from [100] to [111], provided that the electronic Zeeman splitting exceeded any strain splitting of the Γ_{5g} ground state, Leider and Pipkorn[9] indeed observed this effect and moreover found to the accuracy of their experiments that the quantities $\frac{3}{2}|c_3|$ and $2|c_5|$ in Eq. (4.21) were equal. Similar results for $MgO{:}Fe^{2+}$ have also been obtained by Chappert *et al.*[35] These observations indicate, therefore, that the parameters K_E and K_T must be very nearly equal for $MgO{:}Fe^{2+}$. Taking the Jahn-Teller corrections into account in the theory, we see from Table I that, while K_E and K_T are reduced in four of the cases considered there by some 5–15% relative to their crystal-field value, they are found in these cases to differ by only some 5–10%, a difference too small to have been seen in the experimental data. However, the 20% difference given by the fifth case in Table I would probably have been evident in Leider and Pipkorn's data if this case were applicable. On the basis of Leider and Pipkorn's results, therefore, we can say that the first four cases in Table I are consistent with the Mössbauer quadrupole data for $MgO{:}Fe^{2+}$, but that the fifth case apparently is not.

In the absence of an applied magnetic field, Leider and Pipkorn[5,9] found that the Mössbauer spectrum of Fe^{2+} in MgO becomes a resolved quadrupole doublet at temperatures below 14°K. This observation, reported also by Frankel and Blum,[43] and by Chappert *et al.*[35] was explained by Ham[4] as resulting from the instantaneously aspherical charge distribution of the valence electrons on the Fe^{2+} ion in the presence of a weak internal strain in the crystal, and slow electronic relaxation. Corresponding to an electronic (i.e., vibronic) state

$$|\psi\rangle = a|\Gamma_{5g}\xi\rangle + b|\Gamma_{5g}\eta\rangle + c|\Gamma_{5g}\zeta\rangle \tag{4.22}$$

which is an eigenstate of the local strain, where a, b, and c are real coefficients such that $a^2+b^2+c^2=1$, the quadrupole splitting of the Mössbauer doublet given by Eq. (4.19) was shown to be

$$\begin{aligned} \Delta E_Q = 3[&c_3^2 + \tfrac{1}{3}(16c_5^2 - 9c_3^2) \\ &\times (a^2b^2 + b^2c^2 + c^2a^2)]^{1/2}. \end{aligned} \tag{4.23}$$

If $3|c_3|$ were equal to $4|c_5|$, as predicted by crystal-field theory, Ham noted that ΔE_Q would then be independent of the choice of a, b, and c; if the electronic relaxation were sufficiently slow Eq. (4.23) would thus explain the appearance of a resolved doublet in the observed Mössbauer spectrum despite the presumed random nature of the local strains. In our present considerations, because of the Jahn-Teller corrections to K_E and K_T as in Table I, we no longer expect $3|c_3|$ and $4|c_5|$ to be exactly equal, and ΔE_Q as given by Eq. (4.23) will now vary for individual ions between the extremes

$$\Delta E_Q^{(1)} = 3|c_3|$$
and
$$\Delta E_Q^{(2)} = 4|c_5|. \tag{4.24}$$

Since the observed Mössbauer doublet is the superposition of those of the individual ions in the presence of random strains, it will be broadened[44] within these limits, which have values exactly twice the magnitude of the splittings in Eq. (4.21). However, since for the first four cases in Table I the difference between K_E and K_T is only 5–10%, we expect this broadening to have a very modest effect on the observed spectrum of Fe^{2+} in MgO, and we can reasonably take the observed doublet splitting to be given by the mean of Eq. (4.24) or

$$\Delta E_Q \cong (2/7)[\tfrac{1}{2}(K_E + K_T)]\langle r^{-3}\rangle_Q e^2Q. \tag{4.25}$$

Leider and Pipkorn's measurements[9] give for this splitting a value $\Delta E_Q = 0.33$ mm/sec, while Chappert *et al.*[35] obtained the slightly smaller value $\Delta E_Q = 0.30$ mm/sec.

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[41] J. D. Siegwarth, Phys. Rev. **155**, 285 (1967); G. K. Wertheim. H. J. Guggenheim, H. J. Williams, and D. N. E. Buchanan, Phys, Rev. **158**, 446 (1967); U. Ganiel, M. Kestigian, and S. Shtrikman, Phys. Letters **24A**, 577 (1967); M. Eibschutz, S. Shtrikman, and Y. Tenenbaum, Phys. Letters **24A**, 563 (1967); U. Ganiel and S. Shtrikman, Phys. Rev. **167**, 258 (1968); G. R. Hoy and K. P. Singh, Phys. Rev. **172**, 514 (1968).

[42] We define ΔE_Q in Eq. (4.21) in terms of the energies $E(I_\zeta')$ of the nuclear eigenstates of the excited Mössbauer level by $\Delta E_Q \equiv \frac{1}{2}[E(+\frac{3}{2}) + E(-\frac{3}{2}) - E(+\frac{1}{2}) - E(-\frac{1}{2})]$.

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

[44] The value of the quadrupole splitting ΔE_Q in Eq. (4.23) corresponding to a particular value of a, b, and c could be determined experimentally, using an appropriately oriented applied stress at a sufficiently low temperature.

To compare the theoretical expression in Eq. (4.25) with the experimental value, we need a value for $\langle r^{-3}\rangle_Q$. Freeman and Watson[33,34] have obtained a theoretical value $\langle r^{-3}\rangle_Q = 4.93$ a.u. from an unrestricted Hartree-Fock calculation for Fe^{2+} taking into account only the "radial" antishielding. However, Ingalls[45] has calculated, using a perturbation treatment based on restricted Hartree-Fock free-ion functions, that the "angular" corrections to the antishielding make a larger contribution to the Sternheimer factor $1-R_Q$ for Fe^{2+} than do the "radial" corrections. Multiplying Ingalls' value $[1-R_Q(\text{ang.})] \simeq 0.67$ by Freeman and Watson's UHF value $\langle r^{-3}\rangle_Q = 4.93$ a.u., we obtain an estimate[46] $\langle r^{-3}\rangle \simeq 3.3$ a.u. that takes account of both types of antishielding. Combining this estimate, however uncertain, with our result $\frac{1}{2}(K_E+K_T) \simeq +0.09$ from Table I, and the value $Q \simeq +0.29$ b obtained by Ingalls[46] for Fe^{57m}, we calculate from Eq. (4.25) a value $\Delta E_Q \simeq 0.50$ mm/sec, which is substantially larger than the experimental value. Alternatively, if we use Eq. (4.25), together with the values for the other parameters used previously, to determine a value for Q from Leider and Pipkorn's observed[9] $\Delta E_Q = 0.33$ mm/sec, we obtain $Q = +0.19$ b. This value agrees quite well with two other recent determinations of Q by Nozik and Kaplan[47] ($Q = +0.20$ b) and Johnson[48] ($Q = +0.18$ b) from data on ferrous complexes, but no so well with the value $Q = +0.283 \pm 0.035$ b obtained by Artman, Muir, and Wiedersich[49] from a new evaluation of data for the ferric ion in α-Fe$_2$O$_3$. If this latter, larger value for Q is correct, we should evidently have to reduce the estimate of $\langle r^{-3}\rangle_Q$ to a value quite a bit smaller than 3.3 a.u. We should note that we made no explicit provisions for covalency in Eq. (4.25), but, while this would make a further reduction in the value $\langle r^{-3}\rangle_Q$ appropriate to the crystal, this correction is probably less than 10% if our estimates of covalent effects in Sec. IV C are realistic.

The quadrupole splitting of the Mössbauer spectrum of Fe^{2+} in MgO at liquid helium temperature thus appears to offer an excellent opportunity for an accurate determination of the Fe^{57m} quadrupole moment, once uncertainties concerning the proper value for $\langle r^{-3}\rangle_Q$ have been resolved, and the effects of covalency estimated more precisely.

