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Effect of Linear Jahn-Teller Coupling on Paramagnetic Resonance in a ^2E State

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The theory of the effect of a dynamic Jahn–Teller effect on the electron-paramagnetic-resonance spectrum of a ^2E state is developed from the limit of weak Jahn–Teller coupling taking account only of linear coupling. The principal changes produced in the EPR spectrum of the vibronic ground state may be represented simply by introducing appropriate reduction factors into the spin Hamiltonian which describes the splitting of the electronic ^2E state by a magnetic field, strain, or hyperfine interaction. These reduction factors affect the anisotropic part of the spin Hamiltonian but not the isotropic part; they are diminished from unity by the Jahn–Teller coupling; and they are analogous to the reduction factors introduced earlier in the theory of a triplet state. The theory is used to discuss Höchli's data for Sc^{2+} in CaF_2 and SrF_2 and Coffman's data for Cu^{2+} in MgO. While the latter case is consistent with either a moderately strong linear Jahn–Teller coupling or with the tunneling model, the present theory applied to Sc^{2+} in CaF_2 and SrF_2 indicates that in these cases the Jahn–Teller coupling is quite weak.

I. INTRODUCTION

EVER since the discovery[1–3] of the first unambiguous experimental manifestation of the Jahn-Teller effect,[4] in the electron-paramagnetic-resonance (EPR) spectrum of Cu^{2+} in $ZnSiF_6 \cdot 6H_2O$, there has been continuing interest[5] in Jahn-Teller effects of ions having an orbital doublet ground state (belonging to the irreducible representation E of the symmetry group of the cube) in cubic or near-cubic symmetry, particularly as revealed in EPR studies. Numerous observations of such effects have now been reported, particularly for Cu^{2+} and Ni^+ in various host crystals. The typical observation in the cases studied has been of a static Jahn-Teller effect below a temperature typically in the range 10 to 30°K; the EPR spectrum is then the superposition of three axial spectra, each corresponding to a distorted defect with one of the cube axes as its axis of symmetry. At temperatures somewhat above this temperature the spectrum exhibits a dynamic Jahn-Teller effect characterized by a single isotropic spectrum with its g factor and hyperfine interaction given approximately by the average of the corresponding parameters of the three low-temperature spectra. The nature of the configurational instability that leads to the stable configurations characterizing the low-temperature spectrum has been explored theoretically with considerable thoroughness by a number of writers[6–10] beginning with Van Vleck[6] and later Opik and Pryce,[7] and most completely by Liehr.[9] The static Jahn-Teller effect for an orbital doublet state is accordingly now quite well understood, at least in terms of phenomenological parameters. The study of dynamic Jahn-Teller effects for the orbital doublet state, of course, had its inception in Abragam and Pryce's explanation[2] of Bleaney and Ingram's observations,[1] but it has received its principal theoretical development at the hands of Moffitt and his co-workers,[11–13] Longuet-Higgins *et al.*,[14,15] O'Brien,[16] and others.[17–23] Although this theory has accounted for many of the complex features of the spectra observed experimentally, the dynamic effects are still not very well understood in general, and even the detailed nature of the transition to the high-temperature isotropic spectrum remains to a large extent unclear.

Recently what promises to be a major breakthrough for the understanding of dynamic Jahn-Teller effects

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[1] B. Bleaney and D. J. E. Ingram, Proc. Phys. Soc. (London) **A63**, 408 (1950).

[2] A. Abragam and M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 409 (1950).

[3] B. Bleaney and K. D. Bowers, Proc. Phys. Soc. (London) **A65**, 667 (1952).

[4] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).

[5] For a review of relevant work see 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, especially Sec. II.

[6] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

[7] U. Opik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957).

[8] A. D. Liehr and C. J. Ballhausen, Ann. Phys. (N.Y.) **3**, 304 (1958).

[9] A. D. Liehr, J. Phys. Chem. **67**, 389 (1963).

[10] J. B. Goodenough, J. Phys. Chem. Solids **25**, 151 (1964).

[11] W. Moffitt and A. D. Liehr, Phys. Rev. **106**, 1195 (1957).

[12] W. Moffitt and W. Thorson, Phys. Rev. **108**, 1251 (1957).

[13] W. Moffitt and W. Thorson, in *Calcul des Fonctions d'Onde Moleculaire*, edited by R. Daudel (Rec. Mem. Centre Nat. Rech. Sci., Paris, 1958), p. 141.

[14] H. C. Longuet-Higgins, U. Opik, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958).

[15] M. S. Child and H. C. Longuet-Higgins, Phil. Trans. Roy. Soc. (London) **A254**, 259 (1961).

[16] M. C. M. O'Brien, Proc. Roy. Soc. (London) **A281**, 323 (1964).

[17] I. B. Bersuker, Zh. Eksperim. i Teor. Fiz. **43**, 1315 (1962). [English transl.: Soviet Phys.—JETP **16**, 933 (1963)].

[18] J. C. Slonczewski, Phys. Rev. **131**, 1596 (1963).

[19] I. B. Bersuker, Zh. Eksperim. i Teor. Fiz. **44**, 1239 (1963). [English transl.: Soviet Phys—JETP **17**, 836 (1963)].

[20] R. Englman and D. Horn, in *Proceedings of the First International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), p. 329.

[21] I. B. Bersuker, S. S. Budnikov, B. C. Vekhter, and B. I. Chinik, Fiz. Tverd. Tela **6**, 2583 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2059 (1965)].

[22] C. W. Struck and F. Herzfeld, J. Chem. Phys. **44**, 464 (1966).

[23] D. C. Krupka and R. H. Silsbee, Phys. Rev. **152**, 816 (1966)

in the orbital doublet state has occurred in the discovery by Coffman[24] (Cu^{2+} in MgO) and Höchli[25] (Sc^{2+} in CaF_2 and SrF_2) of a new type of low-temperature EPR spectrum showing dynamic effects resulting from the zero-point ionic motion. Instead of the three superimposed axial spectra characteristic of a static Jahn-Teller effect, Coffman and Höchli found a single low-temperature spectrum exhibiting the cubic anisotropy expected for a $^2E(\Gamma_8)$ ground state in full cubic symmetry. Coffman and Höchli independently interpreted their spectra as indicating that appreciable tunneling was occurring between the three tetragonally distorted configurations of the static Jahn-Teller effect, so that as described by Bersuker[17,19] and also by O'Brien,[16] the ground state of the system is split by the tunneling into a doublet (^2E) ground state and a singlet ($^2A_1$ or $^2A_2$) excited state. Coffman found no trace at 1.2°K of the isotropic spectrum expected for the singlet state, so that he concluded this state was not populated appreciably at this temperature, while Höchli interpreted his data to give an estimate for this tunneling splitting as ≈ 10 cm^{-1} for CaF_2:Sc^{2+} and ≈ 8 cm^{-1} for SrF_2:Sc^{2+}.

The purpose of this paper is to develop the theory for an alternative interpretation of spectra such as those found by Coffman and Höchli, in terms of a model different from that used by Bersuker and O'Brien. Both Bersuker[17,19] and O'Brien[16] presupposed that the Jahn-Teller coupling was strong, so that for their work to be applicable one must be near the limiting case of the static Jahn-Teller effect; tunneling between the three distorted configurations, due to a small but finite vibrational overlap, then leads to a small energy separation (Bersuker's "inversion splitting") between the doublet ground state and singlet excited state. However, it is well known from the work of Moffitt and his co-workers[11–13] and that of Longuet-Higgins *et al.*[14,15] that the vibronic ground state is also an orbital doublet belonging to E for a weak or moderately strong Jahn-Teller coupling. One would therefore expect for this case a low-temperature EPR spectrum of the same sort as that obtained on the tunneling model, but we would like to know how the parameters of the spectrum then relate to the strength of the Jahn-Teller coupling, and how they compare quantitatively with those given by the tunneling model. The theory of the EPR spectrum appropriate to a weak or moderately strong Jahn-Teller coupling will accordingly be presented in this paper.

The present theory, as we will see, bridges the gap between static crystal-field theory with zero Jahn-Teller coupling and the strong-coupling theory of Bersuker and O'Brien. It shows clearly therefore how what Coffman[24] has described as a "third type of Jahn-Teller EPR spectrum" for a ^2E state arises as a manifestation of the typical behavior expected of a system exhibiting dynamic Jahn-Teller effects. Moreover, the theory developed from the limit of weak Jahn-Teller coupling has a basic simplicity which is much less evident when the theory is viewed from the strong-coupling limit. Finally, this approach has many features in common with the author's previous treatment[26] of dynamic Jahn-Teller effects for an orbital triplet state, so that a common conceptual basis for interpretation of dynamic effects for doublet and triplet states is thereby established. In particular, we shall show that the Jahn-Teller coupling modifies the electronic parameters of the spin Hamiltonian of the doublet state by introducing reduction factors precisely analogous to the orbital reduction factors which were shown previously[26] to describe the effect of Jahn-Teller coupling in partially quenching the spin-orbit interaction, the orbital part of the g factor, etc., in a triplet state.

We shall limit the analysis of this paper to the case of linear Jahn-Teller coupling—that is, to terms in the vibronic Hamiltonian corresponding to a splitting of the electronic degeneracy linear in the distortion. Our theory then amounts to an application of the theory of the dynamic Jahn-Teller effect for the doublet state developed by Moffitt *et al.*[11–13] and Longuet-Higgins *et al.*[14,15] to the calculation of the EPR spectrum. Indeed, the reduction factors necessary for the present theory have in fact already been calculated numerically by Child and Longuet-Higgins[15] as part of a tabulation of matrix elements needed in connection with their theory of the infrared and Raman spectra of a molecule in an orbital doublet state. Furthermore, Krupka and Silsbee[23] have previously made a similar application of the work of Longuet-Higgins *et al.*[14] to an interpretation of dynamic Jahn-Teller effects in the EPR spectrum of the ^2E ground state of the R center (C_{3v} symmetry) in KCl, and they have also pointed out that the Jahn-Teller coupling modifies the spin Hamiltonian by the introduction of appropriate reduction factors. Nevertheless, despite these close connections with previous work, the results obtained in this paper have not previously been related in their present generality to an interpretation of the EPR spectrum.

A practical reason for the development of the present theory is that evidence is accumulating that a number of transition-metal ions having an orbital doublet ground state in cubic or tetrahedral symmetry may have only a weak or moderately strong Jahn-Teller coupling, so that the present theory would then be directly applicable to these ions. In particular, Höchli[25] found in applying Bersuker's tunneling theory to Sc^{2+} ($3d^1$) in CaF_2 and SrF_2 (eightfold coordination) that he obtained a value of at least 0.20 for the vibrational overlap between the different distorted Jahn-Teller configurations. Such an overlap is remarkably

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[24] R. E. Coffman, Phys. Letters **19**, 475 (1965); **21**, 381 (1966); and (unpublished).

[25] U. T. Höchli and T. L. Estle, Phys. Rev. Letters **18**, 128 (1967); U. T. Höchli, Phys. Rev. **162**, 262 (1967).

