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Dynamical Jahn-Teller Effect in Paramagnetic Resonance Spectra: Orbital Reduction Factors and Partial Quenching of Spin-Orbit Interaction

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It is shown that the dynamical Jahn-Teller effect in a complex having orbital degeneracy may partially quench spin-orbit interaction, the orbital parts of the Zeeman and hyperfine interactions, and other orbital operators governing response to perturbations such as strain or applied electric fields. Such dynamical quenching thus decreases the value of orbital reduction factors usually attributed in paramagnetic resonance studies to covalent bonding, without necessarily causing anisotropy in the spectrum of an individual complex. The dynamical Jahn-Teller effect may also substantially enhance various second-order effects. Such dynamic effects thus may make important changes in the parameters of the spin Hamiltonian without changing its symmetry. It is shown that the dynamical Jahn-Teller effect accounts qualitatively for unusual features in the spectra of interstitial transition-metal ions Cr^0, Mn^+, Mn^0, and Fe^+ in silicon and that it is probably of importance equal to or greater than that of covalent bonding in the interpretation of the spectrum of Fe^{2+} in MgO and CaO. A mathematical analysis of the dynamical effects is given for an orbital triplet state in interaction with a doublet or triplet vibrational mode, and some results are given also when the coupling is with the phonon continuum.

I. INTRODUCTION

As Jahn and Teller[1,2] showed, an electronically degenerate state of a nonlinear complex is unstable (except in the case of simple Kramers degeneracy) with respect to some asymmetric nuclear displacement which lifts the degeneracy. If the coupling between the electrons and such displacements is sufficiently strong relative to the zero-point energy of the associated vibrational modes, the complex undergoes a static distortion to a new configuration of minimum energy.[3–5] If the coupling is less strong, or if the zero-point vibrational energy is comparable with the energy barrier separating equivalent configurations, no static distortion occurs, but the complex exhibits a coupled motion of the electrons and the vibrational modes.[6–8] This latter situation is referred to as the dynamical Jahn-Teller effect.[9–11]

The dynamical Jahn-Teller effect has been the object of a number of studies[12–26] in the time since its unusual features were first pointed out by Abragam and Pryce,[27] Longuet-Higgins, Opik, Pryce and Sack,[8] Moffitt and Liehr,[6] and Moffitt and Thorson.[7] However, little attention has been given within this dynamical regime to the possibility that the Jahn-Teller coupling may change the effect of the spin-orbit interaction, as well as other interactions, in those situations in which spin-orbit interaction is not quenched by static crystal fields. Such changes and their effect on paramagnetic resonance spectra (including several striking effects for which there is now some experimental evidence) will be the topic of this paper; we shall be concerned in particular with the case of a Jahn-Teller interaction that is somewhat stronger than the spin-orbit interaction yet not so strong as to produce a static distortion. The opposite situation has been considered by Opik and Pryce,[4] Van Vleck,[28] and Liehr,[29] who showed that certain complexes

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would be stablized by a strong spin-orbit interaction against a weak Jahn-Teller distortion.

We consider a complex in a state which, in the symmetrical configuration, has orbital degeneracy with an associated orbital angular momentum, as well as spin degeneracy. We find that the Jahn-Teller interaction partially quenches the orbital angular momentum even though it is insufficiently strong to produce a static distortion or to introduce anisotropy into the paramagnetic resonance spectrum. This partial quenching shows up as a reduction in the magnitude of the spin-orbit splitting of the state, and in reduced orbital contributions to the magnetic moment, hyperfine interaction, etc., of the spin-orbit levels.

Such "orbital reduction factors" in matrix elements of orbital angular momentum or spin-orbit interaction of a complex as compared with the appropriate free ion are, of course, well known experimentally and have been discussed extensively.[30–35] Ordinarily, however, they are the direct result of the delocalization of the electronic wave function because of covalent bonding (spin-orbit interaction may, of course, also be changed by expansion or contraction of the radial wave function). Their size has been taken as a measure of the importance of covalency. Our first conclusion, therefore, is that in appropriate cases the dynamical Jahn-Teller effect simulates the effect of covalent bonding in reducing the magnitude of certain parameters of the system. As we shall see, the Jahn-Teller effect may on occasion produce very much greater reductions in such parameters than can reasonably be attributed to covalency.

The possibility that dynamical Jahn-Teller effects may change the values of these orbital reduction factors has been for the most part overlooked in past studies of the Jahn-Teller effect and of such complexes. McConnell and McLachlan[17,18] have noted, however, in their work on the negative radical ion of benzene that the dynamical Jahn-Teller effect reduces matrix elements of orbital angular momentum associated with electronic motion around the ring. Also, in considering "inversion splitting" (dynamical Jahn-Teller effect) of complexes of transition metal ions with a d^1 configuration, Bersuker and Vekhter[25] have taken account of the reduced overlap matrix element between the different equivalent configurations in calculating matrix elements of orbital angular momentum and spin-orbit interaction. No systematic presentation of such dynamical quenching effects has, however, to the best of our knowledge been undertaken before the present work.

In partially quenching the orbital angular momentum $\mathbf{L}$ of a degenerate state, the Jahn-Teller interaction leads to finite matrix elements of $\mathbf{L}$ between the ground state of the coupled electronic-vibrational ("vibronic") system and excited states located higher in energy by an amount $\approx n\hbar\omega$ ($n=1, 2, 3, \cdots$), where $\hbar\omega$ is the energy of the appropriate oscillator (phonon). Accordingly, there are second-order corrections from these relatively low-lying excited states to the spin-orbit splitting, g shifts, etc., in the ground state. Thus second-order effects may be enhanced by the Jahn-Teller interaction over what is expected from coupling to excited states of the electronic system in the symmetrical configuration. In the limit of a static Jahn-Teller distortion these second-order effects go over into the conventional g shifts, etc., for the distorted configuration.

There are a number of experimental situations to which these considerations are relevant, and in several of these, the dynamical Jahn-Teller effect offers a plausible explanation for otherwise puzzling data. Most striking are the cases of the interstitial transition-metal ions Cr^0, Mn^+, Mn^0, and Fe^+ in silicon, the paramagnetic resonance spectra of which were studied by Ludwig and Woodbury.[36–38] These ions are at sites of tetrahedral symmetry, and the ground state of each is an orbital triplet (${}^5T_2$ for $3d^6$, ${}^4T_1$ for $3d^7$). Their resonance spectra show a remarkably large quenching of the orbital contribution to the Zeeman interaction as well as evidence of a strongly reduced spin-orbit splitting and enhanced second-order effects, none of which has been satisfactorily accounted for on the basis of covalent bonding. We believe that these ions offer the clearest examples available so far of the effects of dynamical Jahn-Teller quenching.

Other complexes having orbital triplet ground states in cubic symmetry are Co^{2+}:MgO,[39] Fe^{2+}:MgO,[40] and Fe^{2+}:CaO.[41] The spin-orbit stabilization of Jahn-Teller effects in these complexes has been discussed by Van Vleck,[28] and orbital reduction factors less than unity have been attributed by Low[39,40] and by Shuskus[41] to covalency. We believe that the latter identification is correct for Co^{2+}:MgO, but that for the two Fe^{2+} complexes the dynamical effects may be of at least comparable importance to those of covalency and probably are dominant for Fe^{2+}:CaO. The ions Co^{2+} and Fe^{2+} are of especial interest in the present connection for the historical reason that one justification for their study in octahedral coordination in MgO was the hope that they might offer examples of the Jahn-Teller effect. No such effects for either ion were ever identified, however.

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It will be clear from this paper that such effects appear in fact to be present and significant, at least for the Fe^{2+}, and that their supposed "absence" stemmed from a failure to recognize the form such effects would take in the dynamical Jahn-Teller regime.

The purpose of this paper is to set forth and substantiate the qualitative features of the expected dynamical Jahn-Teller effects, using such mathematical models as permit a rigorous analysis of simplified cases. From these, the general behavior of the effects in realistic cases may be inferred. It is not our purpose here to provide a detailed interpretation for any ion, nor to calculate orbital reduction factors for any realistic case. Such realistic calculations are not yet possible, and more detailed interpretation of existing spectra will be attempted in a later publication.

The dynamical regime with which we shall be specially concerned in this paper corresponds to a Jahn-Teller interaction which is somewhat stronger than the spin-orbit interaction (so that one is justified in treating the former first and then dealing with nondiagonal matrix elements of the latter by perturbation theory). Yet, we shall assume that the reduced spin-orbit splitting is still greater than the splitting of each spin-orbit level in an applied magnetic field. As long as this is the case, each spin-orbit level responds to a magnetic field (and, similarly, to other perturbations) qualitatively the same as it would in the absence of the Jahn-Teller interaction—for example, in cubic symmetry a spin-orbit triplet ($J=1$) gives a cubically symmetric spectrum for *each* single complex despite the Jahn-Teller interaction. If the reverse were the case, the spin would couple more strongly to the magnetic field than to the residual orbital angular momentum; the spectrum then has $g\approx 2$ and is closely related to the superposition of spectra for the various distorted configurations of the complex.

The treatment given in this paper will be confined to the case of an orbital triplet (T_1 or T_2)[42,43] in cubic or tetrahedral symmetry. The effect of partial quenching of $\mathbf{L}$ will, of course, occur, too, in cases of lower symmetry, if $\mathbf{L}$ is not already quenched by crystal fields. The case of the cubic orbital doublet (E) is of less interest in the present work because $\mathbf{L}$ is already quenched by the cubic crystal field. The doublet is, of course, the case that has excited most of the past interest in the dynamical Jahn-Teller effect because of the available spectra for nearly octahedral Cu^{2+} ($3d^9$) complexes[44–46]; our paper thus has no direct relevance to the interpretation of these Cu^{2+} or related spectra.

Our analysis is divided into several parts. In Sec. II we derive the aforementioned dynamical effects for an orbital triplet (T_1 or T_2) coupled to a doubly degenerate E vibrational mode. This case is very simple mathematically, as was noted by Moffitt and Thorson.[7] Accordingly, complete formulas can be obtained for the different effects for an arbitrarily strong Jahn-Teller interaction, and the physical origin of these effects may be seen readily; this is the only case in which a full analysis can at present be given rigorously. Thus, while this case is not a realistic one for quantitative application to practical situations, since it neglects, among other things, all coupling to the T_2 vibrational modes, it is a good one for setting forth the general features of the expected effects.

