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Model for Jahn-Teller Distortions of Ag^{2+} Ions by Odd Modes in Fluorite Crystals

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A model is developed for the Jahn-Teller distortions of Ag^{2+} ions in CaF_2 and SrF_2. Two odd modes of distortion dominate and give rise to hyperfine interaction with a pair of equivalent fluorines as observed in our experiments. The effect of the even mode of distortion is included by using perturbation theory. Near the end of the paper, some estimates are given for the Jahn-Teller energy.

I. INTRODUCTION

In recent years, Jahn-Teller effects[1] have been of increasing interest. A considerable amount of theoretical effort has gone into the study of static and dynamic Jahn-Teller effects for doublet (Γ_3^+) ground states.[2] Bersuker,[3] Ham,[4] and O'Brien[5] have made important contributions beyond the earlier work of Opik, Pryce, and others.[6]

Far less information is available on the distortions of triplet ground states, and the theory seems to be more complicated and less developed. In an important piece of work, Ham[4] has developed a theory of dynamical quenching for triplet states and has successfully explained some reduced g shifts and spin-orbit splittings of certain transition-metal ions. Both Ham[7] and Sturge[8] have recently reviewed the experimental and theoretical status of Jahn-Teller effects.

Our interest in this paper centers on the static Jahn-Teller distortions of the ground-state triplet of the Ag^{2+} ion in CaF_2 and other fluorite crystals. In the previous paper, we presented experimental evidence to show that substitutional Ag^{2+} ions in CaF_2 distort in $\langle 110\rangle$ directions toward pairs of equivalent fluorines. The symmetry of the EPR spectrum indicates that the Ag^{2+} ion and surrounding ions distort from cubic symmetry to a symmetry C_{2v} by an odd mode of distortion. In the distorted position the triplet Γ_5^+ ground state is split and the hole in the d shell is then shared with a pair of neighboring fluorine ions. In pure CaF_2 crystals, a hole can be completely on the fluorine ions and unassociated with a transition-metal ion. In this case, the center is called the V_k center and was first explored by Känzig[9] in the alkali halides. Later, Hayes and Twidell[10] and Sierro[11] examined the center in CaF_2.

We will attempt to develop a model in which the Ag^{2+} ion has a dominant hyperfine interaction with pairs of fluorines that are oriented in $\langle 100\rangle$ directions. To be in accord with experiment we would like the ions to distort in $\langle 110\rangle$ directions. A number of assumptions are involved in the model. First of all, in Sec. II, we treat the hole as being in a one-electron orbital which is spread out over the fluorines. Interactions between electrons are neglected. Second, the spin-orbit interaction is assumed to be weaker than the Jahn-Teller interaction so that g shifts may be calculated by the use of perturbation theory.[12] As a third assumption, we use a *molecular* model in considering the hole wave functions of Sec. II C and the normal vibrations of Sec. II D. To be more exact, the interactions with the whole lattice should be taken into account. Other assumptions are pointed out as the model is developed. Near the end of the paper we attempt to give some estimates of the Jahn-Teller energy.

We might comment that the model given here may eventually have to be evaluated and extended in more detail than presented here. It is only hoped that the presentation of this model will stimulate further interest.

II. MICROSCOPIC MODEL FOR DISTORTIONS

A. Model Hamiltonian

Our discussion will be in terms of a one-electron (or hole) model. Only nearest-neighbor fluorines are included in the Hamiltonian of the system and for simplicity we also omit hyperfine terms.

$$H = p^2/2m + V + \lambda \vec{L} \cdot \vec{S} \ . \qquad (1)$$

The first term is the kinetic energy of the hole while the third term is the spin-orbit interaction. From the beginning we assume that the spin-orbit interaction energy is less than the Jahn-Teller energies. At the end of the paper we estimate the Jahn-Teller energies and find this assumption to be validated. Crystal-field effects are included in the second term which may be expanded in terms of small distortions Q_α from the position of cubic symmetry.

$$V = V_0 + \sum \frac{\partial V}{\partial Q_\alpha}\bigg|_0 Q_\alpha + \tfrac{1}{2} \sum_{\alpha\alpha'} \frac{\partial^2 V}{\partial Q_\alpha \, \partial Q_{\alpha'}}\bigg|_0 Q_\alpha Q_{\alpha'} \ . \qquad (2)$$

All of the derivatives are evaluated at the cubic position which is denoted by the subscript zero. Covalent mixing with the fluorines also arises from this crystal-field potential. A major part of V is the Coulomb interaction of the hole with the nearest-neighbor negative ions and the central ion itself. In calculating the linear term of Eq. (2) it is permissible to limit our considerations to these Coulomb terms:

$$V \cong V_a + \sum_n V_n = \frac{-e^2}{(\vec{r} - \vec{R}_a)} + \sum_{n=1}^{8} \frac{e^2}{(\vec{r} - \vec{R}_n)} . \tag{3}$$

Here R_n is the position of the nth fluorine ion and R_a is the position of the central ion. The ion-ion Coulomb terms are effectively included in the second-order term of (2).

We start our problem by describing the hole states of the Ag^{2+} ion in a cubic crystalline field, then we consider states of the hole on the fluorines with the system in cubic symmetry, introduce the normal coordinates, and finally consider the Jahn-Teller distortions.

B. Central-Ion Hole States

A free Ag^{2+} ion has nine electrons in the $4d$ shell. One electron is missing from filling the d shell so the wave function can be viewed as a hole in the d shell. In the crystal, the Ag^{2+} ion substitutes for an alkaline-earth ion and will be in a position of cubic symmetry when no distorting forces are present. In the cubal symmetry of the substitutional site the orbital d levels of the free ion are split into a Γ_5^+ triplet and a Γ_3^+ doublet with the doublet lowest in energy as in Fig. 1. Electrostatic and covalent interactions together determine the crystal-field splitting of the orbital states. In the $4d^9$ configuration, the hole state will be described by the Γ_5^+ type of wave functions:

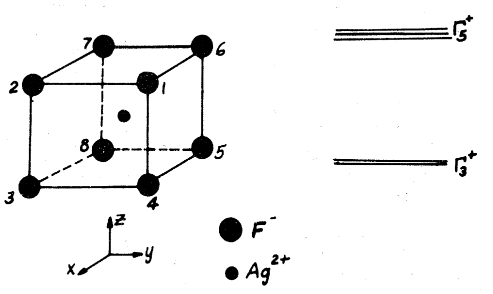

FIG. 1. One-electron energy levels in the undistorted or fully cubic configuration

$$|\Gamma_{5a}^+\rangle = \sqrt{3}\, yz f(r), \quad |\Gamma_{5b}^+\rangle = \sqrt{3}\, zx f(r),$$
$$|\Gamma_{5c}^+\rangle = \sqrt{3}\, xy f(r) . \tag{4}$$

For triplet states, the spin-orbit interaction can also be important since the matrix elements of this interaction do not vanish within the Γ_5^+ manifold as they do in the Γ_3^+ manifold. Our experiment indicates, however, that the Jahn-Teller distortions of the Γ_4^- mode have greater strength than either the spin-orbit interaction or the Jahn-Teller (JT) distortion due to even modes of distortion. In the work that follows, the spin-orbit interaction will be treated as a perturbation. As an example, static effects from the spin-orbit interaction enter into the Abragam-Pryce[13] type of g-shift calculation used in the preceding paper. The spin-orbit interaction together with phonon interactions may also produce dynamic effects such as spin-lattice relaxation.