[26] F. S. Ham, Phys. Rev. **138**, A1727 (1965).

large if the Jahn-Teller coupling is indeed strong enough for simple tunneling theory to be applicable, and, indeed, if we use the present theory to attempt an interpretation of Höchli's data, then, as we shall show, the Jahn-Teller coupling we deduce on this basis is quite weak. In other work, Low and Rosenthal[27] have recently investigated Ti^{3+} in CaF_2 by EPR, and they have found no static Jahn-Teller effect for T as low as 1.4°K. Furthermore, studies by Slack *et al.*[28,29] of the optical spectrum (near- and far-infrared) of Fe^{2+} in tetrahedral coordination in ZnS, CdTe, and $MgAl_2O_4$ revealed that the ${}^5E$ ground state showed the (second-order) spin-orbit splitting expected on the basis of crystal-field theory, with no evidence for any pronounced Jahn-Teller effect. Although we shall not be concerned in detail with a ${}^5E$ state in this paper, many of our results are appropriate to this case as well, and this evidence that Jahn-Teller effects are weak for the E state of Fe^{2+} in tetrahedral coordination suggests that the same may be true for Sc^{2+} and Ti^{3+} if they can be studied in such coordination.

As already noted, the treatment in this paper is limited to linear Jahn-Teller coupling. This coupling should be more important than higher-order effects if the Jahn-Teller coupling is weak or only moderately strong, and in any case it is of interest to know what effects the linear coupling has by itself on the EPR spectrum. However, as Van Vleck[6] originally showed, the linear coupling leads to an infinity of equivalent distortions, and one requires higher-order effects[7-10] to single out the three stable distorted configurations that characterize the static Jahn-Teller effect. Thus, the present theory is not applicable in detail in the limit of strong Jahn-Teller coupling, where the case of a static Jahn-Teller effect is approached, although we shall exhibit some important consequences of O'Brien's theory in this limit which serve to establish limits of applicability of the respective theories.

In Sec. II is presented the basic theory needed to describe the effect of Jahn-Teller coupling on the parameters that determine the EPR spectrum. The detailed mathematical analysis of the vibronic Hamiltonian for the electronic E state is, however, placed in the Appendix. Although this analysis is equivalent in many respects to that given earlier,[11-15] the formulation given here is more convenient than what is given elsewhere for an understanding of the present problem. In Sec. III the relationship of our results to parameters in the strong-coupling theories of O'Brien[16] and Bersuker[17,19] is described

In Secs. IV, V, and VI the conclusions of the general theory are then applied to the g factor, the hyperfine interaction, and the effect of applied strain. Sections VII and VIII consider the effects of random strain and relaxation, since both of these are responsible for very important modifications of the EPR spectrum of a ${}^2E$ state. The paper concludes with a discussion of the applicability of this theory to available experimental data.

II. BASIC THEORY

The vibronic Hamiltonian[12,14,30]

$$\mathcal{H}=\mathcal{H}_0\mathcal{I}+V[Q_\theta U_\theta+Q_\epsilon U_\epsilon], \qquad (1)$$

with

$$\mathcal{H}_0=E_0+(1/2\mu)[P_\theta^2+P_\epsilon^2+\mu^2\omega^2(Q_\theta^2+Q_\epsilon^2)], \qquad (2)$$

describes the linear Jahn-Teller coupling of an orbital doublet electronic state (ψ_θ, ψ_ϵ) belonging to the 2-dimensional irreducible representation E of the rotation group O of the cube (or of the tetrahedral group T_d) with a pair of vibrational modes (Q_θ, Q_ϵ) also belonging to E.[31] 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; E_0 is the energy of the degenerate electronic state in the symmetrical configuration; and V is the coupling coefficient for linear Jahn-Teller coupling. Throughout the paper we shall make use of four Hermitian electronic operators denoted by $\mathcal{I}$, U_θ, U_ϵ, and A_2 which are defined to have matrix elements between the states $\psi_\theta, \psi_\epsilon$ given, respectively, by the unit matrix and

$$U_\theta=\begin{pmatrix}-1 & 0\\ 0 & +1\end{pmatrix},$$

$$U_\epsilon=\begin{pmatrix}0 & +1\\ +1 & 0\end{pmatrix},$$

$$A_2=\begin{pmatrix}0 & -i\\ +i & 0\end{pmatrix} \qquad (3)$$

[rows and columns are labeled in the order θ, ϵ, so that for example $\langle\psi_\theta | U_\theta | \psi_\theta\rangle$ equals -1; note that apart from the sign of U_θ, the matrices (3) are simply the Pauli matrices].

The exact eigenstates and eigenvalues of $\mathcal{H}$ in Eq. (1) may not be obtained by analytic means because U_θ and U_ϵ do not commute and therefore may not be diagonalized simultaneously (in contrast to the simpler

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[27] W. Low and A. Rosenthal, Bull. Am. Phys. Soc. **11**, 906 (1966).

[28] G. A. Slack, F. S. Ham, and R. M. Chrenko, Phys. Rev. **152**, 376 (1966).

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

[30] The subscripts θ and ϵ are used throughout the paper to label the two partners ($\psi_\theta, \psi_\epsilon$; Q_θ, Q_ϵ; P_θ, P_ϵ; U_θ, U_ϵ; etc.) belonging to the irreducible representation E (symmetry group O or T_d) and transforming respectively as $[z^2-\frac{1}{2}(x^2+y^2)]$ and $(\sqrt{3}/2)(x^2-y^2)$, where x, y, z, denote Cartesian coordinates with respect to the cubic (fourfold) axes.

[31] The formal theory of this paper is equally appropriate to the case of an orbital doublet in trigonal symmetry, and our results may be applied directly to this case as well. However, for definiteness, we shall consider explicitly only the cubic case in this paper. For the form of the spin Hamiltonian in the trigonal case, see the paper of Krupka and Silsbee (Ref. 23).

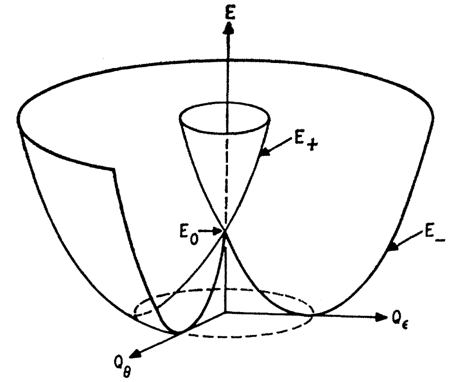

FIG. 1. Potential-energy surfaces $E_\pm(Q_\theta, Q_\epsilon)$ for the vibronic problem of the orbital doublet with linear Jahn-Teller coupling (after Moffitt and Thorson, Ref. 13). The surfaces have rotational symmetry about the energy axis.

case of the triplet[12,26] coupled to Q_θ, Q_ϵ). If, however, we set $Q_\theta=\rho\cos\theta$ and $Q_\epsilon=\rho\sin\theta$, the electronic states[7,13,16] which diagonalize the potential-energy part of $\mathcal{H}$ for fixed values of Q_θ, Q_ϵ are

$$\psi_-(\rho,\theta)=\begin{pmatrix}\cos\frac{1}{2}\theta\\ -\sin\frac{1}{2}\theta\end{pmatrix},\qquad \psi_+(\rho,\theta)=\begin{pmatrix}\sin\frac{1}{2}\theta\\ \cos\frac{1}{2}\theta\end{pmatrix}\tag{4}$$

(where this notation denotes, for example, that $\psi_-=\psi_\theta\cos\frac{1}{2}\theta-\psi_\epsilon\sin\frac{1}{2}\theta$) corresponding, respectively, to the (potential) energies

$$E_\pm(Q_\theta, Q_\epsilon)=E_0\pm V\rho+\tfrac{1}{2}\mu\omega^2\rho^2.\tag{5}$$

Since Eq. (5), plotted as a function of Q_θ, Q_ϵ, has rotational symmetry about the origin, we obtain the well-known potential-energy surfaces[6,9,13] for this vibronic problem as given in Fig. 1, for which the configurations of minimum energy on the lower sheet are all the points on the circle $\rho=|V|/\mu\omega^2$. This minimum defines what we term the Jahn-Teller energy E_{JT},

$$E_{\mathrm{JT}}=V^2/2\mu\omega^2,\tag{6}$$

which is the amount by which the potential energy is lowered when the system is distorted from the symmetrical configuration to a point at the bottom of the trough.

The Hamiltonian of Eq. (1) has full cubic symmetry (under simultaneous transformation of *both* electronic and vibrational operators), so that the exact eigenstates of $\mathcal{H}$ must belong to the irreducible representations of the symmetry group of the original symmetrical configuration and must have the corresponding degeneracies. In particular, the ground state of $\mathcal{H}$ in Eq. (1) is a vibronic doublet belonging to E, whatever the value of V.[13,14] Thus, so long as excited vibronic states are far away in energy from the ground state relative to the size of any perturbation that we may apply, the properties of this vibronic ground state are formally identical, so far as symmetry considerations are concerned, with those of the original electronic orbital doublet state in a fixed environment of cubic symmetry when Jahn-Teller effects are ignored. We may expect, however, that the Jahn-Teller coupling will change the value of the parameters that enter the description of the ground state, just as has been shown previously[26] to be the case in the dynamic Jahn-Teller effect of an orbital triplet, and it is the relationship of such parameters to those for the original electronic state which we now wish to examine.

The direct effect of external perturbations (we consider specific cases in the following parts of the paper), and of interactions involving other dynamic operators (e.g., electronic and nuclear spin), on the electronic orbital doublet $(\psi_\theta, \psi_\epsilon)$ may be represented in a general way by adding to Eq. (1) an operator

$$\mathcal{V}=G_1\mathcal{I}+G_2A_2+G_\theta U_\theta+G_\epsilon G_\epsilon.\tag{7}$$

Here the G's are functions of the components of the external perturbations (magnetic field, strain, etc.) and of the other operators[32]; G_1 is symmetric under cubic transformations of these components, G_2 belongs to the irreducible representation A_2, and G_θ and G_ϵ transform as partners belonging to E. Thus $\mathcal{V}$, as given by Eq. (7), describes the effect that external perturbations, etc., would have in shifting or splitting the electronic energy for the static, perfectly cubic environment when Jahn-Teller effects are ignored.

We now denote by $\Psi_{g\theta}, \Psi_{g\epsilon}$ the two components of the vibronic ground state of $\mathcal{H}$ in Eq. (1), and we define two real parameters q and p in terms of the matrix elements of U_θ, U_ϵ, and A_2 within this ground state as follows[33]:

$$\begin{aligned} q&=-\langle\Psi_{g\theta}\,|\,U_\theta\,|\,\Psi_{g\theta}\rangle\\ &=\langle\Psi_{g\epsilon}\,|\,U_\theta\,|\,\Psi_{g\epsilon}\rangle\\ &=\langle\Psi_{g\epsilon}\,|\,U_\epsilon\,|\,\Psi_{g\theta}\rangle,\end{aligned}\tag{8a}$$

$$p=i\langle\Psi_{g\theta}\,|\,A_2\,|\,\Psi_{g\epsilon}\rangle.\tag{8b}$$

If then we let $U_{g\theta}$, $U_{g\epsilon}$, A_{g2} denote operators having matrix elements between $\Psi_{g\theta}, \Psi_{g\epsilon}$ identical to those of U_θ, U_ϵ, A_2 between ψ_θ, ψ_ϵ as given by Eq. (3) [i.e., $\langle\Psi_{g\theta}\,|\,U_{g\theta}\,|\,\Psi_{g\theta}\rangle=-1$, etc.], then in accord with Eq. (8) the matrix elements of $\mathcal{V}$ from Eq. (7) within this vibronic ground state are identical with those of

$$\mathcal{V}_g=G_1\mathcal{I}+pG_2A_{g2}+q(G_\theta U_{g\theta}+G_\epsilon U_{g\epsilon}).\tag{9}$$

Matrix elements of the symmetric term G_1 are unaffected by the Jahn-Teller coupling, but those of the terms in G_2 and in G_θ, G_ϵ are reduced by the factors p and q, respectively. The parameters p and q are therefore reduction factors analogous to those which par-

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[32] We assume in this paper that the G's are not functions of the vibrational operators Q_θ, Q_ϵ, although a generalization to this case could easily be made.