In Sec. III we consider the mathematically more complicated problem of the orbital triplet coupled to a triply degenerate T_2 mode. We prove that the general features of the quenching are similar to those found with E mode coupling, and we suggest approximate formulas, but we are unable to give rigorous formulas for this case or for the case of both E and T_2 mode coupling.

For a complex in a crystal there is not just a single set of T_2 and E vibrational modes which is involved in the dynamical Jahn-Teller effect, but in reality the entire phonon spectrum. In Sec. IV we formulate this problem in the simplified case in which the triplet is assumed to interact only with the E component of the phonon spectrum, and we write down without derivation the expressions for the energy shift and quenching factor. A more complete treatment of this problem will be given elsewhere; the present results suggest the general form and are useful in permitting estimates of the strength of the Jahn-Teller interaction with the acoustic branch of the phonon spectrum when data are available of the effect of static strain on the resonance spectrum.

The paper is concluded with a discussion and generalization of our results and with a survey of their applicability to cases of experimental interest.

II. ORBITAL TRIPLET (T_1 OR T_2)—E VIBRATIONAL MODE

A. Vibronic States and Matrix Elements

We consider first an orbital triplet electronic state[47] belonging to the irreducible representation T_1 or T_2 of the cubic point group O or the tetrahedral group T_d, in

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[47] Throughout the paper we use as a basis for the triplet state the real functions $\psi_1=\psi_\xi$, $\psi_2=\psi_\eta$, $\psi_3=\psi_\zeta$ which are taken to transform, respectively, for $T_2(O$ or $T_d)$ as yz, zx, xy, for $T_1(O)$ as x, y, z, or for $T_1(T_d)$ as $x(y^2-z^2)$, $y(z^2-x^2)$, $z(x^2-y^2)$, where x, y, z, denote Cartesian coordinates with respect to the cubic axes. The modes Q_θ, Q_ϵ are chosen to transform as $[z^2-\frac{1}{2}(x^2+y^2)]$ and $(\sqrt{3}/2)(x^2-y^2)$. Accordingly, matrices such as $\mathcal{E}_\theta$, $\mathcal{E}_\epsilon$ in (2.2) take the specific form given.

interaction with a single pair of vibrational modes Q_θ, Q_ϵ belonging to the representation E. The vibronic Hamiltonian (neglecting for the moment all effects associated with spin) is given[7] by

$$\mathcal{H}=E_0\mathcal{J}+(1/2\mu)[P_\theta^2+P_\epsilon^2+\mu^2\omega^2(Q_\theta^2+Q_\epsilon^2)]\mathcal{J}+V[Q_\theta\mathcal{E}_\theta+Q_\epsilon\mathcal{E}_\epsilon]. \quad (2.1)$$

Here P_θ, P_ϵ are the momenta conjugate to Q_θ, Q_ϵ; μ is the effective mass of the mode and ω its angular frequency; V is the Jahn-Teller coupling coefficient; and the matrices $\mathcal{J}$, $\mathcal{E}_\theta$, and $\mathcal{E}_\epsilon$ are, respectively, the unit matrix and

$$\mathcal{E}_\theta=\begin{bmatrix}+\frac{1}{2} & 0 & 0\\ 0 & +\frac{1}{2} & 0\\ 0 & 0 & -1\end{bmatrix},\quad \mathcal{E}_\epsilon=\begin{bmatrix}-\sqrt{3}/2 & 0 & 0\\ 0 & +\sqrt{3}/2 & 0\\ 0 & 0 & 0\end{bmatrix}. \quad (2.2)$$

The energy of the degenerate state in the symmetrical configuration is E_0. For simplicity we assume that the electronic states $\psi_i(\mathbf{r})$ are independent of Q, and we ignore coupling to other electronic states.

The simplicity of this case (as contrasted to the other Jahn-Teller problems we have to consider) lies in the fact that the matrices appearing in (2.1) commute and consequently can be simultaneously brought to diagonal form. Accordingly, as noted by Moffitt and Thorson,[7] the vibronic eigenfunctions $\Psi_{in}(\mathbf{Q},\mathbf{r})$ are products of one of the electronic functions $\psi_i(\mathbf{r})$ $(i=\xi,\ \eta,\ \zeta)$ and simple harmonic oscillator wave functions for a displaced two-dimensional oscillator, the equilibrium position of which is

$$Q_{\theta i}=-Ve_{i\theta}/\mu\omega^2,\quad Q_{\epsilon i}=-Ve_{i\epsilon}/\mu\omega^2, \quad (2.3)$$

where $e_{i\theta}$ or $e_{i\epsilon}$ is the appropriate diagonal component of the matrix $\mathcal{E}_\theta$ or $\mathcal{E}_\epsilon$. The potential energy of the oscillator at this position of equilibrium is lower than E_0 by the "Jahn-Teller energy" E_{JT}, which in this case is given by $E_{JT}=V^2/2\mu\omega^2$. We obtain therefore

$$\Psi_{in}(\mathbf{Q},\mathbf{r})=\psi_i(\mathbf{r})F_{n_\theta}\left(Q_\theta+\frac{Ve_{i\theta}}{\mu\omega^2}\right)F_{n_\epsilon}\left(Q_\epsilon+\frac{Ve_{i\epsilon}}{\mu\omega^2}\right), \quad (2.4)$$

$(i=\xi,\ \eta,\ \zeta)$ and the corresponding energy

$$E_{in}=E_0-(V^2/2\mu\omega^2)+(n_\theta+n_\epsilon+1)\hbar\omega,\quad n_\theta,\ n_\epsilon=0,\ 1,\ 2,\ 3,\ \cdots, \quad (2.5)$$

where $F_n(y)$ is a standard harmonic oscillator function which may be defined by the generating relation

$$\exp(-S^2+2S\alpha y-\tfrac{1}{2}\alpha^2y^2)=\pi^{1/4}\alpha^{-1/2}\sum_{n=0}^{\infty}\frac{F_n(y)}{(n!)^{1/2}}(S\sqrt{2})^n, \quad (2.6)$$

with $\alpha=(\mu\omega/\hbar)^{1/2}$.

The vibronic spectrum (2.5) in this case remains the same as in the absence of the Jahn-Teller interaction, except for the displacement $-V^2/2\mu\omega^2$ common to all states. In particular, the vibronic ground state $(n_\theta=n_\epsilon=0)$ remains a triplet for arbitrary sterngth of the Jahn-Teller coupling,[48] and all excited states remain separated from the ground state by at least the finite excitation energy $\hbar\omega$.

However, the equilibrium position (2.3) for the displaced oscillators is different for the three different electronic functions $\psi_i(\mathbf{r})$ corresponding to the three values $i=\xi$, η, ζ. As this separation increases in proportion to $V/\mu\omega^2$, the region of overlap between corresponding oscillator states associated with different electronic functions is diminished, and matrix elements between such states fall off accordingly.

Matrix elements of various operators between the vibronic eigenstates (2.4) may be evaluated explicitly using the generating relation (2.6) for the harmonic oscillator functions. Consider an electronic operator $\mathcal{O}$ which is independent of Q_θ, Q_ϵ. Then a vibronic matrix element of $\mathcal{O}$ is simply the product of an electronic matrix element and the oscillator overlap integrals:

$$\langle\Psi_{in_\theta n_\epsilon}|\mathcal{O}|\Psi_{jn_\theta'n_\epsilon'}\rangle=\langle\psi_i|\mathcal{O}|\psi_j\rangle\langle in_\theta|jn_\theta'\rangle_\theta\langle in_\epsilon|jn_\epsilon'\rangle_\epsilon, \quad (2.7)$$

where

$$\langle in_\theta|jn_\theta'\rangle_\theta=\int_{-\infty}^{\infty}dQ_\theta F_{n_\theta}\left(Q_\theta+\frac{Ve_{i\theta}}{\mu\omega^2}\right)F_{n_\theta'}\left(Q_\theta+\frac{Ve_{j\theta}}{\mu\omega^2}\right), \quad (2.8)$$

and similarly for $\langle in_\epsilon|jn_\epsilon'\rangle_\epsilon$. In particular, matrix elements in which one of the states is in the ground-state triplet involve

$$\langle i0|jn\rangle_\theta=2^{-n/2}(n!)^{-1/2}\left(\frac{V\alpha}{\mu\omega^2}\right)^n(e_{j\theta}-e_{i\theta})^n\times\exp\left[-\frac{1}{4}\frac{V^2\alpha^2}{\mu^2\omega^4}(e_{i\theta}-e_{j\theta})^2\right]. \quad (2.9)$$

An electronic operator $\mathcal{O}_A$ that has only off-diagonal matrix elements among the states ψ_ξ, ψ_η, ψ_ζ, accordingly has matrix elements within the vibronic ground-state triplet

$$\langle\Psi_{i00}|\mathcal{O}_A|\Psi_{j00}\rangle=\langle\psi_i|\mathcal{O}_A|\psi_j\rangle\exp\left[-\frac{3}{4}\frac{V^2\alpha^2}{\mu^2\omega^4}\right]=\langle\psi_i|\mathcal{O}_A|\psi_j\rangle\exp[-3E_{JT}/2\hbar\omega]. \quad (2.10)$$

These are diminished from their value in the absence of the Jahn-Teller coupling by the exponential factor, the argument of which is proportional to the square of the difference in the displacement of the oscillators for the different states or to the ratio of the Jahn-Teller energy

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[48] The treatment of Ref. 24 errs in concluding that "inversion splitting" lifts the threefold degeneracy of the T_2 ground state in this case. Such a splitting is impossible in a system having cubic symmetry.

E_{JT} to $\hbar\omega$. Thus the direct effect of $\mathcal{O}_A$ within the ground-state triplet of the vibronic system is gradually quenched as the overlap of the oscillator wave functions for the different states diminishes as the strength of the Jahn-Teller interaction is increased. The exponential factor in (2.10) is the orbital reduction factor caused by dynamical Jahn-Teller quenching of the operator $\mathcal{O}_A$.