For the purposes of our model the covalent interaction with the surrounding fluorine ions is extremely important. An odd mode of distortion is only allowed by virtue of the hole spending part of its time on the surrounding fluorines.

C. Fluorine Hole States

Let us consider that the hole only spends an appreciable time on the eight nearest-neighbor fluorines. In the alkaline fluoride crystals, the bonding is mainly ionic in a material like CaF_2 but becomes more covalent in a material like CdF_2. Even in CaF_2, there is a small covalent contribution to the bonding. The p-orbital bonds are directed in $\langle 100 \rangle$ directions so that one can think of bonding and antibonding electron orbitals between pairs of fluorines. In our further discussion we will refer to the antibonding and bonding electron orbitals as bonding and antibonding hole orbitals, respectively. These bonding and antibonding hole orbitals are pulled out of the bonding and antibonding valence bands of the crystal. It is precisely these bond energies that allow the hole to lower its energy by a distortion coupling between the hole states on the fluorines. In the alkali halides and many II-VI compounds, our mechanism may not be so important because the hole on the central transition-metal ion mixes with ligand orbitals that are directed toward the central ion. These ligand orbitals have little overlap with each other and thus the energies of the ligand p states can only be lowered by crystal-field effects.

In the undistorted or cubic configuration the 24 orbitals on the eight surrounding flourines are

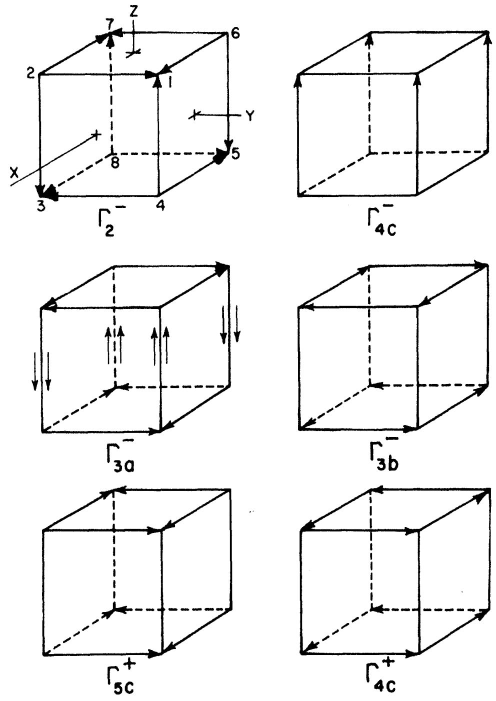

FIG 2. Pictorial representation of the various irreducible wave functions for the bonding hole states on eight fluorines in a cubic arrangement. A double arrow represents a wave function of double amplitude.

split into a set of 12 bonding hole orbitals lowest in energy and 12 antibonding hole orbitals higher in energy. As we shall see, the explanation of the distortion for Ag^{2+} comes mainly from the coupling of the JT distortion operator between bonding hole states.

The fluorine p states that are used in forming the bonding hole orbitals have a very small amount of s character mixed in by the surrounding tetrahedral arrangement of alkaline ions. Further changes in the s character come from the JT distortion. A single bonding hole orbital between a pair of fluorines is described by

$$|nn'\rangle = (|n\rangle - |n'\rangle)/\sqrt{2}$$

with $|n\rangle = \alpha\phi_{2p}(n) + \beta\phi_{3s}(n)$, (5)

where $\phi_{3s}(n)$ is an atomic $3s$ wave function and $\phi_{2p}(n)$ is an atomic $2p$ wave function centered on ion n. $|n'\rangle$ is a wave function identical to $|n\rangle$ but centered on ion n'. As a convenience in writing down the proper wave functions we note that the wave function of Eq. (5) can be pictured (see Fig. 2) as an arrow directed along one of the edges of a cube. The fluorines are located at the corners and the silver ion in the center of the cube. A bonding orbital can be designated by locating the center of an edge with indices i and j that take on values ±1, ±2, ±3 corresponding to the different space directions of the edge from the center of the cube. For example, $|ij\rangle = |12\rangle$ is another way of designating the orbital $|nn'\rangle = |14\rangle$ which is represented in Fig. 2 as an arrow going from fluorine 4 to fluorine 1.

Using a similar notation, an antibonding hole orbital between a pair of fluorines is described by

$$|nn'\rangle_a = (|n\rangle + |n'\rangle)/\sqrt{2}\ . \tag{6}$$

This wave function has a buildup of hole density between the nth and n'th ion and is pictured by circles in Fig. 3. In the undistorted configuration, hole orbitals on the fluorines must transform according to cubic symmetry and may be approximated as linear combinations (LCAO) of the pair orbitals $|nn'\rangle$ and $|nn'\rangle_a$. The reducible representation generated by the 12 pairs of bonding hole orbitals breaks up into five irreducible representations of O_h:

$$\Gamma \rightarrow \Gamma_2^- + \Gamma_3^- + \Gamma_4^- + \Gamma_4^+ + \Gamma_5^+\ . \tag{7}$$

A list of bonding wave functions for holes is given below together with the "tunneling" energy splittings of these states. Interaction between adjacent pair orbitals at 90° is used to calculate the tunneling splittings. Figure 2 shows the bonding hole wave functions of the fluorines in pictorial form.

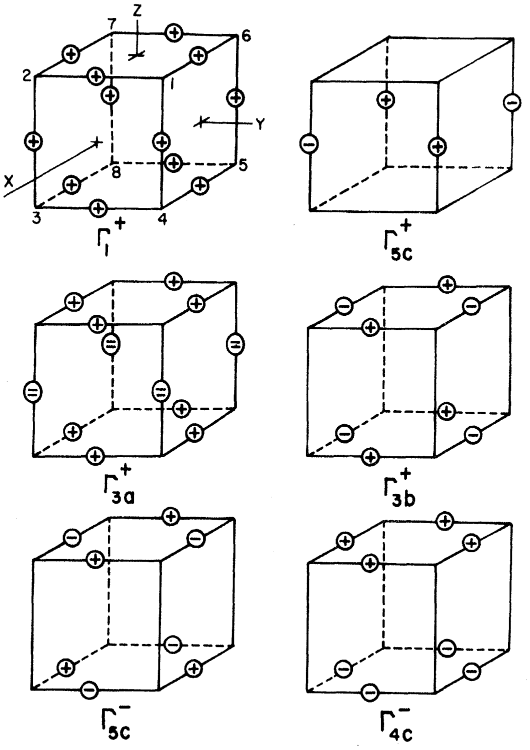

FIG. 3. Similar to Fig. 2 except for the antibonding hole states. The phase of the wave function is represented by + and − signs.