[33] The relations among the matrix elements indicated in Eq. (8) are the consequence of the cubic symmetry and the Wigner-Eckart theorem.

tially quench the spin–orbit interaction, orbital Zeeman interaction, strain coupling, etc., in the dynamic Jahn-Teller effect of an orbital triplet.[26] For small V ($E_{\mathrm{JT}}\ll\hbar\omega$), p and q are found by perturbation theory [Appendix I, Eq. (A9)] to be given by

$$p=1-(2V^2/\mu\hbar\omega^3)+O(V^3)$$

$$=1-(4E_{\mathrm{JT}}/\hbar\omega)+\cdots, \tag{10a}$$

$$q=1-(V^2/\mu\hbar\omega^3)+O(V^3)$$

$$=1-(2E_{\mathrm{JT}}/\hbar\omega)+\cdots, \tag{10b}$$

while for large V ($E_{\mathrm{JT}}\gg\hbar\omega$) p and q are given simply, as shown in Appendix I, by

$$p\simeq 0, \tag{11a}$$

$$q\simeq\tfrac{1}{2}. \tag{11b}$$

Moreover, as shown in Eq. (A18) of Appendix I, the relation

$$q=\tfrac{1}{2}(1+p) \tag{12}$$

is generally valid whatever the value of V so long as only linear Jahn-Teller coupling is considered. An extrapolation of Eq. (10) consistent with Eqs. (11) and (12) is given[34] by

$$p\simeq\exp(-4E_{\mathrm{JT}}/\hbar\omega), \tag{13a}$$

$$q\simeq\tfrac{1}{2}[1+\exp(-4E_{\mathrm{JT}}/\hbar\omega)]. \tag{13b}$$

However, numerical calculations from which values of p and q for intermediate values of $E_{\mathrm{JT}}/\hbar\omega$ may be obtained have been performed by Child and Longuet-Higgins.[15,35] The values for p and q obtained from their tables are given in Fig. 2, where the expressions given in Eq. (13) are also plotted. These expressions, while correct for sufficiently small values of $E_{\mathrm{JT}}/\hbar\omega$, are appreciably in error for $E_{\mathrm{JT}}/\hbar\omega\gtrsim 0.1$. As shown in Fig. 2 a formula approximately reproducing the calculated points for $0.1\lesssim E_{\mathrm{JT}}/\hbar\omega\lesssim 3.0$ is

$$p=\exp[-(1.974)(E_{\mathrm{JT}}/\hbar\omega)^{0.761}]. \tag{14}$$

The first excited state of the Hamiltonian of Eq. (1) is an "accidentally"[36] degenerate doublet with one state belonging to the symmetric representation (A_1) of O and the other to A_2. The energy of this state above the ground state is given by [Appendix I, Eq. (A5)]

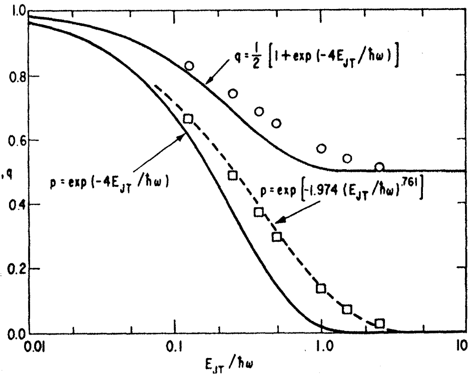

FIG. 2. Reduction factors p and q for the ${}^2E$ ground state of the orbital doublet with linear Jahn-Teller coupling, as a function of the ratio of the Jahn-Teller energy E_{JT} to the mode energy $\hbar\omega$. The solid curves show the approximate expressions given by Eqs. (13a) and (13b) of the text which extend the perturbation results obtained for weak Jahn-Teller coupling. The points are exact values from the calculations of Child and Longuet-Higgins (Ref. 15). The dashed curve is the expression given by Eq. (14) of the text, which is fitted approximately to the calculated points over the range $0.1\leq E_{\mathrm{JT}}/\hbar\omega\lesssim 3.0$.

$$\Delta_1=\hbar\omega-(V^2/\mu\omega^2)=\hbar\omega[1-(2E_{\mathrm{JT}}/\hbar\omega)] \tag{15}$$

for $E_{\mathrm{JT}}\ll\hbar\omega$, and by [Appendix I, Eq. (A23)]

$$\Delta_1=\hbar\omega(\hbar\omega/2E_{\mathrm{JT}}) \tag{16}$$

when $E_{\mathrm{JT}}\gg\hbar\omega$. These limiting expressions (15) and (16) are plotted in Fig. 3, where they are compared with numerical results obtained by Longuet-Higgins *et al.*[14]

In addition to the direct effect of the perturbation $\mathcal{V}$ of Eq. (7) on the ground state, as given by $\mathcal{V}_g$ in Eq. (9), there is a second-order effect of $\mathcal{V}$ on the ground state analogous to the second-order effects found in the case of the triplet.[26] Such a second-order effect has also been considered by Krupka and Silsbee[23] for the particular case of the R center. On grounds of symmetry, this must in general take the form (for simplicity we ignore terms involving G_2)

$$\mathcal{V}_g^{(2)}=a(G_\epsilon^2+G_\theta^2)\mathscr{G}+b[(G_\epsilon^2-G_\theta^2)U_{g\theta}+(G_\theta G_\epsilon+G_\epsilon G_\theta)U_{g\epsilon}]+ci(G_\epsilon G_\theta-G_\theta G_\epsilon)A_{g2}, \tag{17}$$

and of course the term in A_{g2} drops out if G_θ, G_ϵ commute. For the case $E_{\mathrm{JT}}\ll\hbar\omega$, we obtain by perturbation theory, from the matrix elements of Eq. (A8) of Appendix I, that to order V^2, $b=c=0$ and

$$a=-2V^2/\mu\hbar^2\omega^4=-(4/\hbar\omega)(E_{\mathrm{JT}}/\hbar\omega). \tag{18}$$

For $E_{\mathrm{JT}}\gg\hbar\omega$ we obtain instead, from the matrix elements of Eqs. (A19) and (A20), $b=0$ and

$$a=-c\simeq-1/4\Delta_1\simeq-(1/2\hbar\omega)(E_{\mathrm{JT}}/\hbar\omega), \tag{19}$$

where we have used Δ_1 as given by Eq. (16), and

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[34] The formula in Eq. (13b) has been noted previously [Ref. 28, Eq. (4.24)], without derivation, in connection with the second-order spin-orbit splitting of ${}^5E$ for Fe^{2+}.

[35] The value for our parameter p is given by that of the matrix element $d(v_2,\frac{1}{2})$ for $v_2=0$ tabulated in Table A4 by Child and Longuet-Higgins (Ref. 15). Our $E_{\mathrm{JT}}/\hbar\omega$ is equal to the parameter they call D.

[36] This "accidental" degeneracy [all the eigenstates of Eq. (1) are in fact doublets (Refs. 14, 15)] is a result of the fact that $\mathcal{H}$ in Eq. (1) has additional symmetries beyond those imposed by the cubic symmetry of the original problem. This extra symmetry is the cause of the rotational symmetry in Fig. 1, and it is removed by adding to Eq. (1) the terms of cubic symmetry [the quadratic Jahn-Teller terms $V_2\{U_\theta(Q_\epsilon^2-Q_\theta^2)+2U_\epsilon(Q_\theta Q_\epsilon)\}$, or the third-order term $V_3Q_\theta(3Q_\epsilon^2-Q_\theta^2)$] which warp the bottom of the potential-energy trough in Fig. 1 to give three equivalent minima. The addition of such terms therefore splits those eigenstates of Eq. (1) which span A_1 and A_2, but not those like the ground state which belong to E.

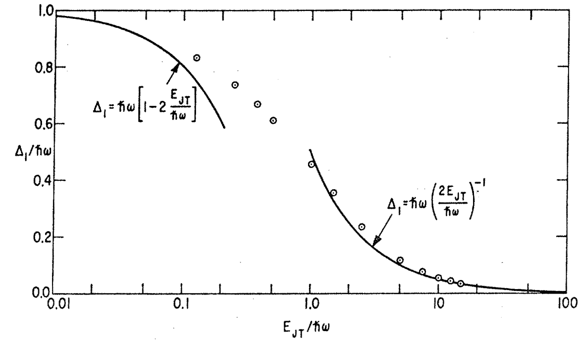

FIG. 3. Excitation energy Δ_1 of the first excited vibronic state for linear Jahn-Teller coupling, in units of the mode energy $\hbar\omega$, as a function of the ratio of the Jahn-Teller energy E_{JT} to $\hbar\omega$. The curves show the limiting behavior given by Eqs. (15) and (16) of the text, while the points are exact values from the calculations of Longuet-Higgins *et al.* (Ref. 14).

$|\eta|\simeq 1$. The vanishing of b is the consequence of the "accidental" degeneracy of the excited doublet (A_1, A_2), and b would be finite if this degeneracy were removed.[36]

III. RELATION TO STRONG-COUPLING THEORIES

The theories of Bersuker[17,19] and O'Brien[16] for dynamic Jahn-Teller effects in the EPR spectrum of an orbital doublet presuppose a strong Jahn-Teller coupling, so that the ground state and low-lying excited states are accurately given by linear combinations of states of the form of Eq. (A22a) (for $V>0$) or of Eq. (A22b) (for $V<0$). In other words, the low-energy vibronic states are Born-Oppenheimer multiples of the electronic state associated with the lower potential energy surface in Fig. 1, that is of ψ_- as given by Eq. (4) if $V>0$ or of ψ_+ if $V<0$. As a result of the warping of the trough in Fig. 1 because of higher-order terms[36] in the Hamiltonian, these vibronic wave functions are not given simply by one term with a single value of $|n|$ as in Eq. (A22); nevertheless a parameter enters these theories which corresponds to our reduction factor q (the parameter corresponding to p is zero). We want here to make this correspondence explicit and to show that the strong-coupling theory leads to a different conclusion from our theory concerning the values which q can assume. This difference offers a basis for an experimental determination as to which theory is more nearly applicable in a given case.