On the other hand, an electronic operator $\mathcal{O}_B$ having only diagonal matrix elements (in terms of ψ_ξ, ψ_η, ψ_ζ) is in this case unaffected by the Jahn-Teller coupling:

$$\langle\Psi_{inm}|\mathcal{O}_B|\Psi_{jn'm'}\rangle=\langle\psi_i|\mathcal{O}_B|\psi_i\rangle\delta_{ij}\delta_{nn'}\delta_{mm'}. \tag{2.11}$$

We must also consider second-order perturbation effects on the ground-state triplet arising from couplings with the excited vibronic states. Because of (2.11), such couplings arise in this case only from off-diagonal operators $\mathcal{O}_A$, $\mathcal{O}_{A'}$, which may belong to either of the representations T_1 or T_2. We have to evaluate sums of the form

$$\langle\Psi_{j00}|\mathcal{O}_{AA'}|\Psi_{k00}\rangle =-\sum_{i\neq j,k}\sum_{n,m}{}'\frac{\langle\Psi_{j00}|\mathcal{O}_A|\Psi_{inm}\rangle\langle\Psi_{inm}|\mathcal{O}_{A'}|\Psi_{k00}\rangle}{\hbar\omega(n+m)} \tag{2.12}$$

for the two cases $j=k$ and $j\neq k$, where the prime on the summation indicates that states with $n=m=0$ are excluded. The relation (2.12) serves to define an operator $\mathcal{O}_{AA'}$ with matrix elements only within the ground-state triplet. We find, using (2.7) and (2.9),

$$\langle\Psi_{j00}|\mathcal{O}_{AA'}|\Psi_{j00}\rangle=-(\hbar\omega)^{-1}\sum_{i\neq j}\langle\psi_j|\mathcal{O}_A|\psi_i\rangle\langle\psi_i|\mathcal{O}_{A'}|\psi_j\rangle \times\exp\left[-\frac{3}{2}\frac{V^2\alpha^2}{\mu^2\omega^4}\right]G\left(\frac{3V^2\alpha^2}{2\mu^2\omega^4}\right) \tag{2.13}$$

and for the case $j\neq k$ (where $i\neq j$ or k)

$$\langle\Psi_{j00}|\mathcal{O}_{AA'}|\Psi_{k00}\rangle=-(\hbar\omega)^{-1}\langle\psi_j|\mathcal{O}_A|\psi_i\rangle\langle\psi_i|\mathcal{O}_{A'}|\psi_k\rangle \times\exp\left[-\frac{3}{2}\frac{V^2\alpha^2}{\mu^2\omega^4}\right]G\left(\frac{3V^2\alpha^2}{4\mu^2\omega^4}\right), \tag{2.14}$$

where $G(x)$ is defined as

$$G(x)=\sum_{n=1}^{\infty}\frac{x^n}{n\times n!}=\int_0^x\frac{1}{u}(e^u-1)du. \tag{2.15}$$

$G(x)$ is equal to the sum

$$\sum_{n,m}{}'\frac{y^nz^m}{(n+m)n!m!} \tag{2.16}$$

if $y+z=x$, and it has the asymptotic expansion

$$G(x)\underset{x\to+\infty}{\sim}\frac{e^x}{x}\left\{1+\frac{1}{x}+\frac{2^2}{2!x^2}+\frac{2^2\times3^2}{3!x^3}+\cdots\right\}. \tag{2.17}$$

TABLE I. Values of $G(x)$ and related functions.

x	$G(x)$	$e^{-x}G(x)$	$e^{-x}G(x/2)$	$e^{-x/2}$
0	0	0	0	1.0
0.5	0.570	0.346		0.779
1.0	1.318	0.485	0.210	0.607
1.5	2.319	0.517		0.472
2.0	3.684	0.499	0.178	0.368
3.0	8.26	0.411	0.115	0.223
4.0	17.68	0.324	0.067	0.135

Representative values of $G(x)$ and $e^{-x}G(x)$ are given in Table I for values of x near unity.

These formulas will suffice to permit calculation in this case of the energy of states derived from the ground-state vibronic triplet when spin and spin-orbit interaction are included, and also to evaluate the response of these states to external pertubations.

B. Quenching of Orbital Angular Momentum and Spin-Orbit Interaction

The electronic orbital angular momentum $\mathbf{L}$ is an operator of the type $\mathcal{O}_A$ with only off-diagonal matrix elements between the states ψ_ξ, ψ_η, ψ_ζ. Accordingly, its matrix elements within the vibronic ground-state triplet are reduced as in (2.10):

$$\langle\Psi_{i00}|L_k|\Psi_{j00}\rangle=\langle\psi_i|L_k|\psi_j\rangle\exp\left[-\frac{3}{4}\frac{V^2\alpha^2}{\mu^2\omega^4}\right]. \tag{2.18}$$

Thus, the orbital angular momentum of the ground-state triplet is partially quenched by the Jahn-Teller interaction. This quenching may be essentially complete if the Jahn-Teller interaction is strong enough, as is, of course, obviously so for the large static tetragonal distortion which is the limiting form of a strong Jahn-Teller interaction in this case. In the dynamical regime, when the overlap of the oscillator wave functions for the different states is still appreciable, the quenching is only partial.

When we include the spin $\mathbf{S}$ of the electronic state, we must add to the Hamiltonian (2.1) the spin-orbit interaction, which we assume takes the simple form

$$\mathcal{H}_{SO}=\lambda\mathbf{S}\cdot\mathbf{L}. \tag{2.19}$$

This complicates the solution of the vibronic problem because $\mathcal{H}_{SO}$ is not diagonal in terms of ψ_ξ, ψ_η, ψ_ζ; however, if $\mathcal{H}_{SO}$ is sufficiently small relative to the Jahn-Teller interaction, we can treat $\mathcal{H}_{SO}$ successfully by perturbation theory using the exact solutions (2.4)–(2.5) of the vibronic problem without spin.

Of course, if spin-orbit interaction is large compared with the Jahn-Teller interaction, we should reverse this procedure, solve the spin-orbit problem first, and then take account of the Jahn-Teller interaction. This is the situation considered by Van Vleck[28] and Liehr,[29] who showed that in appropriate cases a strong spin-orbit interaction could stabilize the system against a Jahn-

Teller distortion. In our present analysis, on the other hand, we shall be concerned primarily with the former situation with the Jahn-Teller interaction stronger than spin-orbit interaction.

Since $\mathcal{H}_{SO}$ is linear in $\mathbf{L}$, its direct effect within the ground-state triplet is reduced by the same exponential factor as in (2.18). Defining an Hermitian operator $\mathfrak{L}=(\mathcal{L}_x,\mathcal{L}_y,\mathcal{L}_z)$ in terms of its nonzero matrix elements

$$\begin{aligned}\langle\Psi_{\xi00}|\mathcal{L}_z|\Psi_{\eta00}\rangle&=\langle\Psi_{\eta00}|\mathcal{L}_x|\Psi_{\zeta00}\rangle\\&=\langle\Psi_{\zeta00}|\mathcal{L}_y|\Psi_{\xi00}\rangle=-i\end{aligned}\quad(2.20)$$

[apart from the Hermitian conjugate of these *all* other matrix elements of $\mathfrak{L}$ are defined to be zero], we can thus express the direct effect of spin-orbit interaction within the vibronic ground state by the equivalent operator

$$\mathcal{H}_{SO}'=\lambda'\mathbf{S}\cdot\mathfrak{L},\quad(2.21)$$

with

$$\lambda'=\lambda g_L\exp\left[-\frac{3}{4}\frac{V^2\alpha^2}{\mu^2\omega^4}\right].\quad(2.22)$$

Here g_L is defined in terms of a typical nonzero electronic matrix element of $\mathbf{L}$

$$g_L=i\langle\psi_\xi|L_z|\psi_\eta\rangle.\quad(2.23)$$

There is, however, a second-order effect of $\mathcal{H}_{SO}$ within the ground state, since $\mathcal{H}_{SO}$ has matrix elements also with excited vibronic states. Using (2.13)–(2.14), we obtain its operator equivalent

$$\begin{aligned}\mathcal{H}_{SO}^{(2)}=&+K_1(\mathfrak{L}\cdot\mathbf{S})^2\\&+K_2(\mathcal{L}_x^2S_x^2+\mathcal{L}_y^2S_y^2+\mathcal{L}_z^2S_z^2),\end{aligned}\quad(2.24)$$

with

$$\begin{aligned}K_1&=-(\lambda^2g_L^2/\hbar\omega)f_a,\\K_2&=-(\lambda^2g_L^2/\hbar\omega)(f_b-f_a),\end{aligned}\quad(2.25)$$

where

$$\begin{aligned}f_a&=\exp\left[-\frac{3}{2}\frac{V^2\alpha^2}{\mu^2\omega^4}\right]G\left(\frac{3}{4}\frac{V^2\alpha^2}{\mu^2\omega^4}\right),\\f_b&=\exp\left[-\frac{3}{2}\frac{V^2\alpha^2}{\mu^2\omega^4}\right[G\left(\frac{3}{2}\frac{V^2\alpha^2}{\mu^2\omega^4}\right).\end{aligned}\quad(2.26)$$

$\mathcal{H}_{SO}^{(2)}$ has the same form as second-order terms arising from spin-orbit coupling to other states of the *electronic* system in a cubic crystal field. However, K_1 and K_2 as given by (2.25)–(2.26) may be substantially larger than corresponding coefficients[43] derived from the cubic field splitting because of the relatively low excitation energy to the excited vibronic states. This is easily seen from the values of $e^{-x}G(x)$ and $e^{-x}G(x/2)$ given in Table I, and from expected values for the coefficient $(\lambda^2g_L^2/\hbar\omega)$, on the assumption that $\hbar\omega$ is much smaller than the cubic field splitting $10Dq$.

The relative energies of the spin-orbit levels derived from the ground-state vibronic triplet depend on the relative magnitudes of λ', K_1, and K_2. If λ' is much larger than K_1, K_2, the levels are grouped according to the eigenvalues $|S-1|$, S, $(S+1)$, of the effective total angular momentum operator (where $\mathcal{L}=1$)

$$\mathbf{J}=\mathfrak{L}+\mathbf{S},\quad(2.27)$$

and we have

$$E(J+1)-E(J)\approx\lambda'(J+1).\quad(2.28)$$

Only the term proportional to $(\mathcal{L}_x^2S_x^2+\mathcal{L}_y^2S_y^2+\mathcal{L}_z^2S_z^2)$ in $\mathcal{H}_{SO}^{(2)}$ (ignoring spin-orbit terms of third order or higher) splits levels of given J (for $J\geqslant2$) or couples states of different J. Thus so long as $\lambda'\gg K_1$, K_2 the levels are much the same as in the absence of Jahn-Teller coupling, but the Jahn-Teller interaction reduces the direct spin-orbit splitting in replacing λ by λ' and enhances the second-order splitting of levels with $J\geqslant2$ in proportion to K_2.