Γ_2^- wave function:

$$|\Gamma_2^-\rangle = \frac{1}{\sqrt{12}} \sum_{i,j=\pm1,\pm2,\pm3} S(i)\, S(j)\,|ij\rangle\,, \tag{8a}$$

$$E(\Gamma_2^-) = 2\Delta;\quad \Delta = \langle 12|H|23\rangle + \langle 23|H|12\rangle\ .$$

Γ_4^- wave functions ($|\Gamma_{4c}^-\rangle$ only):

$$|\Gamma_{4c}^-\rangle = \frac{1}{2} \sum_{i,j=\pm1,\pm2} |ij\rangle\,, \tag{8b}$$

$$E(\Gamma_4^-) = 0.$$

Γ_3^- wave functions:

$$\begin{aligned} |\Gamma_{3a}^-\rangle = \frac{1}{\sqrt{24}}\Big[2 &\sum_{i,j=\pm1,\pm2} S(i)S(j)|ij\rangle \\ &- \sum_{i,j=\pm1,\pm3} S(i)S(j)|ij\rangle \\ &- \sum_{i,j=\pm2,\pm3} S(i)S(j)|ij\rangle\Big]\,, \end{aligned} \tag{8c}$$

$$\begin{aligned} |\Gamma_{3b}^-\rangle = \frac{1}{\sqrt{8}}\Big[&\sum_{i,j=\pm2,\pm3} S(i)S(j)|ij\rangle \\ &- \sum_{i,j=\pm1,\pm3} S(i)S(j)|ij\rangle\Big]\,, \end{aligned}$$

$$E(\Gamma_3^-) = -\Delta\ .$$

Γ_5^+ wave functions ($|\Gamma_{5c}^+\rangle$ only):

$$|\Gamma_{5c}^+\rangle = \frac{1}{\sqrt{8}}\Big[\sum_{i=\pm2,j=\pm3} S(i)|ij\rangle + \sum_{i=\pm1,j=\pm3} S(i)|ij\rangle\Big]\,, \tag{8d}$$

$$E(\Gamma_5^+) = \Delta\ .$$

Γ_4^+ wave function ($|\Gamma_{4c}^+\rangle$ only):

$$|\Gamma_{4c}^+\rangle = \frac{1}{\sqrt{8}}\Big[\sum_{i,j=\pm2,\pm3} S(i)|ij\rangle - \sum_{i,j=\pm1,\pm3} S(i)|ij\rangle\Big]\,,$$

$$E(\Gamma_4^+) = -\Delta\ . \tag{8e}$$

In the above equation, $S(i)$ stands for the sign (±1) of the index i.

The reducible representation of the 12 pairs of antibonding hole orbitals also yields five irreducible representations,

$$\Gamma \rightarrow \Gamma_1^+ + \Gamma_3^+ + \Gamma_5^+ + \Gamma_4^- + \Gamma_5^- \tag{9}$$

with the following set of wave functions.

Γ_1^+ wave function:

$$|\Gamma_1^+\rangle = \frac{1}{\sqrt{12}} \sum_{ij} |ij\rangle_a\ . \tag{10a}$$

Γ_3^+ -type wave functions:

$$|\Gamma_{3a}^+\rangle = \frac{1}{\sqrt{24}}\Big[\sum_{i=\pm1,\pm2,j=\pm3} |ij\rangle_a - 2\sum_{i=\pm1,j=\pm2} |ij\rangle_a\Big]\,,$$

$$|\Gamma_{3b}^+\rangle = \frac{1}{\sqrt{8}}\Big[\sum_{i=\pm1,j=\pm3} |ij\rangle_a - \sum_{i=\pm2,j=\pm3} |ij\rangle_a\Big]. \tag{10b}$$

Triplet wave functions (one of each type):

$$|\Gamma_{5c}^+\rangle = \tfrac{1}{2} \sum_{i=\pm1,j=\pm2} S(i)S(j)|ij\rangle_a\,, \tag{10c}$$

$$|\Gamma_{5c}^-\rangle = \frac{1}{\sqrt{8}}\Big[\sum_{i=\pm3,j=\pm1} S(i)|ij\rangle_a - \sum_{i=\pm3,j=\pm2} S(i)|ij\rangle_a\Big]\,, \tag{10d}$$

$$|\Gamma_{4c}^-\rangle = \frac{1}{\sqrt{8}}\Big[\sum_{i=\pm3,j=\pm1,\pm2} S(i)|ij\rangle_a\Big]. \tag{10e}$$

The wave functions are pictured in Fig. 3.

D. Normal Coordinates

In considering the hole states, we have used a tight-binding model in which the hole wave function only spreads out from the Ag^{2+} to the nearest-neighbor fluorines. Likewise, only the distortions of the nearest-neighbor fluorines will be taken into account. In the fluorite crystal, the Ag^{2+} ion has substituted for the alkaline-earth ion and is surrounded by eight fluorine ions. The possible normal coordinates for the distortion of this molecular unit may be determined by group theory. Rigid-body rotations and translations may be excluded so the distortions can be reduced to the following sum of normal coordinates:

$$\Gamma \rightarrow \Gamma_1^+ + \Gamma_2^- + \Gamma_3^+ + \Gamma_3^- + 2\Gamma_4^- + 2\Gamma_5^+ + \Gamma_5^-\ , \tag{11}$$

where we have used the representation designations as found in Koster *et al.*[2] Liehr has drawn pictures of all of these distortions.[14]

The problem seems complicated with so many possible modes of distortion so we introduce the simplifying assumption of using only the σ modes of distortion, i.e., the modes in which the fluorines move in and out from the central ion. In Fig. 4, we show the modes of distortion of the σ type. Only the Γ_4^-- and Γ_5^+-type distortions can

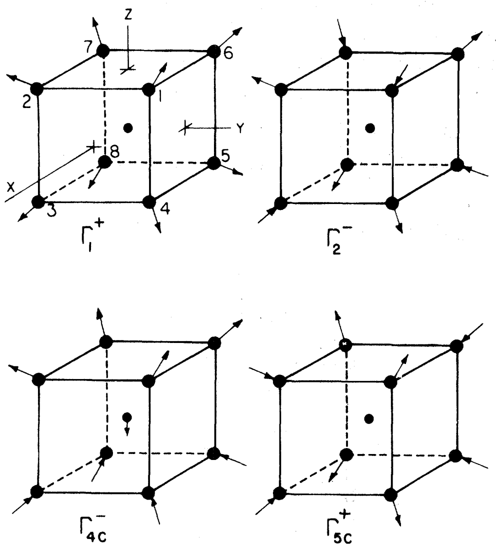

FIG. 4. Possible σ modes of distortion from cubic symmetry for eightfold cubic coordination. Arrows indicate the movement of ions along ⟨111⟩ directions.

cause a splitting of energy levels. A Γ_4^--type distortion can only connect states of opposite parity and hence cannot couple within the ground states of the central ion but can couple between fluorine hole states. Later we will find that the other Γ_4^- mode or π mode of distortion can readily be incorporated into the theory. It is interesting to note that the two Γ_4^- modes correspond to possible vibrational modes of the lattice molecular unit of CaF_2. The π mode is illustrated in Fig. 5.