If a vibronic state is a multiple either of ψ_+ or ψ_-, we are concerned only with the following electronic matrix elements:

$$\langle\psi_+|U_\theta|\psi_+\rangle=\cos\theta,$$
$$\langle\psi_+|U_\epsilon|\psi_+\rangle=\sin\theta \qquad (20a)$$

or

$$\langle\psi_-|U_\theta|\psi_-\rangle=-\cos\theta,$$
$$\langle\psi_-|U_\epsilon|\psi_-\rangle=-\sin\theta \qquad (20b)$$

since

$$\langle\psi_+|A_2|\psi_+\rangle=\langle\psi_-|A_2|\psi_-\rangle=0.$$

Accordingly, within the vibronic E ground state resulting from the tunneling splitting in either O'Brien's theory or that of Bersuker, q is obtained in accordance with Eq. (8a) from the appropriate matrix element of $\pm\cos\theta$ with respect to the vibrational part of the ground-state wave function. We find in this way for O'Brien's theory[16] (where $V<0$, so that we are concerned with ψ_+) that

$$q=c_2 \qquad (21)$$

in terms of the parameters introduced by O'Brien in her Eq. (24). We find similarly that her c_1 corresponds to the parameter η appearing in Eq. (A20) of our theory by

$$|c_1|=\tfrac{1}{2}|\eta| \qquad (22)$$

[because of the warping the degeneracy of A_1 and A_2 is lifted in her case, so that c_1 does not simultaneously relate to the matrix elements of Eq. (A19), which only for linear Jahn-Teller coupling involve the same parameter η as Eq. (A20)].

An explicit evaluation of c_2 from O'Brien's theory[16] leads to the result that $c_2\leq\frac{1}{2}$, as we will show, with $c_2=\frac{1}{2}$ when the warping vanishes, in agreement thus with our result (11b) for strong linear Jahn-Teller coupling. O'Brien's theory thus gives us the result that

$$q<\tfrac{1}{2} \qquad (23)$$

for strong Jahn-Teller coupling when there is appreciable warping of the potential trough, in contrast to our conclusion that

$$1\geq q\geq\tfrac{1}{2} \qquad (24)$$

for linear coupling alone. These contrasting results serve therefore to provide a criterion as to whether a theory of strong coupling with warping or one with weak to moderate Jahn-Teller coupling is the more appropriate in a given case.

The proof of Eq. (23) from O'Brien's theory follows from the explicit form of the most general ground-state wave function which is consistent with an arbitrary warping of a deep trough in the lower-energy surface of Fig. 1. As shown by O'Brien,[16] the θ dependence of the vibrational wave function multiplying ψ_+ in the ground-state vibronic wave function $\Psi_{g\epsilon}$ (her $|E\rangle$) is given by

$$|\Psi_{g\epsilon}\rangle\sim a_{1/2}\cos\tfrac{1}{2}\theta+a_{5/2}\cos\tfrac{5}{2}\theta+a_{7/2}\cos\tfrac{7}{2}\theta$$
$$+a_{11/2}\cos\tfrac{11}{2}\theta+\cdots, \qquad (25)$$

which agrees with the symmetry considerations given in connection with Eq. (A14) in Appendix I. The ρ dependence of $\Psi_{g\epsilon}$ is assumed to be given by a radial function, localized in the bottom of the potential trough, which is approximately the same for all the terms in Eq. (25). Then from the angular average of

$\cos\theta$ with respect to $\Psi_{g\epsilon}$ in accord with Eqs. (8a) and (20a) we obtain the result

$$q=\tfrac{1}{2}(a_{1/2}{}^2+2a_{5/2}a_{7/2}+2a_{11/2}a_{13/2}+\cdots). \tag{26}$$

The normalization condition for the a_n's is given by

$$(a_{1/2}{}^2+a_{5/2}{}^2+a_{7/2}{}^2+a_{11/2}{}^2+\cdots)=1. \tag{27}$$

Because of the inequality

$$2\,|\,a_n\,|\,|\,a_m\,|\leq a_n{}^2+a_m{}^2, \tag{28}$$

the result, Eq. (23), follows immediately from Eqs. (26) and (27).

Bersuker's theory[17,19] of the effect of tunneling between the distorted configurations of the static Jahn-Teller effect makes the tacit assumption that the vibrational wave function associated with each of the three wells is sufficiently well localized in its well that in evaluating matrix elements of $\cos\theta$ we may replace the average of $\cos\theta$ in each well by its value $\cos\theta_0$ at the value of θ corresponding to the bottom of the well. In other words, the electronic wave function entering the vibronic wave function for a given well is taken to be the fixed linear combination of ψ_θ and ψ_ϵ appropriate to θ_0, and this combination is considered to be independent of variations in θ within the well. The vibrational overlap integral γ between the different wells is then taken into account as the origin of the tunneling splitting or "inversion splitting" that leaves the doublet E as the vibronic ground state. As Höchli has shown,[25] Bersuker's theory then leads to a value of q for the ground state given by ($\gamma\ll 1$)

$$q=\tfrac{1}{2}[1+(3/2)\gamma]. \tag{29}$$

However, since γ is positive we see that Eq. (29) conflicts with the result of O'Brien's theory that q must in general be less than $\frac{1}{2}$ for the strong-coupling case. This discrepancy shows therefore that although the overlap between the different configurations acts to increase q as shown by Eq. (29), the spread in θ within each well produces an off-setting reduction in q which is omitted in Bersuker's theory and which always dominates the effect of overlap. Evidence for the importance of this spread in θ has already been found experimentally in Hayes and Wilkens' study[37] of static Jahn-Teller effects for Ni^+ in LiF and NaF, where the data indicate that $\langle\cos\theta\rangle$ must be taken to be $\simeq 0.8$ for the distorted configuration for which $\cos\theta_0=1.0$. The importance of taking into account this spread in θ in changing the admixture of the electronic wave functions from that appropriate to θ_0 was emphasized by O'Brien[16] in her theoretical treatment.

IV. *g* FACTOR

Since the orbital angular-momentum operator has no nonzero matrix elements within an E state, the linear effect of a magnetic field on a ${}^{2S+1}E$ electronic state must take the form of Eq. (7) with $G_2=0$ and

$$\begin{aligned} G_1&=g_1\beta(\mathbf{S}\cdot\mathbf{H}),\\ G_\theta&=g_2\beta[S_zH_z-\tfrac{1}{2}(S_xH_x+S_yH_y)],\\ G_\epsilon&=g_2\beta(\sqrt{3}/2)(S_xH_x-S_yH_y), \end{aligned} \tag{30}$$

where $\hbar\mathbf{S}$ is the spin operator and $\beta=(e\hbar/2mc)$. In particular, for the ${}^2E$ electronic ground state of a d^1 electron configuration in four- or eightfold coordination, or a d^9 configuration in sixfold coordination, we have from crystal-field theory[38]

$$\begin{aligned} g_1&=g_s{}^0-(4\lambda/\Delta),\\ g_2&=-(4\lambda/\Delta), \end{aligned} \tag{31}$$

where $g_s{}^0=2.0023$, $\Delta=10\,|\,Dq\,|$ is the cubic field splitting between ${}^2E$ and the excited state ${}^2T_2$ derived from the ${}^2D$ term of the free ion, and λ is the parameter such that $\lambda(\mathbf{L}\cdot\mathbf{S})$ describes the spin–orbit interaction for ${}^2D$. Taking account of linear Jahn-Teller coupling, then, we obtain, according to Eq. (9), the Hamiltonian for the Zeeman interaction in the ${}^2E$ vibronic ground state (which belongs to the representation Γ_8 of the double group corresponding to O or T_d):

$$\mathcal{H}_{gH}=g_1\beta(\mathbf{S}\cdot\mathbf{H})\mathcal{I}+(qg_2\beta/2)\{[3S_zH_z-(\mathbf{S}\cdot\mathbf{H})]U_{g\theta}+\sqrt{3}(S_xH_x-S_yH_y)U_{g\epsilon}\}. \tag{32}$$

The terms in g_2 have thus been diminished by the Jahn-Teller coupling by the reduction factor q, but the term in g_1 is left unchanged.

The eigenvalues of $\mathcal{H}_{gH}$ in Eq. (32), and thus the g factors for comparison with experiment, are easily obtained in the usual case for which $|\,g_2\,|\ll g_1$, for arbitrary orientation of $\mathbf{H}$. Taking $\hat{\zeta}$ to be a unit vector along $\mathbf{H}$ having components ζ_x, ζ_y, ζ_z and keeping only the part of the g_2 term in Eq. (32) which is diagonal in S_ζ, we may then write Eq. (32) as

$$\mathcal{H}_{gH}=g_1\beta S_\zeta H\mathcal{I}+(qg_2\beta HS_\zeta/2)[(3\zeta_z{}^2-1)U_{g\theta}+\sqrt{3}(\zeta_x{}^2-\zeta_y{}^2)U_{g\epsilon}]. \tag{33}$$

The two-by-two secular equation that one must solve is thus the same for both spin states $S_\zeta=\pm\frac{1}{2}$, except for an over-all sign change, and the vibronic states that diagonalize Eq. (33) are the same for $S_\zeta=\pm\frac{1}{2}$. The g factors for the experimental resonance frequencies thus correspond to spin transitions for a given vibronic state

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[37] W. Hayes and J. Wilkens, Proc. Roy. Soc. (London) **A281**, 340 (1964).

[38] To simplify our presentation of the effects of Jahn-Teller coupling, in this paper we shall ignore all other effects (e.g., covalent bonding) which will change the g shifts, etc., from the predictions of simple crystal-field theory. These other contributions should of course be taken into account, via the appropriate orbital reduction factors for the spin-orbit interaction, orbital Zeeman interaction, etc., when the theoretical formulas are compared with experimental results.

and are therefore given by

$$g_{\pm}=g_1\pm qg_2[1-3(\zeta_x^2\zeta_y^2+\zeta_y^2\zeta_z^2+\zeta_z^2\zeta_x^2)]^{1/2}. \qquad (34)$$

This result agrees in its angular variation with the expression given originally by Abragam and Pryce[2] and more recently by Coffman[24] and by Höchli.[25]

V. HYPERFINE INTERACTION

The hyperfine interaction with the central nucleus has the same form within an E state as the interaction with a magnetic field: the G's entering Eq. (7) are obtained from Eq. (30) by substituting the components of the nuclear spin $\mathbf{I}$ for those of $\mathbf{H}$ and replacing $g_1\beta$, $g_2\beta$ by hyperfine parameters A_1 and A_2. For the ^2E ground state of a d^1 or d^9 configuration, we obtain from crystal-field theory, to second order in perturbation theory,

$$\begin{aligned} A_1&=-P[\kappa+(4\lambda/\Delta)],\\ A_2&=-P[6\xi+(4\lambda/\Delta)+(9\lambda/\Delta)\xi]. \end{aligned} \qquad (35)$$

Here we have represented the hyperfine interaction within the ^2D term by[39]

$$\begin{aligned}\mathcal{H}_I(^2D)=P\{(\mathbf{L}\cdot\mathbf{I})-\kappa(\mathbf{S}\cdot\mathbf{I})+\xi[6(\mathbf{S}\cdot\mathbf{I})\\ -\tfrac{3}{2}(\mathbf{L}\cdot\mathbf{S})(\mathbf{L}\cdot\mathbf{I})-\tfrac{3}{2}(\mathbf{L}\cdot\mathbf{I})(\mathbf{L}\cdot\mathbf{S})]\},\end{aligned} \qquad (36)$$

where $P=2\gamma\beta\beta_N\langle r^{-3}\rangle$, $\xi=+(2/21)$, and γ is the nuclear g factor, β_N the nuclear magneton, $\langle r^{-3}\rangle$ the one-electron average of r^{-3}, and κ the parameter characterizing the contact hyperfine interaction. Taking account of linear Jahn-Teller coupling, we have then for the Hamiltonian for the hyperfine interaction in the ^2E vibronic ground state, just as in Eq. (32),

$$\begin{aligned}\mathcal{H}_{gI}=A_1(\mathbf{S}\cdot\mathbf{I})\mathscr{I}+(qA_2/2)\{[3S_zI_z-(\mathbf{S}\cdot\mathbf{I})]U_{g\theta}\\ +\sqrt{3}(S_xI_x-S_yI_y)U_{g\epsilon}\}.\end{aligned} \qquad (37)$$

The hyperfine splitting of the EPR spectrum is then obtained by combining the Hamiltonians of Eqs. (32) and (37). So long as $g_1 \gg |g_2|$, $|A_1| \gg |A_2|$,[40] we may find the resonance frequencies for arbitrary orientation $(\hat{\zeta})$ of $\mathbf{H}$ by using as in Eq. (33) only those terms that are diagonal in S'_ζ and in the eigenvalue m of I_ζ. We obtain for the resonance frequencies under these conditions

$$\begin{aligned}h\nu_m=(g_1\beta H+A_1m)\pm q(g_2\beta H+A_2m)\\ \times[1-3(\zeta_x^2\zeta_y^2+\zeta_y^2\zeta_z^2+\zeta_z^2\zeta_x^2)]^{1/2}.\end{aligned} \qquad (38)$$

The Jahn-Teller coupling also quenches by the same factor q that part of the superhyperfine interaction with neighboring ions which enters the Hamiltonian as the coefficient of U_θ and U_ϵ, while the isotropic part proportional to $\mathscr{I}$ is unaffected.