If, however, K_1 and K_2 should be comparable with or greater than λ', the spin-orbit levels may be distributed quite differently from what is found in the conventional crystal-field model for an ion in cubic symmetry. This situation will occur if $E_{JT}/\hbar\omega$ is sufficiently large that λ' in (2.22) is suitably quenched. The energy levels in such a case may usually be worked out fairly simply once values for λ', K_1, and K_2 have been assigned, but the states will in general no longer be eigenstates of J.

If $E_{JT}/\hbar\omega\gg1$, we may use the asymptotic expression (2.17) for $G(x)$ in evaluating K_1 and K_2 from (2.25)–(2.26). We find then that both K_1 and λ' decrease exponentially, but that K_2 has the asymptotic value

$$K_2\sim-2\lambda^2\mu\omega^2g_L^2/3V^2.\quad(2.29)$$

In this limit, therefore, the only significant term in $\mathcal{H}_{SO}'+\mathcal{H}_{SO}^{(2)}$ is $K_2(\mathcal{L}_x^2S_x^2+\mathcal{L}_y^2S_y^2+\mathcal{L}_z^2S_z^2)$, which has only diagonal matrix elements among the vibronic states $\Psi_{\xi00}$, $\Psi_{\eta00}$, $\Psi_{\zeta00}$. We obtain, for example,

$$\begin{aligned}&\langle\Psi_{\zeta00}|\mathcal{H}_{SO}'+\mathcal{H}_{SO}^{(2)}|\Psi_{\zeta00}\rangle\\&\qquad\sim\frac{2\lambda^2\mu\omega^2g_L^2}{3V^2}[S_z^2-S(S+1)].\end{aligned}\quad(2.30)$$

But (2.30) is simply the second-order spin-orbit term $D[S_z^2-S(S+1)]$ which we expect in the electronic ground state in the presence of a static tetragonal distortion along the z axis which places ψ_ζ lower than the electronic doublet ψ_ξ, ψ_η by the energy difference

$$\Delta E=3V^2/2\mu\omega^2=3E_{JT}.\quad(2.31)$$

Since this ΔE is precisely the separation of the energy surfaces obtained from the vibronic Hamiltonian (2.1), with neglect of the nuclear kinetic energy terms, at the position (2.3) of the minima in the lowest surface, we see that our result (2.30) agrees completely with that appropriate to the static Jahn-Teller distortion, as of course it should. The fact that in this limit the surviving term in $\mathcal{H}_{SO}'+\mathcal{H}_{SO}^{(2)}$ has only diagonal matrix elements with respect to $\Psi_{\xi00}$, $\Psi_{\eta00}$, $\Psi_{\zeta00}$ is thus the direct reflection of the fact that these three states describe the three possible static tetragonal distortions of the complex with their associated zero-point motion and that the overlap of the zero-point motion about different distortions diminishes rapidly as the strength of the Jahn-Teller coupling increases.

Criteria for the applicability of our procedure in using perturbation theory to find the effect of spin-orbit interaction on the vibronic states are of interest, particularly for contrast to the criteria appropriate to Van Vleck's considerations[28] of spin-orbit stabilization. We evidently desire that λ', K_1 and K_2 as given by (2.22), (2.25), and (2.26) be small compared to $\hbar\omega$ and that spin-orbit perturbation corrections higher than second order be very small or, ideally, negligible. These conditions may be shown usually to be satisfied if

$$V^2/\mu\omega^2 \gg |\lambda| , \tag{2.32}$$

that is if the Jahn-Teller energy is much greater than the spin-orbit splitting in the absence of Jahn-Teller coupling. Van Vleck's considerations, on the other hand, require the reverse, namely

$$V^2/\mu\omega^2 \ll |\lambda| , \tag{2.33}$$

in which case it is legitimate to solve the spin-orbit problem first and to ignore (or treat as perturbations) Jahn-Teller matrix elements coupling levels of different J. In practical examples, of course, one is likely to find that neither limit (2.32) or (2.33) is applicable, but the limiting cases are still useful in suggesting qualitatively the behavior that should be expected.

C. Response to External Perturbations

Magnetic Field

An external magnetic field **H** gives rise to the Zeeman interaction

$$\mathcal{H}_H = \beta \mathbf{L}\cdot\mathbf{H} + g_S{}^0 \beta \mathbf{S}\cdot\mathbf{H} , \tag{2.34}$$

with $\beta = e\hbar/2mc$, $g_S{}^0 = 2.0023$. The direct Zeeman effect on the vibronic ground state is then given, in accordance with (2.18) and (2.23), by

$$\mathcal{H}_H' = g_{\mathcal{L}} \beta \mathfrak{L}\cdot\mathbf{H} + g_S{}^0 \beta \mathbf{S}\cdot\mathbf{H} , \tag{2.35}$$

where

$$g_{\mathcal{L}} = g_L \exp\left[-\frac{3}{4}\frac{V^2\alpha^2}{\mu^2\omega^4} \right] . \tag{2.36}$$

To this we must add the second-order terms arising as in (2.13)–(2.14) from the combined effect of the orbital part of (2.34) and the spin-orbit interaction:

$$\begin{aligned} \mathcal{H}_H{}^{(2)} = g_1\beta[(\mathfrak{L}\cdot\mathbf{S})(\mathfrak{L}\cdot\mathbf{H}) + (\mathfrak{L}\cdot\mathbf{H})(\mathfrak{L}\cdot\mathbf{S})] \\ + g_2\beta[\mathcal{L}_x{}^2 S_x H_x + \mathcal{L}_y{}^2 S_y H_y + \mathcal{L}_z{}^2 S_z H_z] , \end{aligned} \tag{2.37}$$

where

$$\begin{aligned} g_1 &= -(\lambda g_L{}^2/\hbar\omega) f_a , \\ g_2 &= -(2\lambda g_L{}^2/\hbar\omega)(f_b - f_a) , \end{aligned} \tag{2.38}$$

and f_a, f_b were given in (2.26).

In partially quenching the orbital angular momentum of the vibronic ground state, the Jahn-Teller coupling thus reduces the direct orbital contribution to the Zeeman splitting, in accordance with (2.35) and (2.36), enhances the second-order contributions (2.37) with respect to the corresponding terms derived from the cubic-field splitting, and leaves the direct spin contribution $g_S\beta(\mathbf{S}\cdot\mathbf{H})$ unchanged (except possibly for a second-order correction to g_S which in the present case is zero). The resulting g factors for the various spin-orbit levels reflect these changes. For example, in the $3d^6$ configuration in cubic symmetry, if $\lambda' \gg K_1$, K_2 the lowest spin-orbit level is the $J=1$ triplet of ${}^5T_2$, the g factor of which is given by (if also $\lambda' \gg g\beta H$)

$$g(J=1) = \tfrac{3}{2} g_S - \tfrac{1}{2} g_{\mathcal{L}} + 3g_1 + (6/5) g_2 . \tag{2.39}$$

Whereas $g(J=1) \approx 3.5$ for the crystal-field model using free-ion wave functions $[g_{\mathcal{L}} = g_L = -1;\ g_2 = -6g_1 = +12\lambda/(10Dq);\ g_S = g_S{}^0 - 8\lambda/(10Dq)]$, this value is reduced toward 3.0 as the partial quenching of **L** diminishes $g_{\mathcal{L}}$ toward zero, if g_1 and g_2 remain small. [We assume, of course, that the quenching is not so nearly complete that $\lambda' \lesssim g_S \beta H S$; if this happens **S** couples more strongly to **H** than to $\mathfrak{L}$, and the g factor(s) approaches the spin-only value of 2.]

In the limit $E_{JT}/\hbar\omega \gg 1$, $\mathcal{H}_H{}^{(2)}$ in (2.37)–(2.38) takes an asymptotic form consistent with the g shift for a static Jahn-Teller distortion, for example,

$$\begin{aligned} \langle \Psi_{\zeta 00} | \mathcal{H}_H{}^{(2)} | \Psi_{\zeta 00} \rangle \\ \sim -(2\lambda\beta g_L{}^2/\Delta E)(S_x H_x + S_y H_y) , \end{aligned} \tag{2.40}$$

where ΔE is given by (2.31).

Static Uniform Strain

A uniform strain lifts the degeneracy of the electronic states ψ_ξ, ψ_η, ψ_ζ in accordance with the perturbation

$$\begin{aligned} \mathcal{H}_S = V_2[e_\theta \mathcal{E}_\theta + e_\epsilon \mathcal{E}_\epsilon] \\ + V_3[e_{23}\mathcal{T}_{2\xi} + e_{31}\mathcal{T}_{2\eta} + e_{12}\mathcal{T}_{2\zeta}] , \end{aligned} \tag{2.41}$$

where

$$e_{ij} = e_{ji} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \tag{2.42}$$

is a component of the strain tensor (referred to the cubic axes $x_1 = x$, $x_2 = y$, $x_3 = z$) and

$$\begin{aligned} e_\theta &= [e_{33} - \tfrac{1}{2}(e_{11} + e_{22})] , \\ e_\epsilon &= (\sqrt{3}/2)[e_{11} - e_{22}] . \end{aligned} \tag{2.43}$$

The matrices $\mathcal{E}_\theta$, $\mathcal{E}_\epsilon$ are given in (2.2), while

$$\mathcal{T}_{2\xi} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix} , \quad \mathcal{T}_{2\eta} = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix} ,$$

$$\mathcal{T}_{2\zeta} = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} . \tag{2.44}$$

The operator of which V_2 is the coefficient in (2.41) is diagonal in terms of ψ_ξ, ψ_η, ψ_ζ and thus has the form of $\mathcal{O}_B$ in (2.11). Accordingly, within the vibronic ground state it takes the identical form as in (2.41), with the same coefficient V_2, in terms of matrices $\mathcal{E}_\theta'$, $\mathcal{E}_\epsilon'$ which are identical in form with (2.2) but couple the vibronic states $\Psi_{\xi 00}$, $\Psi_{\eta 00}$, $\Psi_{\zeta 00}$ instead of ψ_ξ, ψ_η, ψ_ζ. It has no matrix elements between the ground state and excited vibronic states (in this case) and so gives rise to no higher order terms.