E. JT Distortions

Now we consider the consequences of distortions from cubic symmetry. It is well known that the Γ_5^+ distortion acting alone gives rise to trigonal symmetry as the lowest-energy configuration in the static limit.[15] In this case, one expects to see hyperfine interactions with a pair of equivalent fluorines directed along a $\langle 111\rangle$ direction. A number of systems with static trigonal distortions have been observed.[7] Our experimental results do not give any indication of a trigonal distortion so we will concentrate our attention on the Γ_4^- mode of distortion. Later we will include the effect of the Γ_5^+ mode by using perturbation theory. Also the effect of the second Γ_4^- mode will be accurately incorporated. From parity considerations, we can say that the matrix elements of the Γ_4^- distortion operator vanish within the $4d^9$ ground-state manifold of the central ion. Distortions of the Γ_4^- type become allowed only when one considers that the hole wave function spreads out over the surrounding fluorines. Coupling between the fluorine hole states then allows the distortion to take place. Later on, we will also account for the coupling between the hole states on the fluorines and those on the central ion.

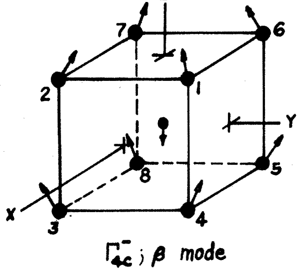

FIG. 5. The second Γ_4^- mode or π mode of distortion. Arrows indicate the movement of ions along $\langle 112\rangle$ directions.

The crystal-field potential including the JT distortion terms may be written as

$$V = V_a + \sum_{n=1}^{8} V_n = \sum_n \left[V_{n0} + \frac{\partial V_n}{\partial Q_a^-}\bigg|_0 Q_a^- + \frac{\partial V_n}{\partial Q_b^-}\bigg|_0 Q_b^- + \frac{\partial V_n}{\partial Q_c^-}\bigg|_0 Q_c^- \right] + V_{a0} + \frac{\partial V_a}{\partial Q_a^-}\bigg|_0 Q_a^- + \frac{\partial V_a}{\partial Q_b^-}\bigg|_0 Q_b^- + \frac{\partial V_a}{\partial Q_c^-}\bigg|_0 Q_c^- , \tag{12}$$

where Q_a^-, Q_b^-, Q_c^- are the coordinates of the Γ_4^- odd mode of distortion. Each derivative may be expanded in terms of displacements of individual fluorines as

$$\frac{\partial V}{\partial Q_a^-} = \sum_n \frac{\partial V}{\partial \sigma_n} \frac{\partial \sigma_n}{\partial Q_a^-} = \frac{1}{\sqrt{8}} \left[\frac{\partial V}{\partial \sigma_1} + \frac{\partial V}{\partial \sigma_2} + \frac{\partial V}{\partial \sigma_3} + \frac{\partial V}{\partial \sigma_4} - \frac{\partial V}{\partial \sigma_5} - \frac{\partial V}{\partial \sigma_6} - \frac{\partial V}{\partial \sigma_7} - \frac{\partial V}{\partial \sigma_8} \right], \tag{13}$$

where the σ_n are displacements of the fluorines in $\langle 111\rangle$ directions.

For the physical systems discussed in this paper the central ion has a fairly weak coupling to the electronic states of the surrounding fluorines. As a result, perturbation theory will be valid so long as we first remove the degeneracies of the fluorine hole states. Bonding hole states on the fluorines are approximately degenerate in energy and have both even- and odd-parity classifications. States of opposite parity may be coupled by the Γ_4^- distortion. We assume that the antibonding states on the fluorines are separated from the bonding states by an appreciable energy gap so that the coupling to antibonding states may be neglected. Our fluorine wave functions can then be represented in the following general form:

$$|\Gamma_\alpha\rangle = \sum_{nn'} |nn'\rangle\langle nn'|\Gamma_\alpha\rangle , \tag{14}$$

where Γ_α belongs to an irreducible representation of the cubic group O_h and $|nn'\rangle$ is the wave function between a pair of fluorines as was described previously. In Eqs. (8), we have listed the various representations $|\Gamma_\alpha\rangle$.

Our first task is to consider the JT coupling between the nearby degenerate fluorine hole states. We use a rigid LCAO model[16] where the atomic orbital on an atom shifts with the position of the atom. Matrix elements of the Hamiltonian will have the following form:

$$\langle \Gamma_{\alpha'}|H|\Gamma_\alpha\rangle = \sum_{n'n''} \langle \Gamma_{\alpha'}|n'n''\rangle\langle n'n''|(p^2/2m) + V_a + \sum_n V_n|n'n''\rangle\langle n'n''|\Gamma_\alpha\rangle . \tag{15}$$

Note that cross coupling of $|n'n''\rangle$ to another state $|n''n'''\rangle$ has been neglected. By using the bonding pair wave functions given in Eq. (5) the matrix element on the right side may be written as

$$E_{n'n''} = \langle n'n''|(p^2/2m) + V_a + \sum_n V_n|n'n''\rangle$$
$$= E_p + \tfrac{1}{2}\langle n'|V_a + \sum_{n\neq n'} V_n|n'\rangle + \tfrac{1}{2}\langle n''|V_a + \sum_{n\neq n''} V_n|n''\rangle$$

$$-\tfrac{1}{2}\langle n''|\,V_a+\sum_{n\neq n'}V_n\,|n'\rangle-\tfrac{1}{2}\langle n'|\,V_a+\sum_{n\neq n''}V_n|n''\rangle\,. \tag{16}$$

These energies are analogous to the terms that arise in the hydrogen-molecule problem. The first term is just the energy of the atomic p state without crystal-field interactions. Crystal-field effects on the atomic p states of the fluorines are expressed in the second and third terms. Finally, the last two terms represent the resonance energy reduction arising from covalent interaction between ions. If the ions are in the cubic configuration then the energy $E_{n'n''}$ has the same value E_F^0 for all fluorine pairs. When distortions of the Γ_{4a}^- type are present, expansion (12) can be used.