[*Note added in proof*. It should be noted in general (M. C. M. O'Brien, private communication) that Eqs. (34) and (38) do not describe accurately the angular variation of the exact g factors or hyperfine splittings when $\mathbf{H}$ is near [111], because in deriving these equations we have neglected the terms in the Hamiltonian which are off-diagonal in S_ζ and I_ζ. Retaining these terms leads to small but nonzero corrections to the g factors and hyperfine splittings when $\mathbf{H}$ is along [111], whereas the anisotropic terms in Eq. (34) and (38) are zero in this orientation. However, for $\mathbf{H}$ near [111], the resonance spectrum should be quite sensitive to effects of random strain and of relaxation, so that a complete description of the angular variation of the spectrum as $\mathbf{H}$ passes through the [111] orientation can be quite complicated.]

VI. APPLIED STRAIN

The splitting of the electronic (orbital) state in uniform strain, when we neglect the Jahn-Teller effect, is described by

$$\mathcal{H}_s=V_2[e_\theta U_\theta+e_\epsilon U_\epsilon], \qquad (39)$$

where

$$\begin{aligned} e_\theta&=e_{zz}-\tfrac{1}{2}(e_{xx}+e_{yy}),\\ e_\epsilon&=(\sqrt{3}/2)(e_{xx}-e_{yy}), \end{aligned} \qquad (40)$$

and

$$e_{ij}=\tfrac{1}{2}[(\partial u_i/\partial x_j)+(\partial u_j/\partial x_i)] \qquad (41)$$

is a component of the strain tensor. When we take account of the Jahn-Teller coupling, the strain splitting of the vibronic ground state is then given, according to Eq. (9), by

$$\mathcal{H}_{gs}=qV_2[e_\theta U_{g\theta}+e_\epsilon U_{g\epsilon}]. \qquad (42)$$

The ground state is thus split by the tetragonal components of the strain, but the strain coefficient that is directly measured experimentally is $V_2'=qV_2$.

There is a close connection between the strain coefficient V_2 and the linear Jahn-Teller coupling coefficient V in the Hamiltonian (1), which we may use to obtain an approximate estimate for the Jahn-Teller energy E_{JT} from the measured value of V_2'. The relation between the amplitudes Q_θ, Q_ϵ of the vibrational coordinates for the E distortion mode of the nearest-neighbor set of ions and a uniform strain given by e_θ, e_ϵ is derived in Appendix II. If we assume that the effect of strain in splitting the electronic state in accord with Eq. (39) is primarily due to this distortion of the nearest-neighbor

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[39] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. **A205**, 135 (1951).

[40] The condition $|A_1| \gg |A_2|$ is not well satisfied for Sc^{2+} in CaF_2 and SrF_2 (Ref. 25); Eq. (38) may then not be accurate except for $\mathbf{H}$ in [100], for which orientation the formula is exact for any values g_1, g_2, A_1, A_2 (apart from second-order corrections of order $A^2/h\nu$).

ions,[41] we then obtain the following relation between V and V_2 [the corresponding value of the mass μ in Eq. (1) is then $\mu = M$, as shown in Appendix II, where M is the mass of a single nearest-neighbor ion and R the nearest-neighbor distance]:

Sixfold cubic coordination:

$$V = \sqrt{3} V_2 / 2R. \tag{43a}$$

Eightfold cubic coordination:

$$V = 3V_2 / 4R. \tag{43b}$$

Fourfold tetrahedral coordination:

$$V = 3V_2 / (2\sqrt{2} R). \tag{43c}$$

Trigonal strain, described by the strain components e_{yz}, e_{zx}, e_{xy} (which transform as T_2), produces no direct splitting of the electronic E state, but in combination with the spin–orbit interaction and the cubic crystal-field splitting it does produce a small linear splitting when spin is taken into account. For the ^2E state derived from ^2D, if electronic matrix elements of trigonal strain within ^2D (e.g., between ^2E and $^2T_2$) are given by those of the operator

$$\begin{aligned} V(\mathrm{trig}) = (V_3/2\sqrt{3}) [& e_{xy}(L_xL_y + L_yL_x) \\ & + e_{yz}(L_yL_z + L_zL_y) + e_{zx}(L_zL_x + L_xL_z)], \end{aligned} \tag{44}$$

we find from second-order perturbation theory that the linear effect of such strain within ^2E is given by

$$\mathcal{H}_s^{(2)} = (2\lambda V_3/\Delta)(S_x e_{yz} + S_y e_{xz} + S_z e_{xy}) A_2. \tag{45}$$

This perturbation has the form of the G_2A_2 term in Eq. (7), so that its effect on the vibronic ground state is given by

$$\mathcal{H}_{gs}^{(2)} = p(2\lambda V_3/\Delta)(S_x e_{yz} + S_y e_{zx} + S_z e_{xy}) A_{g2} \tag{46}$$

according to Eq. (9). The linear splitting of the ground state due to trigonal strain is thus diminished by Jahn-Teller coupling by the reduction factor p.

Similarly, the trigonal strain produces a small change in the Zeeman interaction within ^2E given by

$$\mathcal{H}_{SH}^{(2)} = (2\beta V_3/\Delta)(H_x e_{yz} + H_y e_{xz} + H_z e_{xy}) A_2, \tag{47}$$

which follows if the spin–orbit interaction $\lambda(\mathbf{L}\cdot\mathbf{S})$ is replaced in the derivation of Eq. (45) by the orbital Zeeman interaction $\beta(\mathbf{L}\cdot\mathbf{H})$. The effect of this perturbation on the vibronic ground state is accordingly given by

$$\mathcal{H}_{gSH}^{(2)} = p(2\beta V_3/\Delta)(H_x e_{yz} + H_y e_{xz} + H_z e_{xy}) A_{g2}. \tag{48}$$

These expressions (45) and (47) for the special case of an axial distortion along the [111] axis ($e_{yz} = e_{xz} = e_{xy}$) are identical in form with the spin–orbit and Zeeman interaction terms in the spin Hamiltonian used by Krupka and Silsbee[23] in their analysis of the effect of the Jahn-Teller effect for the R center in KCl.

VII. EFFECT OF RANDOM STRAIN ON EPR

Small random strains in the crystal can alter the resonance spectrum of the ^2E state substantially from what is expected from Eq. (38). Since such changes may be important experimentally, we shall consider them now. We ignore trigonal strain, which has a small effect compared to tetragonal strain because of the factor λ/Δ in Eq. (45).

For a local strain characterized by e_θ, e_ϵ in Eq. (40), the Hamiltonian for the vibronic ground state is obtained by combining Eqs. (32), (37), and (42). Assuming $g_1 \gg |g_2|$, $|A_1| \gg |A_2|$ as done previously, so that only terms diagonal in S_ζ and I_ζ need be kept (and also neglecting the corrections of order $A_1^2/h\nu$), we obtain

$$\begin{aligned} \mathcal{H}_g \simeq & (g_1\beta H S_\zeta + A_1 S_\zeta I_\zeta)\mathcal{G} \\ & + q\{[\tfrac{1}{2}(g_2\beta H S_\zeta + A_2 S_\zeta I_\zeta)(3\zeta_z^2 - 1) + V_2 e_\theta] U_{g\theta} \\ & + [(\sqrt{3}/2)(g_2\beta H S_\zeta + A_2 S_\zeta I_\zeta)(\zeta_x^2 - \zeta_y^2) + V_2 e_\epsilon] U_{g\epsilon}\}, \end{aligned} \tag{49}$$

which has eigenvalues

$$\begin{aligned} E_\pm(S_\zeta', m) = & g_1\beta H S_\zeta' + A_1 S_\zeta' m \\ & \pm q\{[\tfrac{1}{2}(g_2\beta H S_\zeta' + A_2 S_\zeta' m)(3\zeta_z^2 - 1) + V_2 e_\theta]^2 \\ & + [(\sqrt{3}/2)(g_2\beta H S_\zeta' + A_2 S_\zeta' m)(\zeta_x^2 - \zeta_y^2) + V_2 e_\epsilon]^2\}^{1/2}. \end{aligned} \tag{50}$$

There are two pairs of possible transitions among the levels of Eq. (50) for a given value of m, and the relative intensity of these transitions is determined by the magnitude of the terms involving strain in Eq. (49) relative to that of the anisotropic Zeeman and hyperfine terms. If the strains are sufficiently small so that

$$\begin{aligned} |V_2|(e_\theta^2 + e_\epsilon^2)^{1/2} \ll \tfrac{1}{2} & |g_2\beta H + A_2 m| \\ & \times [1 - 3(\zeta_x^2\zeta_y^2 + \zeta_y^2\zeta_z^2 + \zeta_z^2\zeta_x^2)]^{1/2}, \end{aligned} \tag{51}$$

the eigenstates are determined by the Zeeman and hyperfine interactions, and the transitions induced by the microwave field are the pair

$$\begin{aligned} & E_+(+\tfrac{1}{2}, m) \leftrightarrow E_-(-\tfrac{1}{2}, m), \\ & E_-(+\tfrac{1}{2}, m) \leftrightarrow E_+(-\tfrac{1}{2}, m), \end{aligned} \tag{52}$$

with resonance frequencies given approximately by Eq. (38). Expanding Eq. (50) in powers of V_2, we find that the strain displacements of these resonance frequencies are proportional to $V_2^2/|g_2\beta H + A_2 m|$ times the square of the strain. If the strains are random, the EPR lines should be broadened asymmetrically, the lines with

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[41] To simplify the problem of an E state of an ion in a crystal to that described by the Hamiltonian of Eq. (1), we must assume not only that the single distortion mode Q_θ, Q_ϵ of the nearest-neighbor ions provides the dominant coupling, but also that Q_θ, Q_ϵ are normal modes with an appropriate angular frequency ω. This is of course not actually true. A satisfactory analysis of this vibronic problem for a continuum of phonon modes, each coupled to the electronic state, has not yet been given.