The operator multiplying V_3 in (2.41) is of the off-diagonal type $\mathcal{O}_A$, so its effect within the vibronic ground state is partially quenched as in (2.10), and it moreover gives rise to second-order terms linear in strain by working jointly with other type $\mathcal{O}_A$ operators such as the spin-orbit or orbital Zeeman interactions.

We can, therefore, give the effect of both types of strain on the vibronic ground state, including the second-order terms representing the strain-induced change in the spin-orbit and Zeeman interactions, by means of the equivalent operator

$$\begin{aligned}\mathcal{H}_S'=V_2[e_\theta\mathcal{E}_\theta'+e_\epsilon\mathcal{E}_\epsilon']+V_3'[e_{23}\mathcal{T}_{2\xi}'+e_{31}\mathcal{T}_{2\eta}'+e_{12}\mathcal{T}_{2\zeta}']\\ -(\lambda g_L V_3/\hbar\omega)f_a[e_{23}(\mathfrak{L}_yS_z+\mathfrak{L}_zS_y)\\ +e_{31}(\mathfrak{L}_xS_z+\mathfrak{L}_zS_x)+e_{12}(\mathfrak{L}_xS_y+\mathfrak{L}_yS_x)]\\ -(g_LV_3/\hbar\omega)\beta f_a[e_{23}(\mathfrak{L}_yH_z+\mathfrak{L}_zH_y)\\ +e_{31}(\mathfrak{L}_xH_z+\mathfrak{L}_zH_x)+e_{12}(\mathfrak{L}_xH_y+\mathfrak{L}_yH_x)],\end{aligned}\tag{2.45}$$

where

$$V_3'=V_3\exp[-\tfrac{3}{4}(V^2\alpha^2/\mu^2\omega^4)].\tag{2.46}$$

Since both V_3' and f_a decrease exponentially for large $E_{JT}/\hbar\omega$, in the limit of the static Jahn-Teller distortion the only term remaining in (2.45) is the term in V_2, which gives the effect of a uniaxial [100] strain in destroying the equivalence of the three possible tetragonal distortions. The disappearance of V_3' in this limit, of course, is a direct reflection of the fact that a uniaxial [111] strain does not destroy this equivalence.

Other Perturbations

The effect of other perturbations on the vibronic ground state may be written down from the results for those considered above, since these are representative of the three different types of operators, as classified by the irreducible representation of O or T_d to which they belong and by whether they are real or imaginary, which lift the degeneracy of the orbital triplet state. The magnetic field belongs to T_1 and appears in $\beta\mathbf{L}\cdot\mathbf{H}$ associated with an imaginary T_1 operator $\mathbf{L}$, while the [100] and [111] types of uniaxial strain [the V_2 and V_3 terms in (2.41), respectively] belong to E and T_2, respectively, and associate with real operators $\mathcal{E}_\theta$, $\mathcal{T}_{2\xi}$, etc. Since the symmetrized and antisymmetrized direct product of T_1 or T_2 with itself (for either O or T_d) contains, respectively, (A_1, E, T_2) and T_1, these three exhaust the possible types (since A_1 leads to no splitting).

Thus, for example, the effect of the term $P(\mathbf{L}\cdot\mathbf{I})$ in the hyperfine interaction[34,43] follows immediately from our results for the magnetic field, if only we replace β by P and $\mathbf{H}$ by $\mathbf{I}$ in the appropriate terms of expressions such as (2.35), (2.37), and (2.45).

The linear effect of an applied electric field $\mathbf{E}$ for tetrahedral symmetry follows from the above results for the [111] type of strain, since $\mathbf{E}$ belongs to T_2 under T_d (under O it belongs to T_1 and since it is real does not split the triplet in first order).

III. ORBITAL TRIPLET (T_1 OR T_2)—
T_2 VIBRATIONAL MODE

A triplet state in interaction with a set of vibrational modes Q_ξ, Q_η, Q_ζ belonging to T_2 gives rise to the vibronic Hamiltonian[7]

$$\begin{aligned}\mathcal{H}=E_0\mathcal{I}+(2\mu)^{-1}[P_\xi^2+P_\eta^2+P_\zeta^2+\mu^2\omega^2(Q_\xi^2+Q_\eta^2+Q_\zeta^2)]\mathcal{I}\\ +V[Q_\xi\mathcal{T}_{2\xi}+Q_\eta\mathcal{T}_{2\eta}+Q_\zeta\mathcal{T}_{2\zeta}],\end{aligned}\tag{3.1}$$

where $\mathcal{T}_{2\xi}$, $\mathcal{T}_{2\eta}$, $\mathcal{T}_{2\zeta}$ are the matrices given in (2.44), in terms of ψ_ξ, ψ_η, ψ_ζ as basis.

In this case the matrices $\mathcal{T}_{2\xi}$, $\mathcal{T}_{2\eta}$, $\mathcal{T}_{2\zeta}$ do not commute, and it is consequently not possible to find three fixed linear combinations of ψ_ξ, ψ_η, ψ_ζ which diagonalize the linear term in (3.1) for all Q_ξ, Q_η, Q_ζ. The vibronic eigenfunctions, therefore, do not have a simple form analogous to (2.4), and the energy spectrum is no longer essentially unchanged by the Jahn-Teller interaction, as it was in (2.5). The problem is, therefore, very much more complicated than for the E vibrational mode. We shall not attempt here to analyze this case thoroughly, but we shall give enough detail to be able to compare its general properties with those of the E mode case, particularly with respect to the quenching of various operators within the vibronic ground state.

The spectrum of (3.1), to second order in the Jahn-Teller coupling coefficient V, was shown by Moffitt and Thorson[7] to be the same as that of the Hamiltonian obtained from (3.1) by replacing the terms linear in V by

$$(V^2/2\mu\omega^2)(\mathbf{M}\cdot\mathfrak{l}-2),\tag{3.2}$$

where $\mathbf{M}=\hbar^{-1}(\mathbf{Q}\times\mathbf{P})$ and $\mathfrak{l}$ is an Hermitian electronic operator defined [in analogy with (2.20)] by

$$\langle\psi_\xi|\mathfrak{l}_z|\psi_\eta\rangle=-i,\ \text{(etc.)}.\tag{3.3}$$

Defining $\mathfrak{F}=\mathbf{M}+\mathfrak{l}$, we have then

$$\begin{aligned}E=E_0+(n+\tfrac{3}{2})\hbar\omega\\ +(V^2/4\mu\omega^2)[F(F+1)-M(M+1)-6],\\ n=0,1,2,3,\cdots,\end{aligned}\tag{3.4}$$

where F is the eigenvalue of $\mathfrak{F}$ [$F=M-1, M, M+1$ for $M\geqslant 1$; $F=1$ for $M=0$] and M takes the values n, $n-2$, $\cdots$, to 0 or 1. The degeneracy of each vibronic level is $(2F+1)$ in the "spherical" approximation of (3.2) and (3.4), and the ground state is a triplet with

$n=0$, $M=0$, $F=\mathfrak{l}=1$. The Jahn-Teller energy E_{JT} in this case is $(2/3)V^2/\mu\omega^2$.

In the limit of a very strong Jahn-Teller coupling, $E_{JT}\gg\hbar\omega$, the ground state is fourfold degenerate corresponding to four equivalent static distortions[3,4]

$$(Q_\xi^0,Q_\eta^0,Q_\zeta^0)_j=(2V/3\mu\omega^2)(m_1,m_2,m_3)\,, \tag{3.5}$$

with the associated electronic states

$$\psi_j=(1/\sqrt{3})(m_1\psi_\xi+m_2\psi_\eta+m_3\psi_\zeta)\,, \tag{3.6}$$

where for $j=1$, 2, 3, 4, (m_1,m_2,m_3) is the set $(+1, +1, +1)$, $(-1, -1, +1)$, $(+1, -1, -1)$, $(-1, +1, -1)$, respectively. The fourfold vibronic degeneracy spans the irreducible representations T_2+A_1 if the orbital triplet belongs to T_2 (and T_1+A_2 if the triplet belongs to T_1) so that an accidental degeneracy occurs in this limit. Thus, as the strength of the Jahn-Teller coupling increases, the triplet ground state of (3.4) is approached by a singlet state which has the same limiting energy.[49] For a finite coupling strength the ground state is presumably always the triplet, but whereas in the case of the E mode the triplet is always $\hbar\omega$ below the nearest excited state, for the T_2 mode the excitation energy to the singlet may be much less than $\hbar\omega$.

In considering the quenching of operators within the vibronic ground-state triplet, analogous to that found in Sec. II, it is convenient to look first at the case of a very strong Jahn-Teller coupling and to form the wave functions $\Psi_{\xi0}$, $\Psi_{\eta0}$, $\Psi_{\zeta0}$ for the triplet and Ψ_{S0} for the nearby singlet as linear combinations of the lowest vibronic eigenfunctions Ψ_j appropriate to each of the four distorted configurations (3.5):

$$\begin{aligned}
\Psi_{\xi0}&=(2\Lambda)^{-1}(\Psi_1-\Psi_2+\Psi_3-\Psi_4)\,,\\
\Psi_{\eta0}&=(2\Lambda)^{-1}(\Psi_1-\Psi_2-\Psi_3+\Psi_4)\,,\\
\Psi_{\zeta0}&=(2\Lambda)^{-1}(\Psi_1+\Psi_2-\Psi_3-\Psi_4)\,,\\
\Psi_{S0}&=(2\Lambda')^{-1}(\Psi_1+\Psi_2+\Psi_3+\Psi_4)\,.
\end{aligned} \tag{3.7}$$

Each Ψ_j is given approximately for $E_{JT}\gg\hbar\omega$ by ψ_j in (3.6) multiplied by the vibrational function corresponding to zero-point motion about the jth extremum; the nonorthogonality of the Ψ_j arising from a small overlap in this motion about different extrema necessitates the normalization correction factors Λ, Λ' in (3.7). Matrix elements within the triplet or between the triplet and singlet may then be expressed in terms of matrix elements among the Ψ_j. Obviously those operators are completely quenched as $E_{JT}/\hbar\omega$ increases which can be shown to depend only on off-diagonal matrix elements among the Ψ_j, since their overlap eventually diminishes exponentially in $E_{JT}/\hbar\omega$ in analogy to (2.10). Operators depending on diagonal matrix elements may remain finite in the limit.