$$\begin{aligned}E_{n'n''}=E_F^0&+\tfrac{1}{2}\left\langle n'\left|\frac{\partial V_a}{\partial Q_a^-}+\sum_{n\neq n'}\frac{\partial V_n}{\partial Q_a^-}\right|n'\right\rangle Q_a^-\\&+\tfrac{1}{2}\left\langle n''\left|\frac{\partial V_a}{\partial Q_a^-}+\sum_{n\neq n''}\frac{\partial V_n}{\partial Q_a^-}\right|n''\right\rangle Q_a^- -\tfrac{1}{2}\left\langle n''\left|\frac{\partial V_a}{\partial Q_a^-}\right.\right.\\&\left.\left.+\sum_{n\neq n'}\frac{\partial V_n}{\partial Q_a^-}\right|n'\right\rangle Q_a^- -\tfrac{1}{2}\left\langle n'\left|\frac{\partial V_a}{\partial Q_a^-}+\sum_{n\neq n''}\frac{\partial V_n}{\partial Q_a^-}\right|n''\right\rangle Q_a^-\,.\end{aligned} \tag{17}$$

Symmetry can be used to simplify the matrix elements. For a Γ_4^- distortion atoms 1 to 4 (see Fig. 4) experience identical changes in the crystal field while atoms 5 through 8 have the opposite sign but the same magnitude for the change.

$$\begin{aligned}&\left\langle n'\left|\frac{\partial V_a}{\partial Q_a^-}+\sum_{n\neq n'}\frac{\partial V_n}{\partial Q_a^-}\right|n'\right\rangle=-A\quad\text{for } n'=1\text{ to }4,\\&\left\langle n'\left|\frac{\partial V_a}{\partial Q_a^-}+\sum_{n\neq n'}\frac{\partial V_n}{\partial Q_a^-}\right|n'\right\rangle=+A\quad\text{for } n'=5\text{ to }8.\end{aligned} \tag{18}$$

Similar relations may be set down for distortions in the y and z directions. Also the following relationships hold for the energies derived from the resonance integrals:

$$\begin{aligned}&\tfrac{1}{2}\left[\left\langle n''\left|\frac{\partial V_a}{\partial Q_a^-}+\sum_{n\neq n'}\frac{\partial V_n}{\partial Q_a^-}\right|n'\right\rangle\right.\\&\qquad\left.+\left\langle n'\left|\frac{\partial V_a}{\partial Q_a^-}+\sum_{n\neq n''}\frac{\partial V_n}{\partial Q_a^-}\right|n''\right\rangle\right]\\&\qquad=-B\text{ for } n',\ n''=1,\ 4;\ 1,\ 2;\ 2,\ 3;\text{ or }3,\ 4\\&\qquad\cong 0\text{ for } n',\ n''=1,\ 6;\ 2,\ 7;\ 3,\ 8;\text{ or }4,\ 5\\&\qquad=+B\text{ for } n',\ n''=5,\ 6;\ 6,\ 7;\ 7,\ 8;\text{ or }5,\ 8.\end{aligned} \tag{19}$$

Again similar expressions may be written for distortions in the y and z directions.

By using these relationships to calculate couplings between the fluorine hole states one finds that a Γ_4^- distortion in a $\langle 110\rangle$ direction gives the maximum lowering of the energy. For a distortion in a $\langle 110\rangle$ direction a 5×5 secular equation must be solved to find the lowest energy level. This calculation is best accomplished by classifying the wave functions according to representations of C_{2v}. The energy lowerings associated with the different directions of distortion are

$$\begin{aligned}&E^-\langle 110\rangle=-\sqrt{2}\,(A-B)\,Q^-\,,\\&E^-\langle 100\rangle=-(A-B)\,Q^-\,,\\&E^-\langle 111\rangle=-(2/\sqrt{3})(A-B)\,Q^-\,,\end{aligned} \tag{20}$$

where Q^- is the magnitude of the Γ_4^- distortion. The wave function of the fluorine state of lowest energy may be expressed as a linear combination of the wave functions in cubic symmetry. Such a wave function is simply a hole shared by a pair of fluorines labeled by n and n'.

$$\begin{aligned}|\,\Gamma_{4b}\rangle\cong|\,nn'\rangle&=(1/2\sqrt{3})|\,\Gamma_2^-\rangle+(1/\sqrt{6})|\,\Gamma_{3a}^-\rangle\\&+\tfrac{1}{2}|\,\Gamma_{4c}^-\rangle+(1/2\sqrt{2})[\,|\Gamma_{5a}^+\rangle+|\,\Gamma_{5b}^+\rangle+|\,\Gamma_{4a}^+\rangle-|\,\Gamma_{4b}^+\rangle\,].\end{aligned} \tag{21}$$

If "tunneling" coupling is introduced this ground state will be modified by coupling to other Γ_4 states with a corresponding perturbation on the energy.

It is quite simple to include the effect of the second Γ_4^- mode of distortion since the linear JT term will have the same form as given in Eq. (20). We will label this second mode or π mode with a subscript β and the first mode with the subscript α. As seen in Fig. 5 the ions move in $\langle 112\rangle$ directions for the β mode. The extension of Eq. (20) can then be written immediately.

$$\begin{aligned}&E^-\langle 110\rangle=-\sqrt{2}\,(A-B)\,Q_\alpha^- -\sqrt{2}(A'-B')\,Q_\beta^-,\\&E^-\langle 100\rangle=-(A-B)Q_\alpha^- -(A'-B')\,Q_\beta^-,\\&E^-\langle 111\rangle=-(2/\sqrt{3})\,(A-B)\,Q_\alpha^- -(2/\sqrt{3})(A'-B')\,Q_\beta^-.\end{aligned} \tag{22}$$

As before, a maximum reduction in the energy is obtained for a distortion in a $\langle 110\rangle$ direction. The wave function on the fluorines having the lowest energy will remain as in Eq. (21).