$| g_2\beta H + A_2 m |$ the largest being broadened by strain the least. On the other hand, if strain is sufficiently large (or alternatively if **H** is so close to alignment along a [111] axis or $| g_2\beta H + A_2 m |$ so small for a particular m) that the inequality (51) is reversed, the eigenstates are determined by the strain and the transitions induced are the pair

$$E_+(+\tfrac{1}{2}, m) \leftrightarrow E_+(-\tfrac{1}{2}, m),$$
$$E_-(+\tfrac{1}{2}, m) \leftrightarrow E_-(-\tfrac{1}{2}, m). \qquad (53)$$

The resonance frequencies are now given to first order in the anisotropic terms by

$$h\nu_\pm(m) = (g_1\beta H + A_1 m) \pm \tfrac{1}{2} q (g_2\beta H + A_2 m) \times [e_\theta(3\zeta_z^2 - 1) + e_\epsilon\sqrt{3}(\zeta_x^2 - \zeta_y^2)](e_\theta^2 + e_\epsilon^2)^{-1/2}. \qquad (54)$$

If the strains are random, the line centers should be given by the isotropic resonance frequencies

$$h\nu(m) = g_1\beta H + A_1 m, \qquad (55)$$

which coincide with those given by Eq. (38) when **H** is along [111]. However, the lines should now be substantially broadened, with Δg of order

$$\Delta g \simeq q \,| g_2 + (A_2 m/\beta H) | [1 - 3(\zeta_x^2\zeta_y^2 + \zeta_y^2\zeta_z^2 + \zeta_z^2\zeta_x^2)]^{1/2}. \qquad (56)$$

We note that the effect of random strain in broadening the lines vanishes when **H** is along [111]. Moreover, sufficiently rapid relaxation between the states $E_\pm(S_\zeta', m)$ will eliminate the strain broadening by replacing the lines at $h\nu_\pm(m)$ in Eq. (54) for a given strain by the motionally averaged isotropic line with frequency given by Eq. (55) (see Sec. VIII). Finally, for intermediate values of strain, both pairs of transitions (52) and (53) may simultaneously be present in the EPR spectrum.

[*Note added in proof.* If we define angles φ and α through the relations

$$\cos\varphi = e_\theta/(e_\theta^2 + e_\epsilon^2)^{1/2}, \ \sin\varphi = e_\epsilon/(e_\theta^2 + e_\epsilon^2)^{1/2},$$
$$\cos\alpha = \tfrac{1}{2}(3\zeta_z^2 - 1)[1 - 3(\zeta_x^2\zeta_y^2 + \zeta_y^2\zeta_z^2 + \zeta_z^2\zeta_x^2)]^{-1/2},$$
$$\sin\alpha = \tfrac{1}{2}\sqrt{3}(\zeta_x^2 - \zeta_y^2)[1 - 3(\zeta_x^2\zeta_y^2 + \zeta_y^2\zeta_z^2 + \zeta_z^2\zeta_x^2)]^{-1/2},$$

then the resonance frequencies given by Eq. (54) may be expressed as

$$h\nu_\pm(m) = (g_1\beta H + A_1 m) \pm q(g_2\beta H + A_2 m) \times [1 - 3(\zeta_x^2\zeta_y^2 + \zeta_y^2\zeta_z^2 + \zeta_z^2\zeta_x^2)]^{1/2} \cos(\varphi - \alpha).$$

If the strains are random, the angle φ assumes at random values in the range $0 \leq \varphi \leq 2\pi$. The strain-broadened lines corresponding to $h\nu_+(m)$ and $h\nu_-(m)$ then coincide, and the shape function of the resulting line has the form $g(x) = (1/\pi)[y^2 - (x - x_0)^2]^{-1/2}$ for $| x - x_0 | \leq | y |$ and $g(x) = 0$ for $| x - x_0 | > | y |$. The edges of the line are therefore sharp, and they coincide with the resonance frequencies given by Eq. (38). The case of strong but random residual strain thus leads to a spectrum exhibiting absorption peaks which coincide with those expected in the complete absence of strain, and this spectrum will be insensitive to applied stress until the resulting strain becomes comparable to the residual strain. It is probably this spectrum, rather than the no-strain spectrum, which was observed by both Coffman and Höchli.]

VIII. RELAXATION

Rapid relaxation processes, resulting from the strong coupling of a ${}^2E$ state to lattice phonons because of the orbital degeneracy of the state, may lead to a motionally averaged EPR spectrum. Since the resulting isotropic spectrum may be expected to appear at quite low temperatures in place of the anisotropic spectrum described in Secs. IV and V, we shall now obtain an expression for the relaxation time for this process.

The EPR spectrum found in Secs. IV and V and in either limit of the inequality (51) in Sec. VII arises from transitions between states which have opposite spin $S_\zeta' = \pm\frac{1}{2}$ but the same vibronic wave function. There are two such vibronic states given by the two linear combinations of $\Psi_{g\theta}$, $\Psi_{g\epsilon}$ which diagonalize the combined Hamiltonian of Eqs. (33) and (37), or alternatively the strain Hamiltonian of Eq. (42) for a given static strain. These two states may be coupled directly, for a given spin state, by lattice strain, as we have seen in Secs. VI and VII, and therefore transitions between these states may be induced directly by lattice phonons via the strain coupling. When the relaxation time τ for such transitions becomes shorter than $(2\pi\Delta\nu_m)^{-1}$ corresponding to the frequency difference $\Delta\nu_m$ between the resonance frequencies for these two vibronic states as given by Eq. (38) or (54), a motionally averaged spectrum given by the isotropic resonance condition of Eq. (55) replaces the anisotropic spectrum. The relaxation process that we shall consider to estimate τ at low temperatures is that caused by Raman processes. Direct processes in which a single phonon is absorbed or emitted in the transition should not be important for motional narrowing of the EPR spectrum, because the energy separation of the two states involved in the transition is very small, of order $q(g_2\beta H + A_2 m)$ or alternatively $2qV_2(e_\theta^2 + e_\epsilon^2)^{1/2}$.

To estimate the Raman relaxation time for transitions between these two vibronic states, we use the long-wavelength approximation in order to describe the coupling to a phonon by means of Eq. (42) in terms of the local strain produced by the phonon. The resulting transition rate P per unit time from one state to the other is found by a straightforward calculation (the lattice is assumed elastically isotropic) to be given at low temperatures ($T \ll$ Debye temperature) by

$$P \simeq [3\pi q^4 V_2{}^4 (kT)^5 / 125\hbar^7 \rho^2 v_T{}^{10}][1+\tfrac{2}{3}(v_T/v_L)^5]^2, \qquad (57)$$

where k is Boltzmann's constant, ρ the density, and v_T and v_L the velocities of transverse and longitudinal sound waves propagating along [100]. The relaxation time τ for this process is then given by

$$\tau = 1/2P. \qquad (58)$$

The isotropic spectrum produced by rapid relaxation in the ${}^2E$ ground state and given by Eq. (55) unfortunately coincides with the spectrum expected for the excited ${}^2A_1$ and ${}^2A_2$ states which should be appreciably populated when $kT \simeq \Delta_1$. Thus, unless one has an estimate for the excitation energy Δ_1 and finds experimentally that the isotropic spectrum becomes strong while yet $kT \ll \Delta_1$, one cannot safely ascribe the isotropic spectrum to relaxation effects without a detailed study of the temperature dependence of intensities, linewidths, etc., in any given case. This ambiguity concerning the nature of the transition to an isotropic spectrum of course also occurs in connection with the transition to the high-temperature spectrum for an ion which exhibits a static Jahn-Teller effect at low temperature. Although this transition has been much studied,[2,16,20] a full clarification of it has not yet been made in any of the cases in which it has been observed.

IX. DISCUSSION

We have seen that, as the strength of the Jahn-Teller coupling increases starting from zero, the properties of the ground state vary continuously through the regime of the dynamic Jahn-Teller effect. The vibronic ground state remains a ${}^2E(\Gamma_8)$ state, and its splitting under various perturbations is identical, except in magnitude, with the splitting of the ${}^2E$ electronic state when Jahn-Teller effects are ignored. Of course, when the Jahn-Teller coupling becomes very strong the first excited vibronic state approaches more and more closely to the ground state, and when this excitation energy Δ_1 is comparable to the strength of a perturbation this excited state must be included explicitly in the analysis of what should be observed, say, in an EPR experiment. The limiting case when the excited state approaches degeneracy with the ground state (and higher-order effects split the accidental degeneracy of the ${}^2A_1$, ${}^2A_2$ excited state) is, of course, the case that has been analyzed previously in terms of a static Jahn-Teller effect with three equivalent distortions, and the dynamic case for which Δ_1 is small but not zero is the one considered in detail by O'Brien.[16] However, so long as Δ_1 is large compared to the various perturbations, we see that we need only be concerned with the behavior of a ${}^2E$ ground state alone, and that its behavior is formally identical to that of a ${}^2E$ electronic state in simple crystal-field theory.

The magnitude of the response of the ${}^2E$ ground state to various perturbations is affected by the Jahn-Teller coupling, as we have seen, and this change may be described very conveniently by introducing appropriate reduction factors in the formal theory of the electronic ${}^2E$ state. These factors have the value unity for no Jahn-Teller coupling and are diminished as the strength of the Jahn-Teller coupling increases. The factor q has a limiting value of $\frac{1}{2}$ for a strong linear Jahn-Teller coupling and is appropriate to all perturbations such as applied tetragonal strain and the anisotropic parts of the g factor and hyperfine interaction which transform as E (at least to those that are not explicit functions of the distortion). The factor p has a limiting value zero and is appropriate to perturbations transforming as A_2, such as those arising from effects of trigonal strain. Symmetric perturbations such as the isotropic parts of the g factor and hyperfine interactions are, however, quite unaffected by the Jahn-Teller coupling. These reduction factors are the precise analog of those shown previously[26] to be introduced by a Jahn-Teller effect in the behavior of a triplet state, and they have a similar origin in the reduced overlap of the vibrational parts of the wave functions associated with different electronic wave functions in the various vibronic states. We have also shown that there are second-order effects for the doublet analogous to those found for the triplet. Although our analysis in this paper has been simplified by the assumption that the Jahn-Teller coupling may be approximately represented by coupling to a single pair of vibrational modes, we expect that a better analysis using the phonon continuum will lead to similar conclusions concerning the behavior of the ground state, although the values of the reduction factors will then be appropriately modified.

We may now see plainly that Coffman's "third type of Jahn-Teller spectrum"[24] for a ${}^2E$ state is simply the case of a vibronic ${}^2E$ ground state when $q=\frac{1}{2}$. Coffman used Bersuker's theory[17,19] to evaluate the appropriate matrix elements of the Zeeman and hyperfine interaction among the tunneling states, and since he assumed the overlap γ to be negligible, his results are equivalent to taking $q=\frac{1}{2}$ as given by Eq. (29). We have seen that $q=\frac{1}{2}$ is also the limiting case approached for linear Jahn-Teller coupling when $E_{\mathrm{JT}} \gg \hbar\omega$; in fact, when $E_{\mathrm{JT}}/\hbar\omega$ is as small as 2.5, we find from the calculations of Child and Longuet-Higgins[15] that $q=0.512$. Thus it is possible to have $q \simeq \frac{1}{2}$ even though the situation is rather different from one that can be described in terms of tunneling between well-defined distorted configurations [for $E_{\mathrm{JT}}/\hbar\omega = 2.5$, the excitation energy Δ_1 to the first excited state above the ${}^2E$ ground state is still $\simeq (1/5)\hbar\omega$ from Eq. (16), and of course the trough in Fig. 1 preserves its rotational symmetry when only linear Jahn-Teller coupling is present]. On the other hand, Coffman's finding that $q \simeq \frac{1}{2}$ describes the case of Cu^{2+} in MgO is also consistent with his model based on a strong Jahn-Teller coupling with tunneling between well-localized distorted configurations. As we have seen from O'Brien's theory, q should be less than $\frac{1}{2}$ if the Jahn-Teller coupling is strong, but as O'Brien[16] showed explicitly, one obtains $q=c_2=\frac{1}{2}[1-(1/8\omega)]$ if the vibrational wave function varies as $\exp[-\omega(\theta-\theta_0)^2]$ in each well and if the overlap γ is negligible. Thus for well-localized states we should have $q\simeq\frac{1}{2}$, in agreement with Coffman's conclusion. Distinguishing between these alternatives (and other intermediate cases that may also give $q\simeq\frac{1}{2}$) is not possible on the basis of the data so far available for Cu^{2+} in MgO (although from the behavior of Cu^{2+} in other octahedrally coordinated crystals we would of course expect a fairly strong Jahn-Teller coupling in this case).