Finally, it should be noted that the experimental evidence that $\frac{3}{2}|c_3|$ and $2|c_5|$ (and therefore also K_E and K_T) are equal to within ~10% supports the view that both types of Jahn-Teller coupling—one involving the E_g modes and the other the T_{2g}—are of more or less equal importance for the $^5T_{2g}$ terms of Fe^{2+} in MgO. In other words $(E_{JT})_E$ and $\frac{3}{2}(E_{JT})_T$ [or x_E and x_T in Eq. (3.3)] must be of similar size, as is true for the cases in Table I. Were the coupling predominantly with one type of mode, we see from Eq. (3.2) and Table II that there would be a greater difference between the values of K_E and K_T than was found in the cases in Table I, and such a difference should have been evident from the Mössbauer data.

F. Strain Coupling Coefficients

The effect of static strain in the crystal on the orbital states of the $^5T_{2g}$ term may be described phenomenologically by introducing into the Hamiltonian the terms

$$\mathcal{H}_S(^5T_{2g}) = V_2[e_\theta \mathcal{E}_\theta + e_\epsilon \mathcal{E}_\epsilon] + V_3[e_{yz}\mathcal{T}_\xi + e_{zx}\mathcal{T}_\eta + e_{xy}\mathcal{T}_\zeta]. \tag{4.26}$$

Here

$$e_{ij} = e_{ji} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \tag{4.27}$$

denotes a component of the strain tensor, and we define

$$\begin{aligned} e_\theta &= [e_{zz} - \tfrac{1}{2}(e_{xx}+e_{yy})], \\ e_\epsilon &= (\tfrac{1}{2}\sqrt{3})[e_{xx}-e_{yy}]. \end{aligned} \tag{4.28}$$

V_2 and V_3 are strain coupling coefficients. Using the reduction factors (3.1) we find then that Eq. (4.26) is equivalent within the Γ_{5g} vibronic ground state to

$$\begin{aligned} \mathcal{H}_S(\Gamma_{5g}) = (\tfrac{1}{2}V_2K_E)\{e_\theta[3\mathcal{J}_z^2 - \mathcal{J}(\mathcal{J}+1)] \\ + e_\epsilon\sqrt{3}[\mathcal{J}_x^2 - \mathcal{J}_y^2]\} + V_3K_T\{e_{yz}(\mathcal{J}_y\mathcal{J}_z + \mathcal{J}_z\mathcal{J}_y) \\ + e_{zx}(\mathcal{J}_z\mathcal{J}_x + \mathcal{J}_x\mathcal{J}_z) + e_{xy}(\mathcal{J}_x\mathcal{J}_y + \mathcal{J}_y\mathcal{J}_x)\}. \end{aligned} \tag{4.29}$$

The strain coupling coefficients that determine the linear splitting of the Γ_{5g} ground-state triplet are therefore V_2K_E and V_3K_T.

It is, however, esthetically more satisfying in the context of the Jahn-Teller problem to view the effect of strain in the crystal to be that of shifting the equilibrium position of the distortion modes Q_θ, Q_ϵ, etc., that are responsible for the Jahn-Teller coupling. Instead of having the equilibrium position of these modes at $Q=0$ in the elastic energy in Eq. (2.10), in the presence of strain we take it to be displaced to the new positions

$$\begin{aligned} Q_\theta &= Q_\theta^0 = De_\theta, \\ Q_\epsilon &= Q_\epsilon^0 = De_\epsilon, \\ Q_\xi &= Q_\xi^0 = D'e_{yz}, \\ Q_\eta &= Q_\eta^0 = D'e_{zx}, \\ Q_\zeta &= Q_\zeta^0 = D'e_{xy}, \end{aligned} \tag{4.30}$$

where D and D' are coefficients to be discussed below. The elastic energy is accordingly now given by

$$\begin{aligned} \mathcal{H}_{\text{el}}^{(S)} = \tfrac{1}{2}\mu_E\omega_E^2[(Q_\theta - Q_\theta^0)^2 + (Q_\epsilon - Q_\epsilon^0)^2] \\ + \tfrac{1}{2}\mu_T\omega_T^2[(Q_\xi - Q_\xi^0)^2 + (Q_\eta - Q_\eta^0)^2 \\ + (Q_\zeta - Q_\zeta^0)^2], \end{aligned} \tag{4.31}$$

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[45] R. Ingalls, Phys. Rev. **128**, 1155 (1962).

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

[47] A. J. Nozik and M. Kaplan, Phys. Rev. **159**, 273 (1967).

[48] C. E. Johnson, Proc. Phys. Soc. (London) **92**, 748 (1967).

[49] J. O. Artman, A. H. Muir, and H. Wiedersich, Phys. Rev. **173**, 337 (1968).

in place of Eq. (2.10). However, we may now make the change of variable

$$\begin{aligned} Q_\theta' &= Q_\theta - Q_\theta^0, \\ Q_\xi' &= Q_\xi - Q_\xi^0, \end{aligned} \tag{4.32}$$

etc., in Eq. (4.31) and in the Jahn-Teller interaction, Eq. (2.6), as well as the corresponding transformation of the canonical momenta $P_\theta' = P_\theta$, etc., in Eq. (2.11). In terms of the new (primed) variables, the Hamiltonian obtained by combining Eqs. (2.1), (2.6), (2.11), and (4.31) is now identical with Eq. (2.12), except that additional terms appear identical in form to Eq. (4.26) and with coefficients given by

$$\begin{aligned} V_2 &= V_E D \\ \text{and} \qquad V_3 &= V_T D'. \end{aligned} \tag{4.33}$$

These new terms result from making the variable change in the Jahn-Teller interaction, Eq. (2.6), using Eq. (4.30). This procedure, therefore, provides the connection between the phenomenological strain coupling coefficients V_2 and V_3 in Eq. (4.26) and the Jahn-Teller coupling coefficients V_E and V_T.

The coefficients D and D' in Eqs. (4.30) and (4.33) are easily evaluated if the Q's are taken to represent the distortions of the cluster of six oxygen ions surrounding the Fe^{2+} ion, and if the local elastic constants are assumed to be the same as those of the MgO crystal. Defining the Q's by an orthogonal transformation[22,50] of the displacements of these six oxygens, we may take[51] for the effective masses μ_E and μ_T in Eqs. (2.10) and (2.11) the mass M of a single oxygen atom

$$\mu_E = \mu_T = M. \tag{4.34}$$

The displacements of the oxygen ions under a given uniform strain are then easily evaluated, and when the resulting values of the Q's are substituted into Eq. (4.30) we obtain the results

$$\begin{aligned} D &= (2/\sqrt{3})R \\ \text{and} \qquad D' &= 2R, \end{aligned} \tag{4.35}$$

where R is the nearest-neighbor distance. If, however, we were to define the Q's to take into account not only displacements of nearest-neighbor ions but of more distant ions as well, or if the local elastic constants should be different from those of the bulk MgO crystal, the values of D and D' appropriate to Eq. (4.33) might differ appreciably from those given in Eq. (4.35).

The strain coupling coefficients for the Γ_{5g} ground state of $\mathrm{MgO{:}Fe^{2+}}$ have been measured by Watkins and Feher[52] from the splitting of the EPR lines under applied stress. In terms of their notation, the strain splitting of the level is described by $\mathcal{H}_s(\Gamma_{5g}) = \mathfrak{J}\cdot\delta\mathbf{D}\cdot\mathfrak{J}$, where the components of the tensor $\delta\mathbf{D}$ are related to those of the strain (Voigt notation: $\delta D_1 = \delta D_{xx}$, $\delta D_4 = \delta D_{yz}$, etc., but $e_1 = e_{xx}$, $e_4 = 2e_{yz}$, etc.) by $\delta D_i = \sum_j G_{ij} e_j$. Comparing with Eq. (4.29) we thus have the equivalent quantities

$$V_2 K_E = \tfrac{2}{3}(G_{11} - G_{12}), \tag{4.36a}$$

$$V_3 K_T = 2G_{44}, \tag{4.36b}$$

or, if we assume with Watkins and Feher that the trace of δD vanishes so that $G_{11} = -2G_{12}$,

$$V_2 K_E = G_{11}, \tag{4.36a'}$$

Watkins and Feher obtain the values $G_{11} = +800\ \mathrm{cm}^{-1}$, $G_{44} = +540\ \mathrm{cm}^{-1}$. Taking $K_E \cong K_T \cong +0.09$ from Table I, we thus infer for Fe^{2+} in MgO the values[53]

$$\begin{aligned} V_2 &\cong +9000\ \mathrm{cm}^{-1}, \\ V_3 &\cong +12000\ \mathrm{cm}^{-1}. \end{aligned} \tag{4.37}$$