F. Γ_5^+ Mode of Distortion

Earlier, we pointed out that the Γ_5^+ mode of distortion will produce a trigonal static distortion when acting separately. In our experiment, we believe that the odd Γ_4^- modes dominate but the Γ_5^+ mode can still have an effect as determined by perturbation theory. Figure 4 shows the Γ_5^+ mode when the distortion is in the z direction. The linear JT term can be written as

$$H_5^+=\frac{\partial V}{\partial Q_a^+}\Big|_0 Q_a^+ +\frac{\partial V}{\partial Q_b^+}\Big|_0 Q_b^+ +\frac{\partial V}{\partial Q_c^+}\Big|_0 Q_c^+\,, \tag{23}$$

where Q_a^+, Q_b^+, and Q_c^+ are the normal coordinates for distortions in the x, y, and z directions. As before, the derivatives are evaluated at the position of full cubic symmetry. In Sec. II G, we will include the first-order effect of the Γ_5^+ mode on the energy of the central ion. The linear change in the energy for different directions of distortion is as follows:

$$E^+\langle 110\rangle = -V_+ Q_+ , \quad E^+\langle 100\rangle = -V_+ Q_+ , \quad E^+\langle 111\rangle = -(2V_+/\sqrt{3})\, Q_+ , \tag{24}$$

where $V_+ = \langle \Gamma_{4a}^+ \,|\, \partial V/\partial Q_c^+ |_0 |\, \Gamma_{4b}^+\rangle$, and Q_+ is the amplitude of the distortion.

G. Effect on Central-Ion Wave Function

Matrix elements of the Γ_4^- distortion vanish within the Γ_5^+ ground-state manifold of the central ion. Covalent coupling of the wave function of the central ion to the hole states of the surrounding fluorines allows the Γ_4^- distortion to occur with an associated lowering of the energy. We also include the first-order correction arising from the Γ_5^+ mode of distortion.

When the framework of fluorine ions is in the distorted configuration of minimum energy, the symmetry is C_{2v} with the lowest-energy hole state on the fluorines belonging to the Γ_{4b} representation. For the central ion, the wave function $[|\Gamma_{5a}^+\rangle + |\Gamma_{5b}^+\rangle]/\sqrt{2}$ of O_h also transforms according to the Γ_{4a} representation of C_{2v}. Perturbation theory may be applied to the system in this symmetry C_{2v} to obtain the following result for the energy and wave function. The first-order effect of the Γ_5^+ mode of distortion has been included in the expression for the energy.

$$|\Gamma_4\rangle = |\Gamma_{4a}\rangle + \frac{\langle \Gamma_{4b} | H_0 + \partial V/\partial Q_\alpha^- |_0 Q_\alpha^- + \partial V/\partial Q_\beta^- |_0 Q_\beta^- | \Gamma_{4a}\rangle | \Gamma_{4b}\rangle}{E_0(\Gamma_{4a}) - E_F^0 + \sqrt{2}(A-B)(Q_\alpha^-) + \sqrt{2}(A'-B')(Q_\beta^-) - \frac{1}{2}k_F[(Q_\alpha^-)^2 + (Q_\beta^-)^2]}, \tag{25a}$$

$$E(\Gamma_4) = E_0(\Gamma_{4a}) - V_+Q_+ + \tfrac{1}{2}k_+Q_+^2 + \tfrac{1}{2}k_\alpha (Q_\alpha^-)^2 + \tfrac{1}{2}k_\beta (Q_\beta^-)^2$$

$$+ \frac{|\langle \Gamma_{4a} | H_0 + \partial V/\partial Q_\alpha^- |_0 Q_\alpha^- + \partial V/\partial Q_\beta^- |_0 Q_\beta^- | \Gamma_{4b}\rangle|^2}{E_0(\Gamma_{4a}) - E_F^0 + \sqrt{2}(A-B)\, Q_\alpha^- + \sqrt{2}(A'-B')\, Q_\beta^- - \frac{1}{2}k_F[(Q_\alpha^-)^2 + (Q_\beta^-)^2]}, \tag{25b}$$

$$H_0 = p^2/2m + V_0 . \tag{25c}$$

In this expression $|\Gamma_{4b}\rangle$ has the form expressed in Eq. (21) and $|\Gamma_{4a}\rangle$ may be obtained from Eq. (4). For the cubic configuration the Hamiltonian is H_0 and $E_0(\Gamma_{4a})$ is the energy of the central ion in the absence of covalent coupling to the fluorines. Various force constants such as k_α, k_β, k_F, and k_+ determine the elastic energies.

$$k_\alpha = \left\langle \Gamma_{4a} \left| \frac{\partial^2 V}{\partial Q_\alpha^{-2}} \right|_0 \right| \Gamma_{4a} \Big\rangle ; \quad k_\beta = \left\langle \Gamma_{4a} \left| \frac{\partial^2 V}{\partial Q_\beta^{-2}} \right|_0 \right| \Gamma_{4a} \Big\rangle ,$$

$$k_F = \left\langle \Gamma_{4b} \left| \frac{\partial^2 V}{\partial Q_\alpha^{-2}} \right|_0 \right| \Gamma_{4b} \Big\rangle = \left\langle \Gamma_{4b} \left| \frac{\partial^2 V}{\partial Q_\beta^{-2}} \right|_0 \right| \Gamma_{4b} \Big\rangle , \tag{26}$$

$$k_+ = \left\langle \Gamma_{4a} \left| \frac{\partial^2 V}{\partial Q_+^2} \right|_0 \right| \Gamma_{4a} \Big\rangle .$$

In Eq. (25b), we have used an elastic potential energy with spherical symmetry to represent the elastic interaction between fluorine ions. The terms involving k_α and k_β determine the elastic energy between the silver ion and the fluorines.

Other Γ_4 states on the fluorines are much higher in energy and will not couple very strongly to the $|\Gamma_{4a}\rangle$ state of the central ion because of the large energy denominators and the small overlap of the wave functions. Nevertheless this coupling does give rise to the hyperfine coupling to four extra fluorines as observed in our experiment. In writing down Eq. (25b) we have assumed that the off-diagonal matrix elements of the elastic term in the Hamiltonian are negligible. Let us now assume that $E_F^0 - E_0(\Gamma_{4a}) \gg \sqrt{2}(A-B)(Q_\alpha^- + Q_\beta^-)$ so that the energy denominator in Eq. (25b) may be expanded and only linear terms need to be retained.

$$E(\Gamma_4) \cong E_0(\Gamma_{4a}) - \gamma^2/[E_F^0 - E_0(\Gamma_{4a})] - V_+Q_+ + \tfrac{1}{2}k_+Q_+^2$$

$$- V_\alpha^- Q_\alpha^- - V_\beta^- Q_\beta^- + \tfrac{1}{2}k_\alpha (Q_\alpha^-)^2 + \tfrac{1}{2}k_\beta (Q_\beta^-)^2$$

$$+ \tfrac{1}{2}k_F' [(Q_\alpha^-)^2 + (Q_\beta^-)^2], \tag{27}$$

where $k_F' = \gamma^2 k_F/[E_F^0 - E_0(\Gamma_{4a})]^2$,

$$V_\alpha^- = \frac{\sqrt{2}(A-B)\gamma^2}{[E_F^0 - E_0(\Gamma_{4a})]^2} + \frac{2\gamma C_\alpha}{E_F^0 - E_0(\Gamma_{4a})},$$

$$V_\beta^- = \frac{\sqrt{2}(A'-B')\gamma^2}{[E_F^0 - E_0(\Gamma_{4a})]^2} + \frac{2\gamma C_\beta}{E_F^0 - E_0(\Gamma_{4a})},$$

$$\gamma = \langle \Gamma_{4a} | H_0 | \Gamma_{4b}\rangle , \quad C_\alpha = \left\langle \Gamma_{4a} \left| \frac{\partial V}{\partial Q_\alpha^-} \right|_0 \right| \Gamma_{4b} \Big\rangle ,$$

$$C_\beta = \left\langle \Gamma_{4a} \left| \frac{\partial V}{\partial Q_\beta^-} \right|_0 \right| \Gamma_{4b} \Big\rangle .$$

The first two terms on the right side of Eq. (27) represent the energy of the triplet state before the distortion occurs while the remaining terms determine the effect of the JT distortions. From considerations of overlap we expect C_α to be positive and C_β to be negative so the two terms in V_β^- are of opposite sign.