When the Jahn-Teller coupling is sufficiently weak so that q is appreciably greater than $\frac{1}{2}$, the present theory based only on linear coupling should suffice to give a fairly accurate description of the situation. In this case, as we have seen, it is possible to infer the value of $E_{JT}/\hbar\omega$ directly from the value of q using Eqs. (12) and (14). We shall now use this approach to propose an alternative interpretation of Höchli's experimental data[25] for Sc^{2+} in CaF_2 and SrF_2.

Höchli found that his g factors and hyperfine splitting for the Γ_8 ground state showed an anisotropic variation agreeing with that of Eqs. (34) and (38). From his data for the g factors, taking the ratio of the coefficient qg_2 of the anisotropic term in Eq. (34) to the difference between the isotropic part g_1 and the spin-only value 2.0023, we obtain using Eq. (31) the values $q=0.75$ and $q=0.71$, for CaF_2:Sc^{2+} and SrF_2:Sc^{2+}, respectively. Applying our theory for linear Jahn-Teller coupling to these results, we obtain from Eqs. (12) and (14) the values

$$E_{JT}/\hbar\omega=0.25 \quad\text{and}\quad 0.34 \tag{59}$$

for CaF_2:Sc^{2+} and SrF_2:Sc^{2+}, respectively. On the basis of our present theory, therefore, Sc^{2+} in CaF_2 and SrF_2 is not at all near the limit of a static Jahn-Teller effect, which requires $E_{JT}\gg\hbar\omega$; on the contrary, the Jahn-Teller energy is only one-quarter to one-third of the energy of the effective vibrational mode, so that the Jahn-Teller coupling is relatively weak, and we are well within the regime in which the Jahn-Teller effect must be viewed entirely as a dynamic coupling of the electrons to the vibrational modes. For so weak a Jahn-Teller coupling as indicated by Eq. (59), we would expect our theory based on linear Jahn-Teller coupling to be altogether appropriate (apart from the need to generalize the theory to take proper account of the phonon continuum) for a detailed interpretation of the system. Moreover, from our result from O'Brien's theory that q must be less than $\frac{1}{2}$ for a strong Jahn-Teller coupling ($E_{JT}\gg\hbar\omega$) with warping, we see that a model based on this limiting case as in Bersuker or O'Brien's treatment cannot account for the values of q found from the experimental data.

Since the Jahn-Teller coupling for Sc^{2+} in CaF_2 and SrF_2 is thus evidently in fact quite weak, it is not reasonable on the basis of the present theory to suppose that the first excited vibronic state of the Sc^{2+} can be as low as 8 to 10 cm^{-1} above the ground state, if we assume that we should take for $\hbar\omega$ a value of several hundred cm^{-1}. From Fig. 3 we see that for values of $E_{JT}/\hbar\omega$ as given in Eq. (59) we should have $\Delta_1\simeq0.7\,\hbar\omega$. The isotropic EPR spectrum which Höchli found for $T>6°K$ and which he attributed to resonance in a low-lying excited state must then have some other origin if the present theory is the appropriate one.

It seems very plausible that this isotropic spectrum may arise from effects of rapid relaxation within the ^2E ground state itself, although there are features of the experimental data which appear to be not altogether consistent with this proposal. As we have seen in Sec. VIII, exactly such a motionally averaged spectrum is expected in the ^2E state when the relaxation time τ as obtained from Eqs. (57) and (58) becomes short compared to $(2\pi\Delta\nu_m)^{-1}$ as obtained from Eq. (38). Substituting values appropriate to CaF_2 in Eq. (57), we find

$$\tau=(4.3\times10^{-6})/(q^4V_2{}^4T^5), \tag{60}$$

where τ is measured in seconds and V_2 in eV/(unit strain). Taking the value $q\,|\,2g_2\beta H+A_2\,|\simeq1\times10^{-2}\ cm^{-1}$ from Höchli's data, we find that $(2\pi\Delta\nu_{1/2})^{-1}\simeq5\times10^{-10}$ sec for the pair of lines with $m=\frac{1}{2}$. Accordingly for $q=0.75$, if $V_2\simeq1$eV/(unit strain) we find from Eq. (60) that $\tau<(2\pi\Delta\nu_{1/2})^{-1}$ for $T\gtrsim8°K$. It is therefore quite likely that motional narrowing of the low-temperature anisotropic spectrum appears in just the temperature range in which Höchli observed the appearance of the isotropic spectrum. However, the linewidths should be strongly temperature-dependent if the isotropic spectrum is to be accounted for on this basis, and Höchli reports that the linewidths of this spectrum are practically independent of temperature between 6 and 10°K. This feature of the data is of course better accounted for by Höchli's proposal that the isotropic spectrum arises from an excited orbital state. This and other features of the data, particularly the relative extent to which relaxation and random strain influence the onset of the isotropic spectrum and determine linewidths, can only be clarified by further investigation. We may note, however, that an interpretation of the isotropic spectrum in terms of relaxation would account at least qualitatively for the different widths of the different hyperfine lines in the isotropic spectrum at, say, $T=9°K$, since the lines with the larger values of $\Delta\nu_m$ would be motionally narrowed at higher temperatures. The corresponding lines in the isotropic spectrum would thus be the broader ones at temperatures low enough such that the motional narrowing is not complete, in agreement with the observations.

Finally, we may compare the values for $E_{\mathrm{JT}}/\hbar\omega$ obtained in Eq. (59) with what we might expect on the basis of Eq. (6) and the approximate relation (43b) between the Jahn-Teller coupling coefficient V and the strain coefficient V_2. Using $R=2.36$ Å and $\mu=M=3.18\times10^{-23}$ g for CaF$_2$, we obtain (in cm^{-1})

$$E_{\mathrm{JT}}=0.088\ (V_2/\hbar\omega)^2. \tag{61}$$

Thus if V_2 has a value $\simeq$1eV/(unit strain), and if $\hbar\omega\simeq300$ cm^{-1}, we would have $E_{\mathrm{JT}}\simeq60$ cm^{-1}. Thus the values (59) for $E_{\mathrm{JT}}/\hbar\omega$ are certainly consistent with this estimate if V_2 is in the neighborhood of 1eV/(unit strain). Clearly it would be extremely valuable to obtain an experimental determination of V_2 from a measurement of the strain coefficient $V_2'=qV_2$ of the ^2E vibronic ground state of Sc^{2+}, in order to check the consistency of applying our theory to this ion.

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APPENDIX I: EIGENSTATES OF THE VIBRONIC HAMILTONIAN

The transformation

$$\mathcal{H}'=\exp(iS)\mathcal{H}\exp(-iS) \tag{A1}$$

of the Hamiltonian $\mathcal{H}$ of Eq. (1), with

$$S=-(V/\mu\omega^2\hbar)(P_\theta U_\theta+P_\epsilon U_\epsilon), \tag{A2}$$

yields

$$\mathcal{H}'=\mathcal{H}_0\mathcal{I}-(V^2/\mu\omega^2)[\mathcal{I}+A_2M] \tag{A3}$$

as obtained previously by Moffitt and Thorson,[12] plus terms of order V^3 and higher. Here M is the "angular-momentum" operator

$$M=\hbar^{-1}(P_\theta Q_\epsilon-P_\epsilon Q_\theta). \tag{A4}$$

The eigenvalues of $\mathcal{H}$ to order V^2 are therefore[12]

$$E_{nmp}=E_0+(n+1)\hbar\omega-(V^2/\mu\omega^2)(m+1), \tag{A5}$$

where $n=0,\ 1,\ 2,\cdots;\ m=-n,\ -n+2,\cdots,\ n-2,\ n$; and $p=1$, 2, each level being doubly degenerate. Since M commutes with $\mathcal{H}_0$, the exact eigenstates $|\,nmp\rangle'$ of $\mathcal{H}'$ to the order written down in Eq. (A3) are the vibrational eigenfunctions of $\mathcal{H}_0$ (the Hamiltonian of the two-dimensional harmonic oscillator) which are also eigenfunctions of M, multiplied by the electronic functions $\psi_p=(1/\sqrt{2})(\psi_\theta\pm i\psi_\epsilon)$ which diagonalize A_2. The vibronic eigenstates of our original $\mathcal{H}$ are accordingly given by

$$|\,nmp\rangle=\exp(-iS)\,|\,nmp\rangle', \tag{A6}$$

and matrix elements of any operator O among the eigenstates of $\mathcal{H}$ are therefore the same as those of

$$O'=\exp(iS)O\exp(-iS) \tag{A7}$$

among the states $|\,nmp\rangle'$.

Applying the transformation (A7) to the electronic operators U_θ, U_ϵ, and A_2 of Eq. (3), we obtain to order V^2

$$U_\epsilon'=U_\epsilon-(2V/\mu\omega^2\hbar)P_\theta A_2 -(2V^2/\mu^2\omega^4\hbar^2)(P_\theta^2U_\epsilon-P_\epsilon P_\theta U_\theta), \tag{A8a}$$

$$U_\theta'=U_\theta+(2V/\mu\omega^2\hbar)P_\epsilon A_2 -(2V^2/\mu^2\omega^4\hbar^2)(P_\epsilon^2U_\theta-P_\epsilon P_\theta U_\epsilon), \tag{A8b}$$

$$A_2'=A_2+(2V/\mu\omega^2\hbar)(P_\theta U_\epsilon-P_\epsilon U_\theta) -(2V^2/\mu^2\omega^4\hbar^2)(P_\theta^2+P_\epsilon^2)A_2, \tag{A8c}$$

while of course by applying (A7) to the unit matrix $\mathcal{I}$ we obtain simply $\mathcal{I}$. Accordingly, the matrix elements of U_θ, U_ϵ, and A_2 among the vibronic eigenstates $|\,nmp\rangle$ of $\mathcal{H}$ are given to order V^2 by the matrix elements of U_θ', U_ϵ', and A_2' in Eq. (A8) between the eigenstates of the simple harmonic-oscillator Hamiltonian $\mathcal{H}_0$. In particular, for the matrix elements of U_θ within the ground state, we obtain

$$\langle 00p\,|\,U_\theta\,|\,00p'\rangle=[1-(V^2/\mu\omega^3\hbar)]\langle\psi_p\,|\,U_\theta\,|\,\psi_{p'}\rangle \tag{A9a}$$

and similarly for U_ϵ, while for A_2

$$\langle 00p\,|\,A_2\,|\,00p'\rangle=[1-(2V^2/\mu\omega^3\hbar)]\langle\psi_p\,|\,A_2\,|\,\psi_{p'}\rangle. \tag{A9b}$$

These results provide the derivation of the reduction factors of Eq. (8) of the text when $E_{\mathrm{JT}}\ll\hbar\omega$. Since S as given by Eq. (A2) belongs to the symmetric representation (A_1) of the cubic group, the transformation properties of the states $|\,nmp\rangle$ and $|\,nmp\rangle'$ are identical according to Eq. (A6), and similarly those of the operators O' and O according to Eq. (A7). The operators U_θ' and U_ϵ' therefore belong as partners θ, ϵ, respectively, to the representation E, and A_2' to A_2.