G. Jahn-Teller Energies

From the values (4.37) for the strain coupling coefficients V_2 and V_3, the relations given by Eqs. (4.33), (4.34), and (4.35) and the various assumed values for ω_E and ω_T, we may now calculate values for the Jahn-Teller energies $(E_{JT})_E$ and $\frac{3}{2}(E_{JT})_T$ from Eq. (2.9) for comparison with the values given in Table I. These calculated values are given in Table III. We see that they agree very well in size with the values inferred in Table I from the reduced spin-orbit splitting, and this agreement thus supports the self-consistency of our proposed model for the Jahn-Teller effects. Indeed, the agreement is very much better than we have any right to expect, in view of the questionable assumptions that led to the values of D and D' given by Eq. (4.35). The calculated values of the Jahn-Teller energies when compared with Table I appear to favor taking $\hbar\omega_E \cong \hbar\omega_T$ midway in the region (300–400 cm^{-1}) of the principal peaks of the phonon frequency distribution for MgO.[13]

TABLE III. Jahn-Teller energies for $\mathrm{MgO{:}Fe^{2+}}$ calculated[a] from experimental values of the strain coupling coefficients, for various choices of the effective mode frequencies.

$\hbar\omega(\mathrm{cm}^{-1})$	$(E_{JT})_E(\mathrm{cm}^{-1})$	$\frac{3}{2}(E_{JT})_T(\mathrm{cm}^{-1})$
303	155	185
345	120	140
400	90	105

[a] The values of $(E_{JT})_E$ and $\frac{3}{2}(E_{JT})_T$ are calculated from Eq. (2.9) taking μ_E and μ_T equal to the mass of one oxygen atom, and relating V_E and V_T to the values $V_2 \cong +9000\ \mathrm{cm}^{-1}$, $V_3 \cong +12\,000\ \mathrm{cm}^{-1}$ inferred from experiment, using Eqs. (4.30) and (4.32) with $R = 2.10$ Å. The value assumed for $\hbar\omega_E$ or $\hbar\omega_T$ in the calculation is listed under $\hbar\omega$.

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[50] M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York 1967), Vol. 20, p. 91 (see Table II, p. 102).

[51] F. S. Ham, Phys. Rev. **166**, 307 (1968) (see Appendix II).

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

[53] If we calculate V_2 and V_3 directly from the point ion approximation to crystal-field theory, we obtain values which agree approximately with Eq. (4.37) in magnitude, but which have the opposite sign. No explanation has been given for the curious discrepancy in sign from what one naively expects.

They also support our earlier conclusion that both types of Jahn-Teller coupling are of more or less equal importance for the $^5T_{2g}$ terms of Fe^{2+} in MgO.

H. Oscillator Strengths of Far-Infrared Transitions

Optical transitions from the Γ_{5g} ground state of the Fe^{2+} ion to the Γ_{3g} and Γ_{4g} excited states are allowed by the selection rules for magnetic-dipole processes. The oscillator strength $f_m(A,B)$ for a magnetic-dipole transition from level A to level B is given[54] by

$$f_m(A,B)=\frac{\hbar\bar{\nu}_{BA}n^2}{2mcd_A}\left(\frac{\mathcal{E}}{\mathcal{E}_{\text{eff}}}\right)^2 \times\sum_{a,b}|\langle Aa|(\mathbf{L}+2\mathbf{S})\cdot(\hat{e}\times\hat{k})|Bb\rangle|^2, \quad (4.38)$$

where $hc\bar{\nu}_{BA}=(E_B-E_A)$ is the energy difference between the levels, d_A the degeneracy of the initial level A, m the electron mass, c the speed of light in vacuum, n the far-infrared index of refraction of MgO, $(\mathcal{E}_{\text{eff}}/\mathcal{E})$ the local-field correction[55] at the Fe^{2+} site, and $\hat{e}$ and $\hat{k}$ are unit vectors in the direction, respectively, of the polarization and propagation of the light. The summation in Eq. (4.38) extends over the states a and b comprizing the levels A and B. For the $\Gamma_{5g}\to\Gamma_{3g}$ and $\Gamma_{5g}\to\Gamma_{4g}$ transitions, crystal-field theory gives for this summation the values 27/5 and 81/10, respectively. Taking $n^2(\mathcal{E}/\mathcal{E}_{\text{eff}})^2\simeq 9n^2/(n^2+2)^2\simeq 0.64$ from the value of the static dielectric constant of MgO, we thus calculate for these transitions from Eq. (4.38) the oscillator strengths $\sim 1.5\times 10^{-8}$ and $\sim 2.2\times 10^{-8}$, respectively, if we take $\bar{\nu}$ to be given by Wong's observed excitation frequency 105 cm^{-1}. These values should be reduced somewhat to take into account the change caused by the Jahn-Teller coupling in the matrix elements of $(\mathbf{L}+2\mathbf{S})$ between the levels (primarily a reduction in the matrix elements of $\mathbf{L}$), but we have not calculated this correction in detail.

We have noted in Sec. II that the results given in Fig. 1 show that for the cases for which these numerical calculations were made, there are additional levels which are only slightly higher than the lowest Γ_{3g} and Γ_{4g} levels when E_{JT} is as large as $\sim$200–300 cm^{-1}. If such additional levels are present also for Fe^{2+} in MgO, we may ask whether they should not have been observed in Wong's absorption spectrum[2] as additional lines lying above the peak at 105 cm^{-1}, but within the range to 220 cm^{-1} which was examined. Although we have not tried to calculate such levels in detail for Fe^{2+} in MgO, we believe that they would *not* be observed because they would contribute an absorption both much weaker and much broader than the 105-cm^{-1} peak. Such levels originate, in the limit of zero Jahn-Teller coupling, from levels which have one or more vibrational quanta excited or from the $J'=3$ levels [Eq. (2.5)] of the Fe^{2+} ion, and in either case the matrix elements for optical transitions to these levels from the ground state are zero in this limit. With a nonzero Jahn-Teller coupling these matrix elements no longer vanish but should remain small if the coupling is not too strong. In support of this conclusion, we have calculated for the cases considered in Fig. 1 the matrix elements of $\mathbf{L}$ and $\mathbf{S}$ from the Γ_{5g} ground state to the second Γ_{4g} and Γ_{5g} levels, which lie just above the first Γ_{3g} and Γ_{4g} levels, as a function of the Jahn-Teller coupling. Over the range of the coupling in Fig. 1, the combined oscillator strength of the transitions to these higher levels is found to be less than 10% of that to the first Γ_{3g} and Γ_{4g} levels. Moreover, in a more realistic model of Fe^{2+} in MgO (as in the Appendix), the Jahn-Teller coupling is not with a single vibrational mode but with many phonons of different frequencies. The lowest state of each symmetry type Γ_{3g}, Γ_{4g}, and Γ_{5g} is a unique vibronic state which originates for zero Jahn-Teller coupling in the lowest Fe^{2+} electronic state of the same symmetry type, and which reflects in its energy and other properties the effect of the coupling to all of the phonons. There is, however, a multiplicity of higher states of each type which originate in the states with one vibrational quantum excited. As these states individually are probably not strongly perturbed by the Jahn-Teller coupling, such states are probably not so much depressed in energy as the higher states in Fig. 1, and because of the spread in phonon frequencies, the oscillator strength for transitions to these states should be distributed over a range of frequencies. We would, therefore, expect these higher transitions to be not only weak, but also broad and higher in energy than indicated in Fig. 1, so that it is not surprising that such transitions were not observed in Wong's spectra.