Now we can minimize the energy with respect to variations in Q_α^-, Q_β^-, and Q_+ and find the following expressions for the energy and the magnitudes of the static distortions:

$$E(\Gamma_4) \cong E_0(\Gamma_{4a}) - \frac{\gamma^2}{E_F^0 - E_0(\Gamma_{4a})} - \frac{V_+^2}{2k_+} - \frac{1}{2}\frac{(V_\alpha^-)^2}{k_\alpha + k_F'} - \frac{1}{2}\frac{(V_\beta^-)^2}{k_\beta + k_F'} , \tag{28a}$$

$$Q_{+0} = V_+/k_+ , \tag{28b}$$

$$Q_{\alpha 0}^- = V_\alpha^-/(k_\alpha + k_F') , \tag{28c}$$

$$Q_{\beta 0}^- = V_\beta^-/(k_\beta + k_F') . \tag{28d}$$

The ground-state wave function may be found by using these values of the static distortions in Eq. (25a). For this ground-state wave function we have primarily a hyperfine coupling to a pair of equivalent fluorines as observed in the experiment. Futhermore, the interaction with four additional fluorines could be included by taking account of the coupling to fluorine states of higher energy. Perhaps this is one of the stronger arguments for our model.

It is interesting to compare with the reduction in energy obtained when the Γ_5^+ mode of distortion acts alone. When the even mode of distortion acts alone the third equation of (24) holds and together with the elastic term lowers the energy by $\frac{2}{3} V_+^2/k_+$. In comparing this energy with the JT energy in Eq. (28a) we see that the odd mode dominates when the following inequality holds:

$$\frac{1}{2}\frac{(V_\alpha^-)^2}{k_\alpha + k_F'} + \frac{1}{2}\frac{(V_\beta^-)^2}{k_\beta + k_F'} > \frac{1}{6}\frac{V_+{}^2}{k_+} . \tag{29}$$

The term on the right-hand side is just $\frac{1}{4}$ of the JT energy for a trigonal distortion.

III. DISCUSSION

Let us now examine the JT distortions under various assumptions. First of all, the force constant k_β can be quite small because the fluorine ions are moving perpendicular to the lines joining the silver and fluorine ions. Little change in overlap will result so the repulsive potential should be fairly weak. It may also be true that both k_α and k_β are weak because of the nature of the repulsive potential. The repulsive potential becomes important when the electron clouds of ions begin to overlap and some electrons must be promoted into excited states. For ions with saturated shells the excited states are very high in energy thereby making the repulsive potential very strong. On the other hand, for the silver ion the electrons can transfer into the vacant triplet state of the central ion. For the Γ_{4a} orbital the lobes of the hole distribution point exactly toward the fluorine ion so the fluorine can move in considerably before repulsion becomes strong. On these admittedly shaky grounds we assume that k_α and k_β are of the order of k_F' and perhaps smaller. A third possible reason for the repulsive force being weak might be the smaller ionic size of the silver ion. Our estimates indicate however that the ionic radius of the divalent silver ion is comparable to that of the calcium ion.

In order to sort out the possible strength of different energy terms let us assume that k_F' is the approximate elastic constant and that C_α and C_β are negligible. The resulting JT energy has a value of $[(A-B)^2 + (A'-B')^2]\gamma^2/[E_F^0 - E_0(\Gamma_{4a})]^2$ which is related to the JT energy of the V_k center in CaF_2. From our EPR experiment we found the probability density on the fluorines to be 0.09. The factor $\gamma^2/[E_F^0 - E_0(\Gamma_{4a})]^2$ should also have approximately the value of 0.09 since the hole distribution on the fluorines is simply sloshed to one side by the distortion. As a result, the JT energy should be about 0.09 the value found for the V_k center. Hayes and Twidell[10] found the ${}^2\Sigma_u^+ \leftrightarrow {}^2\Sigma_g^+$ transition to be at 3500 Å or approximately 30 000 cm^{-1}. In the JT distortion, the σ_g state goes up as fast as the σ_u state goes down in energy so we expect the JT energy to be approximately one-half of the optical splitting or 15 000 cm^{-1}. From this estimate the contribution to the JT energy of the silver ion would be about 1400 cm^{-1}.

Of course, non-negligible values of k_α and k_β will reduce this estimate but this calculation does point out the importance of this term. In addition the energy can be lowered further when C_α becomes appreciable. We should point out that the energy associated with C_α cannot be as large as the splitting between bonding and antibonding fluorine states for this would cause the fluorine hyperfine interactions to depart from the axial symmetry observed in our experiments. Finally, the even mode of distortion can contribute substantially to the lowering of the energy even though the mode does not dominate. For a static JT distortion to occur it is only necessary that the JT energy be quite a bit larger than the energies of the optical branches of the lattice vibrations. In CaF_2 these energies are approximately 300 cm^{-1} so it becomes reasonable that the JT energy can exceed this value.