When the Jahn-Teller coupling is not weak, we use the fact that any linear combination of ψ_θ and ψ_ϵ which is a single-valued function of Q_θ, Q_ϵ may be expressed as a series of the form

$$\sum\nolimits_n[A_n(\rho)\exp(in\theta)\psi_-+B_n(\rho)\exp(in\theta)\psi_+], \tag{A10}$$

where ψ_-, ψ_+ are the electronic functions defined by Eq. (4), and $A_n(\rho)$, $B_n(\rho)$ are functions only of ρ. Here n must range over all half-odd integers,[14] $n=$

$\cdots -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, \cdots$, the half-integral value being necessary in order that (A10) be single-valued, since ψ_+, ψ_- change sign if θ is replaced by $(\theta+2\pi)$. However, $\mathcal{H}$ of Eq. (1) does not connect terms of (A10) having different values of n. The eigenfunctions of this Hamiltonian accordingly have the form

$$\Psi_n = f_n(\rho)\,\exp(in\theta)\psi_- + ig_n(\rho)\,\exp(in\theta)\psi_+, \quad \text{(A11)}$$

where f_n, g_n satisfy the coupled differential equations[13,22]

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) - \frac{n^2+(1/4)}{\rho^2}\right]\begin{Bmatrix} f_n \\ g_n \end{Bmatrix} + \left(\tfrac{1}{2}\mu\omega^2\rho^2 \mp V\rho - E_n\right)\begin{Bmatrix} f_n \\ g_n \end{Bmatrix} = -\frac{\hbar^2 n}{2\mu\rho^2}\begin{Bmatrix} g_n \\ f_n \end{Bmatrix}. \quad \text{(A12)}$$

Since all the terms in Eq. (A12) are real, we may choose the arbitrary phase factor in Ψ_n in Eq. (A11) such that $f_n(\rho)$ and $g_n(\rho)$ are real functions. All eigenstates are doubly degenerate,[13,14] since if f_n, g_n satisfy Eqs. (A12) for $n = |n|$, a solution of these equations for $n = -|n|$ but the same energy E_n is given by

$$f_{-|n|}(\rho) = f_{|n|}(\rho),$$
$$g_{-|n|}(\rho) = -g_{|n|}(\rho). \quad \text{(A13)}$$

It is convenient to form explicitly the linear combinations of the degenerate eigenfunctions Ψ_n in Eq. (A11) that belong to the irreducible representations E, A_1, and A_2 of the cubic group. Assuming that f_n and g_n are real and that they satisfy Eq. (A13), and defining (where now we take $n>0$)

$$\Psi_n^+ = 2^{-1/2}(\Psi_n + \Psi_{-n}),$$
$$\Psi_n^- = i2^{-1/2}(\Psi_n - \Psi_{-n}), \quad \text{(A14)}$$

we find for $n = \frac{1}{2}+3m$ (m = positive integer or zero) that Ψ_n^+, Ψ_n^- belong to E as partners θ, ϵ, respectively. For $n = \frac{3}{2}+3m$, Ψ_n^+ belongs to A_1 and Ψ_n^- to A_2. For $n = \frac{5}{2}+3m$, Ψ_n^+ and $(-)\Psi_n^-$ belong to E, respectively, as the partners θ, ϵ.

The ground state of $\mathcal{H}$ in Eq. (1) for an arbitrarily strong Jahn-Teller coupling is a doublet having $n = \pm\frac{1}{2}$ and thus belonging to E.[13,14] We may evaluate the matrix elements of U_θ, U_ϵ, and A_2 within this ground state explicitly in terms of $f_{1/2}(\rho)$ and $g_{1/2}(\rho)$, using Eqs. (A11) and (A14), to obtain general expressions for the reduction factors p and q defined in Eq. (8). We obtain in this way

$$p = -4\pi\int_0^\infty \rho f_{1/2}(\rho)\,g_{1/2}(\rho)\,d\rho \quad \text{(A15)}$$

and

$$q = \tfrac{1}{2} - 2\pi\int_0^\infty \rho f_{1/2}(\rho)\,g_{1/2}(\rho)\,d\rho, \quad \text{(A16)}$$

where in obtaining Eq. (A16) we have used the normalization condition

$$2\pi\int_0^\infty \rho[f_n^2(\rho) + g_n^2(\rho)]d\rho = 1. \quad \text{(A17)}$$

From Eqs. (A15) and (A16), we see therefore that the relation

$$q = \tfrac{1}{2}(1+p) \quad \text{(A18)}$$

is an exact relation so long as only linear Jahn-Teller coupling is considered.

In general, it may be shown that U_θ, U_ϵ have nonzero matrix elements between two states Ψ_n, Ψ_n', of the form (A11) only if $|n-n'| = 1$, but that A_2 is diagonal with respect to n. As the first excited state[13,14] has $n = \pm\frac{3}{2}$, it follows that A_2 has no matrix elements between the ground state and first excited state; those of U_θ, U_ϵ are given by

$$\langle\Psi_{1/2}^+ | U_\theta | \Psi_{3/2}^+\rangle = \langle\Psi_{1/2}^- | U_\epsilon | \Psi_{3/2}^+\rangle = -\tfrac{1}{2}\eta, \quad \text{(A19)}$$

$$\langle\Psi_{1/2}^+ | U_\epsilon | \Psi_{3/2}^-\rangle = -\langle\Psi_{1/2}^- | U_\theta | \Psi_{3/2}^-\rangle = +\tfrac{1}{2}\eta, \quad \text{(A20)}$$

where we use the notation of Eq. (A14), and η is given by

$$\eta = 2\pi\int_0^\infty \rho d\rho\,\{f_{1/2}f_{3/2} - g_{1/2}g_{3/2} - f_{1/2}g_{3/2} + g_{1/2}f_{3/2}\}. \quad \text{(A21)}$$

When the Jahn-Teller coupling is strong, so that $E_{\mathrm{JT}} \gg \hbar\omega$, the separation $4E_{\mathrm{JT}}$ of the potential-energy surfaces in Fig. 1 in the region of the minimum at $\rho = |V|/\mu\omega^2$ is large compared to $(\hbar^2 n/2\mu\rho^2)$, the coefficient of the term on the right-hand side of Eq. (A12), for small n. Accordingly, a state with E_n near the minimum is predominantly the electronic state for the lower potential-energy surface, so that for this state we have

$$\Psi_n \simeq f_n(\rho)\,\exp(in\theta)\psi_-, \qquad (V>0) \quad \text{(A22a)}$$

or

$$\Psi_n \simeq ig_n(\rho)\,\exp(in\theta)\psi_+, \qquad (V<0) \quad \text{(A22b)}$$

and we may omit the right-hand side of Eq. (A12) in solving for the wave functions and energies. The remaining dependence on n is then through the term in (n^2/ρ^2), so that it is clear that the ground state has $n = \pm\frac{1}{2}$ and that the first excited state has $n = \pm\frac{3}{2}$ with an excitation energy above the ground state given to an excellent approximation when $E_{\mathrm{JT}}/\hbar\omega \gg 1$ by

$$\Delta_1 \simeq (\hbar^2/\mu)\,\langle\rho^{-2}\rangle$$
$$\simeq (\hbar^2\mu\omega^4/V^2) = \hbar\omega\,(\hbar\omega/2E_{\mathrm{JT}}). \quad \text{(A23)}$$

Since in this limit the ground-state eigenfunctions as given by Eq. (A22) are multiples either of ψ_- or of ψ_+, so that in Eq. (A11) either $f_n(\rho)$ or $g_n(\rho)$ is negligibly small, we see from Eqs. (A15) and (A16) that in this limit $p=0$ and $q=\frac{1}{2}$. This result provides the proof of Eq. (11) of the text. Moreover, in this limit the radial functions $f_{1/2}(\rho)$ and $f_{3/2}(\rho)$ (or $g_{1/2}$ and $g_{3/2}$) for the ground state and first excited state are approximately equal, since the term n^2/ρ^2 in Eq. (A12) is then small in the vicinity of the minimum. Accordingly for $E_{\mathrm{JT}}\gg\hbar\omega$ we find from Eqs. (A17) and (A21) that $|\eta|\sim 1$ in the matrix elements (A19), with the sign of η the same as that of V.

APPENDIX II: RELATION OF STRAIN TO DISTORTION MODES

We derive here the relation between strain and the amplitude of the distortion modes of the set of nearest-neighbor ions, in order to relate the coefficient for linear Jahn-Teller coupling to the strain coefficient.

Let $R_n=(X_{n1}, X_{n2}, X_{n3})$ denote the Cartesian coordinates of the nth nearest-neighbor ion, and X_{ni}^0 the equilibrium value of the coordinate. The kinetic energy of these ions is then given by

$$K=\tfrac{1}{2}M\sum_{n,i}\dot{X}_{ni}^2, \tag{A24}$$

where M is the mass of one ion. Introducing a transformation

$$Q_p=\sum_{n,i}\alpha_{p;ni}(X_{ni}-X_{ni}^0), \tag{A25}$$

we have thus

$$K=\tfrac{1}{2}M\sum_{p}\dot{Q}_p^2, \tag{A26}$$

provided the transformation (A25) is orthogonal. Accordingly, if we use such a transformation to define vibrational coordinates Q_θ, Q_ϵ, the vibronic Hamiltonian describing the interaction of these modes with the electronic state E is given by Eq. (1) of the text[36] with

$$\mu=M. \tag{A27}$$

We now introduce a tetragonal strain, given in accord with Eq. (40) by $e_{xx}=e_{yy}=-\frac{1}{3}e_\theta$, $e_{zz}=+\frac{2}{3}e_\theta$. The nth ion is accordingly displaced to

$$R_n'=[X_{n1}^0(1-\tfrac{1}{3}e_\theta), X_{n2}^0(1-\tfrac{1}{3}e_\theta), X_{n3}^0(1+\tfrac{2}{3}e_\theta)]. \tag{A28}$$

Substituting these displacements into Eq. (A25), we obtain the following relation between e_θ and the even vibrational mode Q_θ that transforms as $E(\theta)$, for six- and eightfold cubic coordination and fourfold tetrahedral coordination, respectively:

Sixfold,

$$Q_\theta=(2/\sqrt{3})Re_\theta. \tag{A29a}$$

Eightfold,

$$Q_\theta=(\tfrac{4}{3})Re_\theta. \tag{A29b}$$

Fourfold,

$$Q_\theta=(2\sqrt{2}/3)Re_\theta, \tag{A29c}$$

Here R is the nearest-neighbor distance. Identical relations between Q_ϵ and e_ϵ of course also hold.