V. DISCUSSION

We have seen that we may reasonably attribute the reduced spin-orbit splitting of the $^5T_{2g}$ term of Fe^{2+} in MgO primarily to a Jahn-Teller effect, while we are unable to account for so large a reduction solely on the basis of the effects of covalent bonding. Moreover, it has proved possible to develop a model which accounts quantitatively for this reduction on the basis of the Jahn-Teller coupling, and which is also consistent with other data available from EPR and Mössbauer measurements. We have concluded from these calculations that there are significant Jahn-Teller corrections to many of the parameters such as the g factor and nuclear quadrupole and hyperfine coupling coefficients which characterise the EPR and Mössbauer spectra of MgO:Fe^{2+}. Moreover we have found that many of these Jahn-

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[54] G. A. Slack, S. Roberts, and F. S. Ham, Phys. Rev. **155**, 170 (1967).

[55] The factor $(\mathcal{E}/\mathcal{E}_{\text{eff}})^2$ appears in Eq. (4.38) for a magnetic-dipole process, because the oscillator strength of the transition is defined in terms of the strength of the equivalent classical *electric*-dipole oscillator. This factor is cancelled[54] by the factor $(\mathcal{E}_{\text{eff}}/\mathcal{E})^2$ in the relation giving the optical absorption coefficient in terms of $f_m(A,B)$.

Teller corrections appear to be larger than the corresponding corrections from covalent bonding.

The model which has been used in our calculations has involved Jahn-Teller coupling with two vibrational modes, one E_g and one T_{2g}, with frequencies in the range 300–400 cm^{-1}. An important question is the legitimacy of a calculation that uses only two discrete modes, when we know that the Fe^{2+} couples with the entire spectrum of phonons of the MgO lattice. In the Appendix we have formulated the Jahn-Teller problem when the coupling is with a continuous spectrum of phonons, for the case in which a second-order perturbation treatment of the Jahn-Teller coupling suffices, as for MgO:Fe^{2+}, to give the energy level displacements and reduction factors. We have obtained explicit expressions, Eqs. (A22) and (A23), for these energy shifts and reduction factors for the simplified case of a Debye spectrum. These results show that the terms giving the Jahn-Teller corrections to the energy shifts, Eq. (2.14), and reduction factors, Eq. (3.2), in the case of the discrete modes must be replaced for the continuous case by integrals of the appropriate quantities over the phonon frequency spectrum. Long-wavelength acoustic modes are, however, relatively ineffective in contributing to these integrals, compared with modes of higher frequency, because of the factors $\sin(\frac{1}{2}aq_x)$, etc., in Eq. (A13) which lead to the factor $1-(aq)^{-1}\sin aq$ in Eqs. (A22) and (A23), where a is the lattice constant and $\mathbf{q}$ the phonon wave vector.[56] Moreover, comparing Eq. (A23) with Eq. (A22), we see that the expressions for the reduction factors may be obtained from those for the energy shifts by replacing the $F_n(\zeta,\omega)$ by the appropriate $G_n(\zeta,\omega)$ and dividing the integrand by $\hbar\omega$. This is, of course, the same replacement procedure that provides the relationship between the energy shifts and reduction factors for the case of the discrete modes. Accordingly, if the main contribution to the integrals in Eqs. (A22) and (A23) comes from a band of relatively high-frequency phonons, it is a good approximation to replace these by one E_g and one T_{2g} mode with frequencies taken to be an average of the band, and coupling coefficients taken to represent the combined contribution of all the phonons of each type to the energy shifts and reduction factors. We may expect in such a situation that the absolute and relative values of these energy shifts and reduction factors will thus be given fairly accurately by the phenomenological model using discrete modes, even though the coupling in reality is with the continuous spectrum. The apparent success of our phenomenological treatment of MgO:Fe^{2+} in this paper leads us to the speculation that whatever the complexities of the coupling to the actual phonon spectrum of MgO as distorted by the presence of the Fe^{2+}, the predominant coupling is with the band of phonons lying roughly in the range ($\sim$300–$\sim$400 cm^{-1}) of the prominent peaks in the frequency distribution function of MgO lattice phonons.[13] We should note, however, as discussed in Sec. IV H, that we should not expect the model with discrete modes to be equally satisfactory in describing states of MgO:Fe^{2+} with energies above those of the lowest Γ_{3g}, Γ_{4g}, and Γ_{5g} levels. We must also note that we have not considered in our calculations the thermal excitation of the lattice, which not only introduces relaxation effects but may also cause a temperature dependence of some of the parameters of the experimental spectra, analogous to that of the Debye-Waller factor. So long as the principal contribution from the lattice zero-point motion to, say, the reduction factors comes from phonons of relatively high frequency, we do not, however, expect a major change in these factors below a temperature sufficiently high to excite these modes appreciably. The theory of temperature-dependent Jahn-Teller effects is not yet in an altogether satisfactory state, and we will not pursue these effects further in this paper.

There has been interest in MgO:Fe^{2+} for a number of years as a system that might exhibit a Jahn-Teller effect, since Fe^{2+} in cubic symmetry with octahedral coordination not only has an orbital triplet state lowest but has a triply degenerate Γ_{5g} spin-orbit ground state, and consequently clearly should be subject in principle to a Jahn-Teller instability. Indeed, the search for a Jahn-Teller effect was one justification given by Low and Weger[1] for initiating their detailed theoretical and experimental study of MgO:Fe^{2+}. No such effect was identified in this early work, however, because it was not recognized at that time what form Jahn-Teller effects would take in the dynamic Jahn-Teller regime. Moreover, an explanation for the apparent absence of an observable Jahn-Teller effect in MgO:Fe^{2+} was put forward by Van Vleck[57] and Liehr,[58] who noted that matrix elements of the Jahn-Teller interaction within the Γ_{5g} spin-orbit ground state were reduced, according to crystal field theory, by a factor $\frac{1}{10}$, compared with matrix elements among the *orbital* triplet states of ${}^5T_{2g}$ [the same factor $\frac{1}{10}$ that gives the crystal-field value for K_E and K_T in Eq. (3.2)]. The stabilization energy of a Jahn-Teller distortion, calculated for the Γ_{5g} level alone, would thus be only 1/100 of that one would obtain for the orbital triplet if the spin-orbit interaction were negligible. Van Vleck noted that the zero-point motion would suffice to carry the system over such a small barrier between equivalent distortions, so that one would expect that no static Jahn-Teller distortion would occur, and that crystal-field theory would accurately describe the system's magnetic behavior. The Fe^{2+} ion in octahedral coordination was thus concluded to be a case in which the spin-orbit

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[56] Inspection of the frequency dependence of $F_n(\zeta,\omega)$ and $G_n(\zeta,\omega)$ in Eqs. (2.15) and (3.4) shows that these quantities do not offset the effect of the factor $[1-(aq)^{-1}\sin aq]$ in substantially suppressing the contribution of the long-wavelength acoustic phonons to Eqs. (A22) and (A23).

[57] J. H. Van Vleck, Discussions Faraday Soc. **26**, 96 (1958); Physica **26**, 544 (1960).

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

interaction stabilized the system against a Jahn-Teller distortion.[23]

McMahon and Silsbee[59] subsequently recognized that even in the situation considered by Van Vleck[57] and Liehr,[58] in which matrix elements of the Jahn-Teller interaction between nondegenerate spin-orbit levels were assumed to have a negligible effect, there might be an observable change in the ground-state g factor of MgO:Fe^{2+} as a result of the spin-phonon coupling, which has its origin in the Jahn-Teller interaction. They calculated this g shift using a perturbation treatment and treating the phonons in the long-wavelength approximation. Their result has the same form as what we obtain for $2K_S-K_L$ from our Eq. (A23) if we ignore all but the first term in the expressions for $G_1(\zeta,\omega)$ and $G_2(\zeta,\omega)$ in Eq. (3.4) (this term is the one that arises from coupling *within* the Γ_{5g} electronic level) and if we approximate $1-(aq)^{-1}\sin aq \simeq \frac{1}{6}(aq)^2$ in Eq. (A23). McMahon and Silsbee also calculated the corresponding change in g with temperature that results from the thermal excitation of the phonons. They concluded, however, that both contributions of the spin-phonon coupling to the g shift were too small to be identified experimentally in view of the large strain-broadened EPR linewidths of MgO:Fe^{2+}. This calculation was subsequently reconsidered by O'Brien,[60] without making the long-wavelength approximation; her resulting estimate of the g shift was smaller than that obtained by McMahon and Silsbee.