IV. EFFECTS OF STRESS

A uniaxial stress in a ⟨001⟩ direction will lower the energies of some of the vibronic states while others go higher in energy. For CaF_2: Ag^{2+} with a uniaxial stress along a ⟨001⟩ direction the strain Hamiltonian may be represented by

$$H_s = \frac{\partial V}{\partial e_\theta}\, e_\theta \ , \tag{30}$$

where $e_\theta = e_3 - \frac{1}{2}(e_1 + e_2)$ is defined in terms of the usual strains e_1, e_2, and e_3. The stress T_j is related to the strain by the familiar formula

$$e_i = \sum_{j=1}^{6} S_{ij}\, T_j \, . \tag{31}$$

For CaF_2, $S_{11} = 0.71 \times 10^{-12}$ cm^2/dyn and $S_{12} = -0.166 \times 10^{-12}$ cm^2/dyn.[17] Consequently, for $T_3 \neq 0$ and $T_1 = T_2 = 0$,

$$e_\theta = 0.876 \times 10^{-12}\, T_3 \ , \quad e_3 = 0.710 \times 10^{-12}\, T_3, \\ e_1 = -0.166 \times 10^{-12}\, T_3. \tag{32}$$

Changes of energy resulting from strain may arise from changes in either the crystal field or the resonance energies of covalent bonding. The strain e_θ causes the fluorine ions to move in $\langle 112 \rangle$ directions which is precisely the direction of motion of the fluorine ions for the Q_β^- mode. On the other hand, the e_θ strain does not directly involve a motion of the Ag^{2+} ion but only indirectly in that the Ag^{2+} ion may adjust its position so as to maintain the center of gravity. For the case of the heavy silver ion the shift of the silver ion will not be as great as the shift of the fluorines. With this in mind we approximately have a proportionality between Q_β^- and e_θ and the linear term in the JT energy will also determine the energy splittings produced by strain. The proportionality would be exact if C_β were equal to zero. In the limit where the part of the wave function on the fluorines is localized to a pair of fluorines, we can write the following relationship between Q_β^- and e_θ:

$$Q_{\beta\parallel}^- = (1/\sqrt{6})\, a e_\theta \, . \tag{33}$$

This relationship holds when the axis of the fluorine pair is parallel to T_3. The spacing a between the pair of fluorines has the value of 2.73 Å in the CaF_2 lattice. For T_3 perpendicular to the axis of the fluorine pair a different relationship holds between Q_β^- and e_θ:

$$Q_{\beta\perp}^- = -\,(1/2\sqrt{6})\, a e_\theta \, . \tag{34}$$

From these relations we can calculate the energy changes for T_3 parallel or perpendicular to the axis of the fluorine pairs.

$$\Delta E_\parallel = -V_\beta^- Q_{\beta\parallel}^- = -\,(V_\beta^- a/\sqrt{6})\, e_\theta \, , \quad T_3 \parallel \hat{n} \\ \Delta E_\perp = -V_\beta^-\, Q_{\beta\perp}^- = +\,(V_\beta^- a/2\sqrt{6})\, e_\theta \, , \quad T_3 \perp \hat{n} \tag{35}$$

where $\hat{n}$ gives the direction of the axis of a fluorine pair. From these expressions we can determine the energy splitting ΔE between the different vibronic states and estimate some parameters from experiment.

$$\Delta E = \Delta E_\parallel - \Delta E_\perp = -\,(3/2\sqrt{6})\, a V_\beta^-\, e_\theta \ , \\ \text{or} \quad \Delta E = -\,(3/2\sqrt{6})\,(S_{11} - S_{12})\, a V_\beta^-\, T_3 \, . \tag{36}$$

Again we should remind ourselves that this is only an approximate expression because we have neglected the motion of the silver ion in arriving at this result. Nevertheless, the result provides us with an estimate of V_β^- when we compare with the experimental stress measurements. The initial slope of the experimental ΔE-versus-T_3 plot is 315 cm^2 sec^{-1} dyn^{-1}. From this slope we estimate the value of V_β^- to be 1.4×10^{-4} erg/cm or 0.89×10^8 eV/cm. If we take the value of k_F to be 3.9×10^4 erg/cm^2 as can be calculated from the parameters of Ganesan and Srinivasan,[18] we can then estimate the JT energy of the Q_β^- mode to be 1.5 eV. In making this estimate we have assumed k_β to be zero. If we cannot make this assumption then we must calculate the JT energy as $(V_\beta^-)^2 / 2(k_\alpha + k_F')$ and our estimate will be reduced accordingly. Our estimates again show that the JT energy is sufficient to produce a static distortion.

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Zeeman Splitting between Nondegenerate Crystalline Stark Levels of Tm^3 $(4f^{12})$ in Monoclinic Single Crystals*

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Optical Zeeman absorption and electron-paramagnetic-resonance experiments reveal that the ground crystalline Stark levels of Tm^{3+} in $YCl_3 \cdot 6H_2O$ and $TmCl_3 \cdot 6H_2O$ and Tm^{3+} in $Y_2(SO_4)_3 \cdot 8H_2O$ and $Tm_2(SO_4)_3 \cdot 8H_2O$ are nearly accidentally degenerate. Extrapolation of the data to zero magnetic field gives the lowest Stark levels of the $^3H_6$ state of Tm^{3+} as 0 and 1.12 cm^{-1} for the chloride salts; 0 and 0.61 cm^{-1} for the sulfate salts. It is also found from the EPR data that the sulfate has two magnetically inequivalent lattice sites.

INTRODUCTION

Recent experiments and the subsequent interpretation of the pseudoquadrupole shift of recoilless nuclear-resonance spectra of tripositive thulium-169 in crystals of low cation-site symmetry by Clauser and Mössbauer[1] have suggested that one or more electronic crystalline Stark levels of Tm^{3+} may be nearly accidentally degenerate with the ground Stark level. A crystal field splitting calculation by Harrop[2] also predicts that the two lowest crystalline Stark levels of the $^3H_6$ ground state of Tm^{3+} in $TmCl_3 \cdot 6H_2O$ are nearly accidentally degenerate. Previously unpublished optical Zeeman spectra[3] of thulium in various salts have led us to the same conclusion. We wish to report here the results and interpretation of the electron-paramagnetic-resonance spectra together with the optical Zeeman spectra of Tm^{3+} in $YCl_3 \cdot 6H_2O$ and $TmCl_3 \cdot 6H_2O$ and Tm^{3+} in $Y_2(SO_4)_3 \cdot 8H_2O$ and $Tm_2(SO_4)_3 \cdot 8H_2O$ which confirm the supposition of a near accidental degeneracy in the ground state of Tm^{3+} in these salts. We also wish to report the zero magnetic field splitting of the nearly degenerate ground Stark levels for Tm^{3+} in these salts deduced from the EPR and optical Zeeman data.

OPTICAL ABSORPTION STUDIES

Absorption spectra of the hydrated chloride and sulfate single crystals have been taken between 2500 and 8000 Å at liquid-nitrogen temperature and from zero magnetic field to nearly 24 kG in regular intervals and for specific crystal orientations. The spectrometer used was a 3.4-m Jarrel-Ash Ebert scanning spectrometer/spectrograph with a resolution of 0.07 Å in first order in the region of 5000 Å. An L-96 Magnion magnet with a power supply stable to 0.1% was used for the Zeeman studies. The magnetic field strength was measured with a Rawson rotating coil accurate to 0.1%.

The cation point-group symmetry of Tm^{3+} in the hydrated chloride and sulfate salts is reported as C_2 and m, respectively.[4,5] Both crystals have monoclinic unit-cell symmetry.[6,7] For a non-Kramer's