Real operators belonging to E or T_2 and imaginary operators belonging to T_1 are the only ones leading to a first-order splitting of the triplet. We may show from the general transformation properties of these operators that when the triplet states have the form (3.7) (the Ψ_j are real) matrix elements of E and T_1 operators within the triplet may be given in terms of a single off-diagonal matrix element among the Ψ_j; a T_2 operator requires one diagonal and one off-diagonal matrix element among the Ψ_j to be specified completely. Representative matrix elements for each case are the following:

$$\langle\Psi_{\xi0}|T_{1z}|\Psi_{\eta0}\rangle=2\Lambda^{-2}\langle\Psi_3|T_{1z}|\Psi_1\rangle\,, \tag{3.8a}$$

$$\langle\Psi_{\xi0}|E_\epsilon|\Psi_{\xi0}\rangle=2\Lambda^{-2}\langle\Psi_3|E_\epsilon|\Psi_1\rangle\,, \tag{3.8b}$$

$$\langle\Psi_{\xi0}|T_{2\zeta}|\Psi_{\eta0}\rangle=\Lambda^{-2}\{\langle\Psi_1|T_{2\zeta}|\Psi_1\rangle-\langle\Psi_1|T_{2\zeta}|\Psi_2\rangle\}\,. \tag{3.8c}$$

Thus the electronic orbital angular momentum, which belongs to T_1, is strongly quenched within the vibronic triplet ground state by a strong T_2 mode Jahn-Teller coupling, just as it was in (2.18) for the E mode. An operator belonging to E is also strongly quenched this time [for example, the V_2 part of the strain interaction (2.41)], while one belonging to T_2 [the V_3 part of (2.41), say] may remain finite in the limit because of the diagonal matrix element on the right-hand side of (3.8c); for E mode coupling the reverse was true. This behavior is of course just a reflection of the fact that in the static limit all four distorted configurations are equivalent with respect to a [100] uniaxial strain (E) which thus causes no splitting, while a [111] strain (T_2) distinguishes one of the four.

It has so far not been possible to derive a rigorous quantitative expression for the quenching in this case, like (2.18) and (2.46) for the E mode, because the overlap integrals needed in (3.8) are difficult to evaluate even if we can make use of the Born-Oppenheimer approximation over most of the configuration space. However, it is quite simple to evaluate the quenching to the accuracy represented by Moffitt and Thorson's approximate Hamiltonian (3.2) and the energies (3.4). We obtain for representative matrix elements of electronic operators the following:

$$\langle\Psi_{\xi0}|L_z|\Psi_{\eta0}\rangle=\langle\psi_\xi|L_z|\psi_\eta\rangle \times\{1-\tfrac{3}{2}(V\alpha/\mu\omega^2)^2+\cdots\}\,, \tag{3.9a}$$

$$\langle\Psi_{\xi0}|E_\theta|\Psi_{\xi0}\rangle=\langle\psi_\xi|E_\theta|\psi_\xi\rangle \times\{1-\tfrac{3}{2}(V\alpha/\mu\omega^2)^2+\cdots\}\,, \tag{3.9b}$$

$$\langle\Psi_{\xi0}|T_{2\zeta}|\Psi_{\eta0}\rangle=\langle\psi_\xi|T_{2\zeta}|\psi_\eta\rangle \times\{1-\tfrac{1}{2}(V\alpha/\mu\omega^2)^2+\cdots\}\,. \tag{3.9c}$$

As seen from (3.8), the limiting value of the bracketed functions in (3.9a) and (3.9b) must decrease exponentially to zero $E_{JT}/\hbar\omega\to\infty$, while that in (3.9c) may be shown from (3.8c) and (3.6) to approach (2/3). These results suggest the following extrapolation of (3.9):

$$\langle\Psi_{i0}|L_k|\Psi_{j0}\rangle=\langle\psi_i|L_k|\psi_j\rangle\exp[-\tfrac{3}{2}(V\alpha/\mu\omega^2)^2]\,, \tag{3.10a}$$

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[49] The energy difference between the singlet and triplet is the "inversion splitting" referred to by Bersuker (Ref. 24).

$$\langle\Psi_{i0}|E_k|\Psi_{j0}\rangle=\langle\psi_i|E_k|\psi_j\rangle\exp[-\tfrac{3}{2}(V\alpha/\mu\omega^2)^2], \quad (3.10b)$$

$$\langle\Psi_{i0}|T_{2k}|\Psi_{j0}\rangle=\langle\psi_i|T_{2k}|\psi_j\rangle \times\{\tfrac{2}{3}+\tfrac{1}{3}\exp[-\tfrac{3}{2}(V\alpha/\mu\omega^2)^2]\}. \quad (3.10c)$$

These expressions have the correct general behavior, but they are certainly not correct in detail and *may* be in substantial relative error for both intermediate and large values of $E_{JT}/\hbar\omega$.

Second-order effects on the ground state from perturbations coupling to the excited vibronic states, like those derived in the case of the E mode, will be enhanced here too by the Jahn-Teller interaction. In this case, in fact, all three of the operator types (T_1, E, and T_2) give rise to second-order effects, since even the T_2 operator is partially quenched (for the E mode, an E operator was not affected at all and, therefore, did not couple the ground state and excited states). A rigorous calculation of these effects would, of course, be very much more difficult than it was for the E mode, although expressions may be derived quite simply (we do not give the results here) for the two limits: (a) the limit corresponding to Moffitt and Thorson's approximate Hamiltonian (3.2), and (b) the static limit. The general form of the operator equivalents of these second-order effects on the ground-state triplet is, of course, known on symmetry grounds. The second-order spin-orbit and Zeeman effects take the form (2.24) and (2.37) [additional terms proportional to S^2 and $(\mathbf{S}\cdot\mathbf{H})$ may, in general, also appear]; the relative asymptotic behavior of the coefficients as $E_{JT}/\hbar\omega$ increases must this time be compatible with the limiting trigonal distortion. Similarly, the second-order effects of strain take the general form given in (2.45), except that we must now add to this expression terms arising because the E type of strain also couples to excited states. These take the form

$$[e_\theta(\mathcal{L}_zS_z-\tfrac{1}{2}\mathcal{L}_xS_x-\tfrac{1}{2}\mathcal{L}_yS_y)+e_\epsilon(\sqrt{3}/2)(\mathcal{L}_xS_x-\mathcal{L}_yS_y)]$$

and

$$[e_\theta(\mathcal{L}_zH_z-\tfrac{1}{2}\mathcal{L}_xH_x-\tfrac{1}{2}\mathcal{L}_yH_y)+e_\epsilon(\sqrt{3}/2)(\mathcal{L}_xH_x-\mathcal{L}_yH_y)].$$

There is a further source of second-order effects in this case which was not present for the E mode, namely the singlet state which may be quite close to the ground-state triplet. Since the triplet belongs to T_2 and the singlet to A_1, however (or to T_1 and A_2), only operators belonging to T_2 can couple the triplet and the singlet. Thus there is in particular no spin-orbit or Zeeman coupling between these states and no consequent second-order effect on the g factor of the triplet. There may, however, be large second-order (and higher) effects on the triplet due to a T_2 strain coupling with the singlet.

IV. CONTINUOUS PHONON SPECTRUM

A complex in a crystal interacts with the entire phonon spectrum, not just with a few localized modes, and it is evident that the phonons collectively must produce effects via the Jahn-Teller interaction which are similar to those obtained in Secs. II and III for the simpler cases of single modes. In particular, it is of interest to know at least qualitatively the effect of the continuous phonon spectrum in quenching orbital angular momentum and other operators.

We shall not go into any detail with this problem at this time but shall simply cite a few results. A more complete treatment will be reserved for a later publication. As a guide to the general form of the result for the continuous phonon case, we may take the analog of the case of a single E mode in Sec. II and consider the orbital triplet in interaction with the phonon spectrum only through the E part of each mode. In terms of annihilation and creation operators of the phonon field, the Hamiltonian analogous to (2.1) then takes the form

$$\begin{aligned}\mathcal{H}=E_0\mathcal{I}+\sum_{qt}\hbar\omega(qt)[a^\dagger(qt)a(qt)+\tfrac{1}{2}]\mathcal{I}\\ +\sum_{qt}\{[V_\theta(qt)a(qt)+V_\theta{}^*(qt)a^\dagger(qt)]\mathcal{E}_\theta\\ +[V_\epsilon(qt)a(qt)+V_\epsilon{}^*(qt)a^\dagger(qt)]\mathcal{E}_\epsilon\}. \quad (4.1)\end{aligned}$$

Here q denotes the propagation vector of the phonon, t its mode of polarization, and $\omega(qt)$ its frequency, while $V_\theta(qt)$, $V_\epsilon(qt)$ are Jahn-Teller coupling coefficients which are mutually related so that the Hamiltonian has the full symmetry of O or T_d.

The spectrum of (4.1) may be easily shown to be identical with that of the decoupled problem in which the Jahn-Teller interaction is zero, except for an energy shift δE which is common to all states of the full system and is given by

$$\delta E=-\tfrac{1}{2}\sum_{qt}[\hbar\omega(qt)]^{-1}[|V_\theta(qt)|^2+|V_\epsilon(qt)|^2]. \quad (4.2)$$

We may also show in this case that operators with only diagonal matrix elements with respect to the electronic states ψ_ξ, ψ_η, ψ_ζ are unaffected by the Jahn-Teller coupling, just as was true for $\mathcal{O}_B$ in Sec. II, while those like $\mathcal{O}_A$ with only off-diagonal matrix elements are partially quenched. The quenching factor for $\mathcal{O}_A$ in the ground state of the system may now be shown to be

$$\exp\{-\tfrac{3}{4}\sum_{qt}[\hbar\omega(qt)]^{-2}[|V_\theta(qt)|^2+|V_\epsilon(qt)|^2]\} \quad (4.3)$$

in place of the exponential factor in (2.10).

When the T_2 part of the Jahn-Teller interaction with each mode is included in the Hamiltonian, the problem no longer admits a simple rigorous result like (4.3), any more than it did for the localized modes. Qualitatively, however, the behavior is similar, except that, of course, operators of both types $\mathcal{O}_A$ and $\mathcal{O}_B$ are now partially quenched. Second-order effects are enhanced by a continuous phonon spectrum in both cases, just as they were for the single vibrational modes.