The possibility that the Jahn-Teller coupling might be at least as important as covalent bonding in causing the observed g shift of Fe^{2+} in MgO was first suggested by Ham[10] in connection with his treatment of dynamic Jahn-Teller effects in paramagnetic resonance spectra. In this work, it was shown that when the Jahn-Teller interaction was strong compared with the spin-orbit interaction (but not yet so strong as to lead to a static Jahn-Teller effect), a large reduction in the orbital contribution to the g factor (as well as in the spin-orbit splitting and in some other interactions depending on orbital operators) could occur without any apparent lowering of local symmetry such as would be associated with a static Jahn-Teller distortion. Although his calculations were not applicable in detail to Fe^{2+} in MgO and CaO, Ham suggested that the difference between the g factors in these cases ($g=3.30$ for CaO:Fe^{2+} [61] compared with $g=3.428$ for MgO:Fe^{2+} [1,12]) was more likely to be the result of a dynamic Jahn-Teller effect than of covalent bonding. On the basis of a rough estimate from Watkins and Feher's measured strain-coupling coefficients,[52] he suggested that for MgO:Fe^{2+} the Jahn-Teller interaction (within $^5T_{2g}$) might be comparable in strength to the spin-orbit coupling, so that the conditions of weak Jahn-Teller coupling might not hold which were assumed by Van Vleck,[57] Liehr,[58] McMahon, and Silsbee[59] in neglecting the Jahn-Teller coupling between nondegenerate spin-orbit levels. Under such circumstances, Ham noted that Jahn-Teller corrections to the g factor should be significant, but he gave no calculations for this case.

In addition to the work reported in the present paper, another calculation to estimate these Jahn-Teller contributions to the g shift of MgO:Fe^{2+}, when account is taken of the Jahn-Teller coupling between the nondegenerate spin-orbit levels, has recently been made by Koloskova and Kochelaev.[14] Their calculation considered the coupling of the Fe^{2+} ion, via its interaction with the displacements of the nearest-neighbor oxygen ions, to the full spectrum of lattice phonons, which was treated in the Debye approximation. Since Koloskova and Kochelaev's approximations are essentially the same as those we have used in obtaining Eqs. (A22) and (A23) of the Appendix, and since their calculation was also done treating the Jahn-Teller coupling by second-order perturbation theory, their calculated g factor should agree with the result we obtain for $2K_S-K_L$ using Eq. (A23) [replacing $G_1(\zeta,\omega)$ in the integrand of Eq. (A23) by $2G_2-G_1$ in order to get the expression for $2K_S-K_L$]. These results *are* in agreement in their general form, but there are substantial discrepancies in the numerical coefficients of the terms corresponding to those in u_{22} and u_{55} in the expression for $(2G_1-G_1)$ from Eq. (3.4), while Koloskova and Kochelaev omit altogether the "off-diagonal" terms in u_{25} and v_{25} in this expression, which are by no means negligible. Apart from these algebraic errors in their work, Koloskova and Kochelaev's result for the g shift is however essentially equivalent to ours, and in agreement with our result Koloskova and Kochelaev conclude that a substantial fraction of the observed g shift for MgO:Fe^{2+} is in fact due to the Jahn-Teller coupling. The numerical discrepancies aside, we are, however, dubious that Koloskova and Kochelaev's calculation [or our Eq. (A23)] can be used for an accurate estimate of the vibronic g shift, even though the measured strain-coupling coefficients are used to determine the strength of the Jahn-Teller coupling, because of the uncertainties in treating the important high-frequency phonons in the Debye approximation. We prefer, therefore, to estimate the g shift and the change in the other reduction factors (not considered by Koloskova and Kochelaev) using our phenomenological model with the coupling strength adjusted to give Wong's observed spin-orbit splitting (the latter result was not known to Koloskova and Kochelaev at the time of their work).

The results of the present paper, together with those of Koloskova and Kochelaev,[14] indeed bear out Ham's earlier suggestion[10] concerning the importance of the Jahn-Teller contribution to the g shift of MgO:Fe^{2+}, and Koloskova and Kochelaev estimate that the vibronic g shift is appreciable also for MgO:Co^{2+}. That

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[59] D. H. McMahon and R. H. Silsbee, Phys. Rev. **135**, A91 (1964).

[60] M. C. M. O'Brien, Proc. Phys. Soc. (London) **86**, 847 (1965).

[61] A. J. Shuskus, J. Chem. Phys. **40**, 1602 (1964).

our result for this vibronic g shift for MgO:Fe^{2+} is much larger than what was estimated by McMahon and Silsbee[59] and by O'Brien[60] is due in part to the fact that the effective Jahn-Teller interaction required to account for Wong's reduced spin-orbit splitting is somewhat stronger than that assumed in these earlier calculations, and in part this difference results from neglect of the Jahn-Teller coupling between different nondegenerate spin-orbit levels in the earlier work. It is important to recognize that this coupling between nondegenerate electronic levels *must* be included if accurate estimates of the vibronic corrections are to be made, unless the separation of these levels is large compared not only with the Jahn-Teller energy but also with $\hbar\omega$ of the important vibrational modes. For the calculation of the reduction factors for MgO:Fe^{2+}, the relative importance of the coupling within the Γ_{5g} spin-orbit ground state and the coupling to the higher spin-orbit levels may be seen by comparing the value of the term independent of u_{22}, u_{55}, u_{25}, and v_{25} in the expression for $G_n(\zeta,\omega)$ in Eq. (3.4) (this term arises from coupling within the Γ_{5g} level) with the full value of $G_n(\zeta,\omega)$ given in Table II. Neglecting the coupling with the higher levels of the $^5T_{2g}$ term, as in the interpretation of MgO:Fe^{2+} or MgO:Co^{2+} proposed by Van Vleck[57] and Liehr,[58] is thus seen not to be justified unless the Jahn-Teller coupling is in any case altogether negligible.

Another situation in which a fairly weak vibronic coupling between nondegenerate electronic levels has been shown to be important in determining g shifts, etc., has been examined by Inoue.[62] She has shown that such a coupling between nondegenerate Kramers doublets of certain rare-earth ions provides an explanation, as a result of the lattice zero-point motion, for small differences between the observed g factors and the values calculated on the assumption of a rigid lattice. Since a Kramers doublet is not split by any distortion, in this case it is *only* the coupling with *other* levels that results in the change in the g factor. A striking example of this effect has recently been pointed out by Birgeneau[63] for Ce^{3+} in the ethyl sulfates, for which the vibronic g shift is ~10%. The second-order perturbation calculation given by Inoue[62] and Birgeneau[63] for the g shift resulting from the coupling to the phonons is in principle the same as our calculation for the contribution to the g shift of MgO:Fe^{2+} arising from the higher spin-orbit levels. Another ion for which vibronic coupling between nondegenerate Kramers doublets has been shown to be important is the low-spin ferric ion in ferri-hemoglobin compounds, studied by Kamimura and Mizuhashi.[64] In these molecules the symmetry is nearly tetragonal but there is a weak rhombic-field splitting of the ^2E ground state. Kamimura and Mizuhashi considered interaction with a single nondegenerate mode of vibration, and found that they could account for the highly anisotropic ground state g factor of ferrihaemoglobin azide using values for the rhombic-field and spin-orbit splittings of roughly the same size as $\hbar\omega$ and the Jahn-Teller energy. Their analysis of the dynamic Jahn-Teller effect in this case was done by a numerical diagonalization of the infinite-order secular equation of the vibronic problem including all these interactions. Kamimura and Mizuhashi's work is thus quite similar to our numerical diagonalization of the vibronic secular equation for MgO:Fe^{2+} described in Secs. II and III, except of course that we had higher symmetry and were concerned with a doubly degenerate vibrational mode.

On the basis of the calculations for the Fe^{2+} ion in MgO reported in this paper, we can make a number of speculations concerning the properties of Fe^{2+} in some other crystals. For the reasons suggested by Ham,[10] it is likely that the difference between the g factors of Fe^{2+} in CaO ($g=3.30$) and MgO ($g=3.428$) results not from greater covalency, but from a larger Jahn-Teller g shift in CaO. This view is supported by the observation of Chappert *et al.*,[35] from their Mössbauer studies that the orbital contribution to the hyperfine field at the Fe^{2+} nucleus is smaller in CaO (corresponding to a reduction factor ~0.5) than in MgO, while the isomer shift indicates *less* covalency for CaO:Fe^{2+}. These results indicate a stronger Jahn-Teller interaction in CaO than in MgO, and we are then led to speculate on the basis of Eq. (2.14) or Fig. 1 that for CaO the energy of the first excited spin-orbit levels Γ_{3g} and Γ_{4g} of Fe^{2+} may be even closer to the ground state than the value 105 cm^{-1} found by Wong[2] for both of these levels in MgO. In another case, Wigmore *et al.*[65] have obtained from acoustic paramagnetic resonance studies values for the strain-coupling coefficients for KMgF$_3$:Fe^{2+}, $|G_{11}|=1340\pm100$ cm^{-1} and $|G_{44}|=1000\pm100$ cm^{-1}, which are nearly twice as large as Watkins and Feher's values[52] for MgO:Fe^{2+}. Since the Jahn-Teller energy is proportional to the square of the coupling coefficients, these results suggest that KMgF$_3$:Fe^{2+} may show substantially larger Jahn-Teller effects than MgO:Fe^{2+}.

Note added in proof. The EPR spectrum of KMgF$_3$:Fe^{2+} has now been observed by J. T. Vallin and W. W. Piper (private communication) and found to be similar to the spectrum for MgO:Fe^{2+} reported by McMahon (Ref. 12, Fig. 1). The g factor is found to be $g=3.37\pm0.02$.

VI. CONCLUSION

It is our conclusion that the reduction in the spin-orbit splitting between Γ_{5g} and Γ_{3g}, Γ_{4g} to 105 cm^{-1}, as observed in MgO:Fe^{2+} by Wong, is predominantly the result of the Jahn-Teller coupling, and that significant Jahn-Teller corrections occur also for other parameters

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that characterize the EPR and Mössbauer spectra of MgO:Fe^{2+}. We estimate that covalent bonding reduces the spin-orbit splitting in this system by at most some 10%. If we attribute the observed reduction entirely to the Jahn-Teller coupling, we thus calculate for the g factor of the Γ_{5g} ground state a value $g(\Gamma_{5g})\simeq 3.45 \pm 0.01$, corresponding to a Jahn-Teller g shift -0.08 ± 0.01 from the crystal-field value $g(\Gamma_{5g})=3.53$. In order to be in agreement with the observed value $g(\Gamma_{5g})=3.428$, this would leave a covalency g shift of only ~ -0.02, resulting from the covalent reduction in the orbital contribution to $g(\Gamma_{5g})$. We believe that these values do represent a fair estimate of the relative importance of covalent bonding and of a dynamic Jahn-Teller effect in causing the g shift for MgO:Fe^{2+}.

Our calculations are consistent with Wong's conclusion that the Γ_{3g} and Γ_{4g} levels are almost degenerate for MgO:Fe^{2+} and that both contribute to the 105-cm^{-1} absorption line. To account for this result, we find that the Jahn-Teller coupling with E_g and T_{2g} vibrational modes must be more or less equally strong, and we calculate that we must have a Jahn-Teller energy of roughly 100 cm^{-1} corresponding to each of these types of coupling. These values are consistent with estimates of Jahn-Teller energies obtained from the observed values of the strain-coupling coefficients.

For Jahn-Teller corrections to the parameters of the Fe^{57} Mössbauer spectrum at undistorted cubic sites in MgO, we calculate for the Γ_{5g} level a 12–16% reduction in the orbital contribution to the hyperfine field at the nucleus, and a 5–15% reduction in the parameters c_3 and c_5 that characterize the quadrupole interaction. Our analysis is consistent with the following breakdown of the observed value -120 kOe for the saturation hyperfine field: core polarization contribution, -360 kOe (corresponding to $H_c/2S=-120$ kOe); orbital contribution, $+215$ kOe; spin-dipolar and second-order contributions combined, $+25$ kOe. From this value for the orbital contribution we obtain the estimate $\langle r^{-3}\rangle_{LI} \simeq 4.0$ a.u. for the effective one-electron average of r^{-3} that enters the orbital interaction (this estimate includes any reduction in $\langle r^{-3}\rangle$ that results from covalency). Using current estimates for $\langle r^{-3}\rangle_Q$ including the Sternheimer factors, but omitting any correction for covalency, we would be led from the quadrupole interaction data on MgO:Fe^{2+} to a value $Q\simeq +0.19$ b for the Fe^{57m} quadrupole moment; this value will be increased when account is taken of covalency, but according to our estimates this correction is probably less than 10%.

APPENDIX A: JAHN-TELLER COUPLING WITH A CONTINUOUS SPECTRUM OF PHONONS: PERTURBATION TREATMENT

In a more rigorous formulation of the Jahn-Teller problem for an ion in a crystal, we must consider coupling not with just a single vibrational mode of each type E_g and T_{2g}, as in Eq. (2.6), but with many such modes of different frequencies. However, in a second-order perturbation treatment of the Jahn-Teller coupling as in Secs. II and III, the effect of these modes on the energy level displacements and reduction factors is simply additive. If the Jahn-Teller coupling is not so strong as to make such a perturbation treatment inaccurate, we may therefore obtain these energy shifts and reduction factors for the lowest vibronic level originating from each electronic level of the ion by simply summing the correction terms in expressions of the form of Eqs. (2.15) and (3.2), using the appropriate frequency and coupling coefficients for each mode.

Treating the crystal containing the Jahn-Teller ion in the harmonic approximation[66] (but omitting the part of the energy of the system resulting from the Jahn-Teller coupling with the degenerate electronic level), it is possible in principle to analyze the displacements of the ions from the symmetrical configuration in terms of normal modes of vibration classified by symmetry type. For an orbital triplet electronic level (T_1 or T_2) in O_h symmetry, it is only the even modes belonging to E_g or T_{2g} that can give rise to linear Jahn-Teller coupling as in Eq. (2.6), so that it is only these modes with which we are concerned so long as we do not go beyond linear coupling. We will now illustrate such a calculation of the Jahn-Teller effects using the case in which the vibrational spectrum of the host crystal is considered not to be perturbed by the presence of the Jahn-Teller impurity ion, and we will indicate how this calculation may be applied to MgO:Fe^{2+}.

We denote by $u_{\kappa l;\alpha}$ the αth component of the displacement of the κth ion in the lth cell of the perfect host crystal, and we let $\mathbf{R}_l$ denote the position of this cell and M_κ the mass of the κth ion. We then introduce the expansion[67]

$$u_{\kappa l;\alpha}=(N\Omega M_\kappa)^{-\frac{1}{2}}\sum_{\mathbf{q},j} e_{\kappa j;\alpha}(\mathbf{q})Q_j(\mathbf{q})e^{i\mathbf{q}\cdot R_l}, \qquad \text{(A1)}$$

where N is the number of cells in unit volume, Ω is the volume of the crystal, and the quantities $e_{\kappa j;\alpha}(\mathbf{q})$ are the components of the jth eigenvector of the dynamical matrix of the crystal corresponding to the propagation vector $\mathbf{q}$. The mode frequency corresponding to $e_{\kappa j;\alpha}(\mathbf{q})$ is $\omega_j(\mathbf{q})$. The $e_{\kappa j;\alpha}(\mathbf{q})$ satisfy the relations

$$\sum_{\kappa,\alpha} e_{\kappa j;\alpha}{}^*(\mathbf{q})e_{\kappa j';\alpha}(\mathbf{q})=\delta_{jj'}, \qquad \text{(A2a)}$$

$$\sum_{j} e_{\kappa' j;\beta}{}^*(\mathbf{q})e_{\kappa j;\alpha}(\mathbf{q})=\delta_{\alpha\beta}\delta_{\kappa\kappa'}, \qquad \text{(A2b)}$$