V. DISCUSSION

We have considered several idealized situations in which the dynamical Jahn-Teller effect has been shown to cause a partial quenching of spin-orbit interaction, orbital angular momentum, and other orbital operators, within the degenerate ground state of the vibronic system. This quenching is the result of the coupled motion of the electrons and the vibrational modes which characterizes the dynamical Jahn-Teller regime, and it occurs even though the Jahn-Teller coupling is insufficiently strong to produce a static distortion of the complex. So long as the residual spin-orbit interaction is larger than the splitting of the degenerate levels in a magnetic field, the paramagnetic resonance spectrum of each complex shows no departure from the symmetry of the undistorted configuration, but the Jahn-Teller coupling introduces orbital reduction factors in the response of the complex to perturbing fields, and it may enhance the corresponding second-order effects.

The examples we have considered were chosen because their mathematical simplicity permits a more complete analysis over the full range of the strength of the Jahn-Teller interaction than is possible in other cases. They are, of course, not quantitatively applicable to actual molecules or complexes. We must now consider how these results may be generalized and to what extent they may be relevant to actual experimental cases.

We have shown in the case of an orbital triplet in interaction with a pair of localized E vibrational modes that quenching occurs for orbital operators belonging to both T_1 (orbital angular momentum, spin-orbit and orbital Zeeman interactions, etc.) and T_2 [e.g., response to [111] uniaxial strain or (in tetrahedral symmetry) to an applied electric field]. The orbital reduction factors describing this quenching vary as a function of theJahn-Teller coupling coefficient V in proportion to a simple describing this quenching vary as a function of the Jahn-Teller coupling coefficient V in proportion to $\exp[-\frac{3}{4}(V\alpha/\mu\omega^2)^2]=\exp[-\frac{3}{2}E_{JT}/\hbar\omega]$. In this case, operators belonging to E (e.g., response to [100] uniaxial strain) are unaffected by the Jahn-Teller coupling. On the other hand, for the triplet in interaction with a set of T_2 vibrational modes, T_1 and E operators are quenched [this time in proportion to a complicated function of $(V\alpha/\mu\omega^2)^2$ which we have suggested may be represented approximately as a descending exponential], while T_2 operators are only partially quenched, remaining finite in the limit of large $E_{JT}/\hbar\omega$ with a value $\frac{2}{3}$ their original value.

It is evident from these results that if interaction is with *both* E and T_2 modes, then all types of orbital operators T_1, T_2 and E are quenched at least partially. Whether it is the E or the T_2 operator that has a finite value in the limit of the static Jahn-Teller distortion depends on which mode of distortion dominates in determining the limiting configuration of minimum energy.[4,5] Since in realistic situations with an orbital triplet the Jahn-Teller coupling *is* with both types of modes, we may expect in general in the dynamical regime that all types of operators will display orbital reduction factors less than unity as a consequence of the Jahn-Teller interaction. Moreover, all types of perturbing operators correspondingly should give rise to enhanced second-order effects in the ground state, due to interaction with excited vibronic states. Similar conclusions should apply to other degenerate cases besides the orbital triplet, including those of lower symmetry; the relevant operators in each case are those having nonzero matrix elements between the degenerate states.

The dynamical Jahn-Teller situation for a complex in a crystal is complicated further by the fact that interaction is with the continuum of phonons and not only with a few localized modes of vibration. We have given expressions for the Jahn-Teller energy (4.2) and quenching factor (4.3) for a simple example of the continuum case. These may be evaluated for the acoustic branch of the phonon spectrum, in the long-wavelength approximation, using data obtained from the effect of static strain in splitting the orbital degeneracy of the complex. It is obvious, from (4.2) and (4.3), however, that the important regions of the phonon spectrum are those near critical points, where the density of states is high. Thus, critical points in the continuum act much like localized modes of similar frequency, and their effect may be analyzed approximately in these terms. Unfortunately, this approximation is of limited help in making a quantitative analysis in actual cases, for we rarely would know values for the Jahn-Teller coupling coefficients appropriate to the vairous critical points.

Therefore, while our considerations have sufficed to demonstrate the general occurrence of these consequences of the dynamical Jahn-Teller effect, and to provide a guide to the general form and magnitude of these effects, it will be difficult to give a quantitative analysis for actual complexes of experimental importance. We must probably be content in most cases to analyze the situation in terms of an effective generalized spin Hamiltonian [containing terms like (2.21), (2.24), (2.35), (2.37), (2.45), etc.] which takes account of orbital reduction factors and enhanced second-order effects through phenomenological coefficients chosen to fit the data. The values found for these coefficients may be markedly affected by the Jahn-Teller effect, however, and they may differ considerably from what one expects from ligand field theory taking account of covalent bonding.

In the model cases we have considered we find that even a weak Jahn-Teller coupling causes an appreciable decrease from unity in the various orbital reduction factors. For example, if $V^2/\mu\omega^2=(1/10)\hbar\omega$, the factor appropriate to $\mathbf{L}$ or to spin-orbit interaction is given by (2.18) and (2.22) to be 0.93 in the case of the E mode, and from (3.10a) to be ≈ 0.86 for the T_2 mode. However, these values are correct only if the Jahn-Teller coupling is much stronger than the spin-orbit interaction, $E_{JT}\gg|\lambda|$, as discussed in Sec. IIB. For a weak Jahn-

Teller coupling, this inequality is very likely to be reversed, as in (2.33), and we must then follow Van Vleck[28] and Liehr[29] in examining each spin-orbit level separately for Jahn-Teller instability. If a level is a singlet or a Kramers doublet, there is no instability, and the only effect of terms linear in Q in the Hamiltonian (2.1) or (3.1) is to couple the states of this level to *other* levels. Such coupling introduces a small energy shift in the level quadratic in Q (no splitting) and for the doublet produces a g-shift linear in Q which averages to zero under the zero-point motion. Thus, the spin-orbit interaction stabilizes such levels against a weak Jahn-Teller coupling, and apart from higher order perturbation effects (assumed small) it eliminates the effect of the Jahn-Teller coupling on g factors, hyperfine interaction, etc. On the other hand, if a spin-orbit level has degeneracy greater than 2 ($J\geqslant 1$), Jahn-Teller instability remains. In these cases one may get significant quenching from the dynamical Jahn-Teller effect for those operators which have matrix elements among the degenerate states, and one obtains reduction factors for these operators quite analogous to the orbital reduction factors we have found for orbital operators. Thus with a sufficiently strong spin-orbit interaction even the spin angular momentum can be at least partially quenched by the dynamical Jahn-Teller effect. Substantial quenching in such cases requires, however, $V_J{}^2/\mu\omega^2\approx\hbar\omega$, where V_J is the Jahn-Teller coupling coefficient appropriate to the Jth spin-orbit level. Since V_J is simply some numerical multiple γ_J of the corresponding Jahn-Teller coefficient V for orbital operators, substantial quenching can occur under Van Vleck's condition (2.33) only if the relations

$$|\lambda|\gg V^2/\mu\omega^2\approx\hbar\omega/\gamma_J{}^2$$

are simultaneously satisfied. This is a difficult condition to fulfill, since for the iron group of transition metals λ is comparable with typical values of $\hbar\omega$ for the relevant modes. In the case considered by Van Vleck[28] of the lowest level ($J=1$) of the $3d^6$ configuration in octahedral coordination, γ_J is 1/10 for both E and T_2 modes, so that if the Jahn-Teller coupling is weaker than the spin-orbit interaction, and if $\hbar\omega\gtrsim|\lambda|$, then we have $V_J{}^2/\mu\omega^2<(1/100)\hbar\omega$, and Jahn-Teller reduction factors are within one percent of unity. In this case, therefore, as Van Vleck has noted, a sufficiently strong spin-orbit interaction suppresses for all practical purposes any manifestation of Jahn-Teller instability of this level.

To sum up, the dynamical quenching effects we have calculated for orbital operators are correct even in our model cases only if $V^2/\mu\omega^2\gg|\lambda|$, but within this range they affect matrix elements of all orbital operators among the several spin-orbit levels derived from the vibronic ground state. In the reverse situation appropriate to Van Vleck's considerations, strong spin-orbit coupling may eliminate such effects in certain levels by stabilizing the level against Jahn-Teller instability, either in an essential fashion as for a Kramers doublet, or "accidentally" by reducing the coupling coefficient to a small value. We may, however, still get dynamical quenching effects with $|\lambda|\gg V^2/\mu\omega^2$ (for $J\geqslant 1$), and because of the strong spin-orbit coupling these then quench at least partially both orbital and spin operators within a level. Finally, dynamical quenching effects certainly occur if $V^2/\mu\omega^2\approx|\lambda|$, in which case it is difficult to predict in general what values various parameters might assume. We shall not consider these other situations further, and we shall now present general arguments and cite experimental evidence to support our contention that the range of interest for dynamical Jahn-Teller quenching not only is likely to occur in practice but in fact has been realized in several complexes involving transition metal ions of the iron group.

The general argument that such cases are likely to occur is based on the observation that the range of interest represents an intermediate one with respect to the strength of the Jahn-Teller coupling and the spin-orbit interaction, and that examples from both extremes have been observed. On one hand, we have the examples of Co^{2+} ($3d^7$)[39] and Fe^{2+} ($3d^6$)[40] octahedrally coordinated in MgO. Neither of these show any indication of Jahn-Teller distortions, and both have g values (see Table II) close to the values for the lowest spin-orbit level ($J=\frac{1}{2}$ and 1, respectively) expected on the basis of ligand field theory for the cubic configuraton. These are the two cases cited by Van Vleck[28] as displaying spin-orbit stabilization against Jahn-Teller instability. They evidently correspond to $V^2/\mu\omega^2\gg|\lambda|$ (although as we'll see below there is some reason to think that this inequality is poorly satisfied for Fe^{2+}).

TABLE II. Experimental g factors of transition metal ions in orbital triplet states.

	Ion	g	Reference
$3d^6$: $^5T_2$	Fe^{2+}: MgO	3.428	b
	Fe^{2+}: CaO	3.30	c
	Mn^+: Si[a]	3.01	d
	Cr^0: Si[a]	2.97	d
$3d^7$: $^4T_1$	Co^{2+}: MgO	4.278	e
	Fe^+: MgO	4.15	f
	Fe^+: NaF	4.344	g
	Mn^0: Si[a]	3.362	d
	Fe^+: Si[a]	3.524	d

[a] These values are for ions occupying interstitial sites in the silicon lattice.
[b] W. Low and M. Weger, Ref. 40.
[c] A. Shuskus, Ref. 41.
[d] G. W. Ludwig and H. H. Woodbury, Ref. 37.
[e] W. Low, Ref. 39.
[f] J. W. Orton, P. Auzins, J. H. E. Griffiths, and J. E. Wertz, Proc. Phys. Soc. (London) **78**, 554 (1961).
[g] B. Bleaney and W. Hayes, Proc. Phys. Soc. (London) **B70**, 626 (1957).