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[67] Our treatment of the transformation from $u_{\kappa l;\alpha}$ to the dynamical variables $Q_j(\mathbf{q})$ of the normal modes is taken from that in Chap. 2 of Ref. 67, apart from some changes of notation.

and

$$e_{\kappa j;\alpha}{}^*(-\mathbf{q})=e_{\kappa j;\alpha}(\mathbf{q}). \qquad \text{(A2c)}$$

In terms of the new dynamical variables $Q_j(\mathbf{q})$ and the canonical momenta $P_j(\mathbf{q})$, the vibrational Hamiltonian of the lattice takes the form

$$\mathcal{H}_{\text{lat}}=\tfrac{1}{2}\sum_{\mathbf{q},j}[P_j(\mathbf{q})P_j(-\mathbf{q})+\omega_j{}^2(\mathbf{q})Q_j(\mathbf{q})Q_j(-\mathbf{q})], \qquad \text{(A3)}$$

and we have the commutator relation

$$[Q_j(\mathbf{q}),P_{j'}(-\mathbf{q}')]=i\hbar\delta_{jj'}\Delta(\mathbf{q}-\mathbf{q}'), \qquad \text{(A4)}$$

where $\Delta(\mathbf{q}-\mathbf{q}')$ is zero if $\mathbf{q}\neq\mathbf{q}'$ and unity if $\mathbf{q}=\mathbf{q}'$. All commutators involving other combinations of the P's and Q's are zero.

The $Q_j(\mathbf{q})$ are, however, not the most convenient variables for our Jahn-Teller problem because we cannot classify them directly according to the irreducible representations of the point symmetry group of the site of the Jahn-Teller ion. We may, however, introduce a unitary transformation of all the $Q_j(\mathbf{q})$ having the same mode frequency,

$$Q_\gamma(\omega)=\sum_{j,\mathbf{q}}\Gamma_{\gamma;j,\mathbf{q}}(\omega)Q_j(\mathbf{q}), \qquad \text{(A5)}$$

such that the new variables $Q_\gamma(\omega)$ may be so classified. In the summation in Eq. (A5) the quantities $\Gamma_{\gamma;j,\mathbf{q}}(\omega)$ are nonzero only for those values of j, $\mathbf{q}$ for which $\omega_j(\mathbf{q})=\omega$, and we may choose the transformation such that

$$\Gamma_{\gamma;j-\mathbf{q}}(\omega)=\Gamma_{\gamma;j\mathbf{q}}{}^*(\omega). \qquad \text{(A6)}$$

This latter condition corresponds to the fact that we may choose the transformation matrix from the displacements $u_{\kappa l;\alpha}$ to the $Q_\gamma(\omega)$ to be real, and Eq. (A6) then follows from Eqs. (A1) and (A5) when we use Eq. (A2c). We also make the corresponding transformation of $P_j(\mathbf{q})$,

$$P_\gamma(\omega)=\sum_{j,\mathbf{q}}\Gamma_{\gamma;j,\mathbf{q}}(\omega)P_j(\mathbf{q}). \qquad \text{(A7)}$$

Using the unitary character of the transformation matrices $\Gamma_{\gamma;j\mathbf{q}}(\omega)$ and the relation (A6), we then find from Eq. (A4) that $Q_\gamma(\omega)$ and $P_{\gamma'}(\omega')$ satisfy the commutator relation

$$[Q_\gamma(\omega),P_{\gamma}{}'(\omega')]=i\hbar\delta_{\gamma\gamma'}\Delta(\omega-\omega'), \qquad \text{(A8)}$$

while from Eq. (A3), we obtain the lattice Hamiltonian in terms of the new dynamic variables

$$\mathcal{H}_{\text{lat}}=\sum_{\gamma,\omega}\tfrac{1}{2}[P_\gamma{}^2(\omega)+\omega^2Q_\gamma{}^2(\omega)]. \qquad \text{(A9)}$$

Comparing Eq. (A9) with the vibrational Hamiltonian in Eqs. (2.10) and (2.11) used in our Jahn-Teller calculations, we see that the $Q_\gamma(\omega)$ represent suitable modes of vibration for use in such calculations if we take the effective mass μ to be equal to unity. The coupling of the Jahn-Teller ion to those $Q_\gamma(\omega)$ belonging to E_g and T_{2g} then has the form of Eq. (2.6) for each set of such modes. We may obtain explicit coupling coefficients for each such mode if we use Eqs. (A1) and (A5) to relate the $Q_\gamma(\omega)$ to the atomic displacements $u_{\kappa l;\alpha}$, and if we can estimate the coupling of the Jahn-Teller ion to each such displacement. Carrying this procedure through of course requires that we know the $e_{\kappa j;\alpha}(\mathbf{q})$, and that we have worked out the appropriate $\Gamma_{\gamma;j\mathbf{q}}(\omega)$.

Let us suppose for MgO:Fe^{2+} that the Jahn-Teller coupling is only with the displacements of the octahedron of six oxygen ions surrounding the Fe^{2+}. We define E_g and T_{2g} symmetrized coordinates in terms of these displacements as follows:[22,50]

$$Q_\theta{}^c=(12)^{-\frac{1}{2}}(2Z_3-2Z_6-X_1+X_4-Y_2+Y_5), \qquad \text{(A10a)}$$

$$Q_\epsilon{}^c=\tfrac{1}{2}(X_1-X_4-Y_2+Y_5), \qquad \text{(A10b)}$$

$$Q_\xi{}^c=\tfrac{1}{2}(Z_2-Z_5+Y_3-Y_6), \qquad \text{(A10c)}$$

etc., where X_n, Y_n, and Z_n denote the displacement of the nth oxygen ion from its equilibrium position, and the ions numbered one through six are at the sites $(\frac{1}{2}a,0,0)$, $(0,\frac{1}{2}a,0)$, $(0,0,\frac{1}{2}a)$, $(-\frac{1}{2}a,0,0)$, $(0,-\frac{1}{2}a,0)$, and $(0,0,-\frac{1}{2}a)$, respectively, relative to the Fe^{2+}, a being the lattice constant of MgO. As in Eq. (2.6) ,the Jahn-Teller coupling is given[68] by

$$\mathcal{H}_{\text{JT}}=V_E{}^c(Q_\theta{}^c\mathcal{E}_\theta+Q_\epsilon{}^c\mathcal{E}_\epsilon)+V_T{}^c(Q_\xi{}^c\mathcal{T}_\xi+Q_\eta{}^c\mathcal{T}_\eta+Q_\zeta{}^c\mathcal{T}_\zeta). \qquad \text{(A11)}$$

We now substitute from Eq. (A1) into Eq. (A10) obtaining

$$Q_i{}^c=(N\Omega M_{\text{O}})^{-1/2}\sum_{\mathbf{q},j}A_{ij}(\mathbf{q})Q_j(\mathbf{q}), \qquad \text{(A12)}$$

where

$$A_{\theta j}(\mathbf{q})=2i(3)^{-1/2}[e_{\text{O}j;z}(\mathbf{q})\sin\tfrac{1}{2}aq_z-\tfrac{1}{2}e_{\text{O}j;x}(\mathbf{q})\sin\tfrac{1}{2}aq_x-\tfrac{1}{2}e_{\text{O}j;y}(\mathbf{q})\sin\tfrac{1}{2}aq_y], \qquad \text{(A13a)}$$

$$A_{\epsilon j}(\mathbf{q})=i[e_{\text{O}j;x}(\mathbf{q})\sin\tfrac{1}{2}aq_x-e_{\text{O}j;y}(\mathbf{q})\sin\tfrac{1}{2}aq_y], \qquad \text{(A13b)}$$

$$\text{A}_{\xi j}(\mathbf{q})=i[e_{\text{O}j:z}(\mathbf{q})\sin\tfrac{1}{2}aq_y+e_{\text{O}j;y}(\mathbf{q})\sin\tfrac{1}{2}aq_z], \qquad \text{(A13c)}$$

etc., and we have replaced κ by O in $e_{\kappa j;\alpha}(\mathbf{q})$ to indicate that we are now concerned only with the displacements of the oxygen ions. Substituting from Eqs. (A12) and (A13) into Eq. (A11), we would therefore obtain the Jahn-Teller coupling expressed in terms of the propagating normal modes $Q_j(\mathbf{q})$ of the lattice.

Before making the final transformation of Eq. (A5), we will introduce several simplifications into our model in order that the results of the calculation can be put

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[68] The coupling coefficients $V_E{}^c$ and $V_T{}^c$ in Eq. (A11) are identical with the coefficients V_E and V_T that are appropriate to Eq. (2.6) when the Jahn-Teller vibrational modes are considered to be normal modes of the octahedron of nearest-neighbor oxygen ions. Therefore, $V_E{}^c$ and $V_T{}^c$ may be related to the strain coefficients as in Eq. (4.33) with D and D' given under the appropriate assumptions by Eq. (4.35).

in an explicit and simple form. These simplifying assumptions are not accurately fulfilled for a crystal such as MgO, so that our result will be at best illustrative, and should therefore not be applied quantitatively for Fe^{2+} in MgO. We assume that the phonon spectrum of the crystal is an isotropic Debye spectrum with a cut off frequency ω_D, and that the transverse and longitudinal sound velocities have the same value v_s. We also assume that we can put $e_{0j;\alpha}(\mathbf{q})$ in Eq. (A13) proportional to the components of a unit vector $e_j(\mathbf{q})$

$$e_{0j;\alpha}(\mathbf{q})=f(\omega)e_{j\alpha}(\mathbf{q})\,, \qquad \text{(A14)}$$

where we have

$$\mathbf{e}_j(\mathbf{q})\cdot\mathbf{e}_{j'}(\mathbf{q})=\delta_{jj'} \qquad \text{(A15)}$$

for the three degenerate modes of a given $\mathbf{q}$, and where we assume that $f(\omega)$ depends only on the frequency, and satisfies $f(\omega)\leq 1$ to be consistent with Eq. (A2). In order that, for a given frequency ω ,there be a single symmetrized vibrational mode $Q_\gamma(\omega)$ of each type ($\gamma=\theta$, ϵ, ξ, η, ζ) with which the Jahn-Teller coupling occurs, we then choose *for these modes* in Eq. (A5)

$$\Gamma_{\gamma;j\mathbf{q}}(\omega)=C_\gamma(\omega)A_{\gamma j}(\mathbf{q})\Delta[\omega_j(\mathbf{q})-\omega]\,, \qquad \text{(A16)}$$

where $C_\gamma(\omega)$ is given by $C_1(\omega)$ for $\gamma=\theta$, ϵ, and by $C_2(\omega)$ for $\gamma=\xi$, η, ζ. It may be verified from Eq. (A13) and symmetry considerations that for these five modes the requirement

$$\sum_{j,\mathbf{q}}\Gamma_{\gamma;j\mathbf{q}}(\omega)\Gamma_{\gamma';j\mathbf{q}}^{*}(\omega)=\delta_{\gamma\gamma'} \qquad \text{(A17)}$$

is satisfied if the real numbers $C_1(\omega)$ and $C_2(\omega)$ are chosen to make the normalization correct; that is if

$$C_1^{-2}(\omega)=f^2(\omega)\sum_{j,\mathbf{q}}\left[e_{jx}(\mathbf{q})\sin\tfrac{1}{2}aq_x-e_{jy}(\mathbf{q})\sin\tfrac{1}{2}aq_y\right]^2 \times\Delta[\omega-\omega_j(\mathbf{q})]\,, \qquad \text{(A18a)}$$

$$C_2^{-2}(\omega)=f^2(\omega)\sum_{j,\mathbf{q}}\left[e_{jz}(\mathbf{q})\sin\tfrac{1}{2}aq_y+e_{jy}(\mathbf{q})\sin\tfrac{1}{2}aq_z\right]^2 \times\Delta[\omega-\omega_j(\mathbf{q})]\,. \qquad \text{(A18b)}$$

Other modes of the same frequency ω are formed by other orthonormal combinations of the $Q_j(\mathbf{q})$, but since these do not participate in the Jahn-Teller coupling, we do not have to consider them.

Substituting the inverse of the transformation (A5) into Eq. (A12), and using Eq. (A16) and the unitary property of the $\Gamma_{\gamma;j\mathbf{q}}(\omega)$, we obtain the expansion

$$Q_\gamma{}^c=(N\Omega M_{\mathrm{O}})^{-1/2}\sum_\omega C_\gamma^{-1}(\omega)Q_\gamma(\omega)\,. \qquad \text{(A19)}$$

Inserting this in Eq. (A11), we obtain finally the interaction Hamiltonian

$$\mathcal{H}_{\mathrm{JT}}=(N\Omega M_{\mathrm{O}})^{-1/2}\sum_\omega\{V_E{}^cC_1^{-1}(\omega)\times[Q_\theta(\omega)\mathcal{E}_\theta+Q_\epsilon(\omega)\mathcal{E}_\epsilon]+V_T{}^cC_2^{-1}(\omega)\times[Q_\xi(\omega)\mathcal{T}_\xi+Q_\eta(\omega)\mathcal{T}_\eta+Q_\zeta(\omega)\mathcal{T}_\zeta]\}\,, \qquad \text{(A20)}$$

expressed in terms of the normal modes of the lattice Hamiltonian (A9), with one such mode of each type E_g and T_{2g} for each frequency ω. We may, therefore, apply the perturbation results of Secs. II and III directly to the present calculation if we identify V_E and V_T in Eq. (2.6) for each set of modes with $(N\Omega M_{\mathrm{O}})^{-1/2}V_E{}^cC_1^{-1}(\omega)$ and $(N\Omega M_{\mathrm{O}})^{-1/2}V_T{}^cC_2^{-1}(\omega)$, respectively, take $\mu_E=\mu_T=1$ in Eq. (2.9), and sum the effects for the modes of different ω. For the energy shift of the Γ_{5g} ground state of the Fe^{2+} ion, for example, we obtain from Eq. (2.14a)

$$\Delta E(\Gamma_{5g})=-[(V_E{}^c)^2/2N\Omega M_{\mathrm{O}}]\sum_\omega\omega^{-2}C_1^{-2}(\omega)F_1(\zeta,\omega)-[(V_T{}^c)^2/N\Omega M_{\mathrm{O}}]\sum_\omega\omega^{-2}C_2^{-2}(\omega)F_1(\zeta,\omega)\,, \qquad \text{(A21)}$$

or, on substituting from Eq. (A18), replacing the summation by integration, and carrying out the angular integrals over $\mathbf{q}$ space we have

$$\Delta E(\Gamma_{5g})=-\frac{(V_E{}^c)^2+2(V_T{}^c)^2}{4\pi^2v_s{}^3NM_O}\times\int_0^{\omega_D}f^2(\omega)F_1(\zeta,\omega)\left[1-\frac{\sin(a\omega/v_s)}{a\omega/v_s}\right]d\omega\,. \qquad \text{(A22)}$$

Similar results are obtained for $\Delta E(\Gamma_{3g})$ and$\Delta E(\Gamma_{4g})$, with the integral over ω being given its principal value for those terms in $F_3(\zeta,\omega)$ and $F_4(\zeta,\omega)$ for which the denominators have zeros within the range of integration. Taking the principal value corresponds to cutting out the narrow band of phonons having the same energy as the separation of the Γ_{3g} and Γ_{4g} levels from Γ_{5g}. These resonant phonons contribute to the lifetime of the Γ_{3g} and Γ_{4g} levels and therefore give these levels a nonzero width. In a similar way, we obtain from Eq. (3.2) the reduction factor K_L in the Γ_{5g} ground state,

$$K_L=-\tfrac{1}{2}+\frac{(V_E{}^c)^2+2(V_T{}^c)^2}{4\pi^2\hbar NM_Ov_s{}^3}\int_0^{\omega_D}\omega^{-1}f^2(\omega)G_1(\zeta,\omega)\times\left[1-\frac{\sin(a\omega/v_s)}{a\omega/v_s}\right]d\omega\,,$$

and corresponding results for the other reduction factors.