On the other hand, as examples from the other extreme, $V^2/\mu\omega^2\gg|\lambda|$, we may cite cases in which the Jahn-Teller coupling is so strong that it leads to a static distortion despite a stabilizing influence of the spin-orbit interaction. Two ions giving such an effect are Cu^{2+} ($3d^9$) and Ni^{2+} ($3d^8$) at the tetrahedral A sites of the chromite spinels $Cu_xCo_{1-x}Cr_2O_4$, $Ni_xCo_{1-x}Cr_2O_4$, and $Cu_xNi_{1-x}Cr_2O_4$ studied by Arnott, *et al.*[50] In tetrahedral coordination Cu^{2+} and Ni^{2+} should be in the orbital triplet states ${}^2T_2$ and ${}^3T_1$, respectively, but a strong spin-orbit interaction would stabilize both in ground states having, respectively, $J=\frac{1}{2}$ and 0. However, tetragonal distortions of these compounds do in fact occur[51] in the appropriate ranges of the composition parameter x, and they accord with Dunitz and Orgel's suggestion[52] that these macroscopic distortions arise cooperatively from Jahn-Teller distortions occurring at the sites of the individual Cu^{2+} and Ni^{2+} ions (Co^{2+} at the A site is in the state ${}^4A_2$ and so has no Jahn-Teller instability due to orbital degeneracy). Thus the Jahn-Teller coupling in these cases is evidently sufficiently strong to override the stabilizing effect of the spin-orbit coupling, even though for Cu^{2+} and Ni^{2+} the values for λ should be among the largest of those for the ions of the first transition group. These examples also confirm that the Jahn-Teller coupling of t_2 electrons can be quite strong in tetrahedral coordination (in the octahedral case t_2 electrons are "nonbonding" and should thereby be but weakly coupled to the vibrational modes).

Since the strength of both spin-orbit and Jahn-Teller coupling varies over a considerable range for different ions and different environments, the experimental verification that examples exist from both extremes makes it likely that other cases may occur in the range where dynamical Jahn-Teller quenching occurs. Thus on these general grounds we may hope to find cases with $V^2/\mu\omega^2 \gtrsim |\lambda|$ (ideally $\gg |\lambda|$) but with $V^2/\mu\omega^2 \approx \hbar\omega$ so that no static distortion occurs (ω here is, of course, some effective frequency which approximately characterizes the vibrational modes which are important for the Jahn-Teller coupling). These cases should reveal the expected effects of dynamical quenching in the values found for their orbital reduction factors.

In Table II are presented experimental values of the g factor of the lowest spin-orbit level of an orbital triplet term of various ions in cubic or tetrahedral symmetry. For the ${}^5T_2$ terms of the $3d^6$ configuration the lowest level has $J=1$ and as discussed in connection with (2.39) has a g factor near 3.5 in the crystal-field model which is diminished toward 3.0 by Jahn-Teller quenching of the orbital Zeeman energy (assuming the residual spin-orbit splitting is still larger than the Zeeman splitting). For $3d^7$ ${}^4T_1$ the $J=\frac{1}{2}$ level is lowest with the corresponding values of g near 4.3 and 3.3, respectively.

The most striking cases in Table II are the four interstitial ions Cr^0, Mn^+, Mn^0, and Fe^+ in silicon studied by Ludwig and Woodbury.[37,38] None of these ions have spectra indicating any departure from tetrahedral symmetry at the site of an individual ion, yet the first three appear to have almost entirely suppressed the orbital contribution to the g factor, while the corresponding orbital reduction factor for Fe^+ is about 0.2. A detailed analysis of these and other data for these ions will be presented in another publication[38]; we believe that these results can plausibly be attributed to dynamical Jahn-Teller quenching. All of these ions show evidence that the spin-orbit splitting has been drastically reduced from free-ion values (yet remaining larger than the Zeeman splitting), and that second-order effects are enhanced over what would be expected from the ligand field model using a λ reduced by covalent bonding. Indeed these spectra show a large isotropic hyperfine interaction with the transition metal nucleus which would be difficult to reconcile with the great decrease in the orbital reduction factors if this decrease were due to the spread of the wave function onto neighboring silicon atoms. These features are all compatible with dynamical Jahn-Teller quenching, which is able to effect a much larger decrease in the orbital reduction factors for these ions than could thus reasonably be attributed to covalent bonding.

Among the other ions listed in Table II, the g factor of Co^{2+}:MgO has been accounted for by Low,[39] taking account of the second-order g shift and of mixing with ${}^4P$, on the basis of an orbital reduction factor 0.89–0.85 for the orbital Zeeman interactions. This value is similar to others which have been attributed to covalent bonding,[31–33] and we believe that dynamical quenching probably plays no substantial role in this case. Since λ is large for Co^{2+}, and since in octahedral coordination the t_2 electrons are nonbonding and may be but weakly coupled to the vibrations, Co^{2+}:MgO seems quite likely to be a case to which Van Vleck's considerations rather than ours apply.

For Fe^{2+}:MgO[40] and Fe^{2+}:CaO,[41] we may, however, have complexes in which dynamical Jahn-Teller quenching is as important as covalent bonding in affecting the orbital reduction factors, which for the Zeeman interaction are 0.8 and 0.6, respectively. These values are somewhat smaller than we might have expected as a result of covalency, and we suggest in particular that the difference between them may be due primarily to the Jahn-Teller effect. The spin-orbit interaction is significantly smaller for Fe^{2+} than for Co^{2+}, so that Fe^{2+} on this account would be less likely than Co^{2+} to fulfill Van Vleck's condition for spin-orbit stabilization. Moreover, the lattice constant is *larger* in CaO than in MgO,

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[50] R. J. Arnott, A. Wold, and D. B. Rogers, J. Phys. Chem. Solids 25, 161 (1964).

[51] Arnott *et al.* (Ref. 50) report the following cubic and tetragonally distorted structures in the indicated ranges of the composition parameter x:

$Cu_xCo_{1-x}Cr_2O_4$: cubic, $0 \leqslant x \leqslant 0.43$
tetragonal, $c/a < 1$, $0.48 \leqslant x < 1$
$Ni_xCo_{1-x}Cr_2O_4$: cubic, $0 < x < 0.5$
tetragonal, $c/a > 1$, $0.6 < x < 1$
$Cu_xNi_{1-x}Cr_2O_4$: tetragonal, $c/a > 1$, $0 < x < 0.125$
tetragonal, $c/a < 1$, $0.175 < x < 1$.

[52] J. D. Dunitz and L. E. Orgel, J. Phys. Chem. Solids 3, 20 (1957).

so that we would expect *less* covalent bonding for Fe^{2+} in CaO. The opposite conclusion would be required if the covalent interpretation of the difference in the g factors were correct. The looser lattice should, on the other hand, enhance the dynamical quenching by lowering the relevant vibrational frequencies.

To get a rough idea how well Van Vleck's stabilization criterion may be satisfied for Fe^{2+} in MgO, we have evaluated the Jahn-Teller energy (4.2) arising from the coupling of Fe^{2+} to the E component of the acoustic branch of the phonon spectrum, using a coupling coefficient determined from the data of Watkins and Feher[53] on the effect of static strain in splitting the degeneracy of Fe^{2+} ($J=1$). We obtain $\delta E \approx -45$ cm^{-1}. Added to a similar value arising from the T_2 component, this is already comparable to the spin-orbit coupling parameter $|\lambda| \approx 100$ cm^{-1}. Moreover, localized vibrational modes and higher branches of the phonon spectrum (or coupling coefficients at critical points in the acoustic branch which may be larger than those obtained in the long-wavelength limit) are likely to give the dominant contribution to the Jahn-Teller interaction. Thus it appears that Van Vleck's condition $|\lambda| \gg V^2/\mu\omega^2$ is not well satisfied, and it is likely that Fe^{2+}:MgO is a marginal case in which dynamical quenching is at least as important as the reduction due to covalency.

Evaluation of the orbital reduction factor (4.3) for Fe^{2+}:MgO from the data of Watkins and Feher gives the result that dynamical quenching due to the E component of the acoustic branch alone would reduce the spin-orbit and orbital Zeeman energies by the factor 0.83, if, on the other hand, *our* condition $V^2/\mu\omega^2 \gg |\lambda|$ were satisfied. It is clear that this is not the case either, since the combined quenching effect of all parts of the phonon spectrum cannot result in a factor smaller than the observed[40] value of 0.8. However, if $V^2/\mu\omega^2 \approx |\lambda|$, as appears to be the case, then an over-all dynamical quenching effect of $\approx 10\%$ (that is a reduction factor ≈ 0.9) for Fe^{2+}:MgO seems quite possible, which together with a similar 10% reduction due to covalency as in Co^{2+}:MgO would then account for the value 0.8 found experimentally for the reduction factor. We suggest, therefore, that the two effects are comparable in this case and that for Fe^{2+}:CaO[41] the dynamical quenching accounts for some three-quarters of the observed reduction.

While a more detailed interpretation of the evidence for dynamical quenching in the spectra of the interstitial ions in silicon will be presented in a later publication, we believe the data of Table II suffice to show that dynamical quenching is important for the understanding of these ions and also for at least some of the Fe complexes. We expect that other complexes will be found exhibiting this manifestation of the dynamical Jahn-Teller effect, not only in the paramagnetic resonance spectra of ions having orbitally degenerate ground states, but also in optical spectra involving an excited state with such degeneracy.

VI. CONCLUSION

We have shown that the dynamical Jahn-Teller effect for complexes having orbital degeneracy can substantially diminish the orbital reduction factors appropriate to spin-orbit splitting, orbital Zeeman interaction, and the response of the system to other perturbations such as strain or applied electric fields, without lowering the effective symmetry of the complex. These dynamical effects simulate effects usually associated with covalent bonding, and where they are significant they may radically alter conclusions which otherwise would be drawn about the importance of covalency. As a result of couplings to excited vibronic states of relatively low energy, such dynamical quenching may also enhance various second-order effects to a considerable extent over what would be expected from couplings to excited electronic states of the symmetrical configuration. The importance of all such dynamical effects on the parameters of a phenomenological spin Hamiltonian must be recognized in any interpretation of the paramagnetic or optical spectra of such systems.

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