

Strain-Induced Zero-Field Splitting of d^3 and d^8 Ions in Cubic Crystals

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The zero-field splitting of ions with d^3 and d^8 electron configurations is calculated by the perturbation theory. We consider the ionic and covalent contributions and that of anisotropic spin-spin coupling due to covalency effects. For comparison with experiment, the numerical values for V^{2+} , Cr^{3+} , and Ni^{2+} ions in uniaxially stressed MgO crystals are estimated.

1. INTRODUCTION

RECENTLY, the effect of uniaxial stress on the ground state of iron-group ions was investigated by the EPR method.^{1,2,3} The parameter measured on ions with spin greater than $\frac{1}{2}$ is the zero-field splitting induced by uniaxial stress applied in different directions with respect to the cubic axes of the crystal. This problem was treated theoretically within the framework of point-charge model in the case of d^5 ions, e.g., Mn^{2+} .⁴ It is the purpose of this paper to discuss the origins of the zero-field splitting of d^3 and d^8 ions in tetragonal and trigonal fields. A uniaxially stressed cubic crystal seems to us to be very attractive as a model for this discussion. It has several advantages: (1) The crystal field acting on the transition-metal ion has an inversion symmetry. This is not true, for example, in ruby, for which nevertheless many theoretical treatments exist. The deviation of the metal ion from the center of symmetry would involve complications in the calculation, and therefore it is usually neglected, though it might have a great effect on the zero-field splitting. (2) The effect of the trigonal, as well as of the tetragonal, distortion of the octahedron can be investigated on the same crystal. (3) The strain-induced crystal field is very small in comparison with other terms in the Hamiltonian; consequently, it may be considered as a perturbation without making any obvious mistake. (4) The induced dipole moments of the oxygen ions are zero because of the inversion symmetry of crystal field.⁵ It was shown that in corundum,⁶ the induced dipole moments of the oxygens may have a considerable effect on the resulting crystal field.

The calculation of zero-field splitting has been performed in the strong-field coupling scheme for the trigonal and for the tetragonal crystal field. The main mechanism leading to this splitting is a simultaneous

action of low-symmetry crystal field and spin-orbit coupling. The calculation is performed by a method of perturbation theory up to the third order. In the case of a tetragonal field, only diagonal matrix elements of the crystal-field operator within the manifold of excited T_2 states lead to the zero-field splitting, according to Pryce's mechanism.⁷ In the case of a trigonal field, there are also nondiagonal loops arising from the nonzero matrix element of trigonal field between the ground state 4A_2 and the excited state 4T_1 , leading also to a third-order zero-field splitting. All these third-order contributions to the zero-field splitting were calculated by perturbation theory. The value of zero-field splitting was parametrized by the well-known four reduced elements of trigonal and tetragonal field: the one-electron matrix elements between the $3e$ and $3t_2$ orbitals of the transition-metal ion. This facilitates comparison of the present results with optical measurements of the excited-state splittings.^{8,9}

Three contributions to the zero-field splitting were considered in the calculation: ionic and covalent contributions, and an effect of the anisotropy of spin-spin coupling due to the covalency effects in the distorted octahedron. All these contributions to the zero-field splitting were calculated by perturbation theory. Numerical values were estimated for V^{2+} , Cr^{3+} , and Ni^{2+} ions in stressed MgO crystals, and compared with the experimental values.

2. AXIAL-FIELD SPLITTING OF $d^3(t_2^3) ^4A_2$ STATE

The zero-field splitting induced by the uniaxial stress applied in an arbitrary direction with respect to the crystal cubic axes may be expressed by two parameters called strain coefficients.² To find the values of both these strain coefficients, it is advantageous to apply the uniaxial stress in two specific directions: that of the tetragonal and that of the trigonal axis. Then the crystal field acting on the paramagnetic ion in crystal is of axial symmetry.

The Hamiltonian of paramagnetic ion in axially deformed crystalline surrounding is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{so} + \mathcal{H}_{ss} + V_{axial}, \quad (1)$$

⁷ M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

⁸ A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. **122**, 1469 (1961).

⁹ M. D. Sturge, Phys. Rev. **131**, 1456 (1963).

¹ G. D. Watkins and Elsa Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).

² Elsa Feher, Phys. Rev. **136**, A145 (1964).

³ Elsa Feher, Bull. Am. Phys. Soc. **10**, 699 (1965).

⁴ M. Blume and R. Orbach, Phys. Rev. **127**, 1587 (1962).

⁵ This is not true when an ion with different charge substitutes the lattice ion, as e.g., a Cr^{3+} ion in MgO. Then the extra positive charge of the Cr^{3+} as compared to the Mg^{2+} induces dipole moments on the surrounding oxygen ions. Nevertheless, the extra charge of the Cr^{3+} is reduced, and the effect of induced dipole moments on the zero-field splitting is supposed to be small, since the covalency of the trivalent ion is greater than that of the divalent ion.

⁶ R. R. Sharma and T. P. Das, J. Chem. Phys. **41**, 3581 (1964).

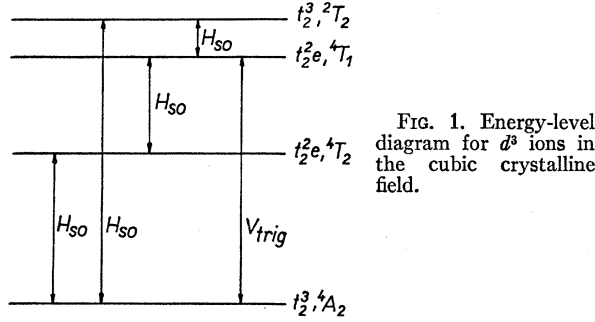


FIG. 1. Energy-level diagram for d^3 ions in the cubic crystalline field.

where \mathcal{H}_0 represents the Hamiltonian of the ion in cubic crystalline field. \mathcal{H}_{so} is the spin-orbit coupling

$$\mathcal{H}_{so} = \sum_i \zeta(\bar{r}_i) \bar{l}_i \cdot \bar{s}_i. \quad (2)$$

The third term on the right of Eq. (1) is the spin-spin interaction:

$$\mathcal{H}_{ss} = g^2 \beta^2 \sum_{i \neq j} \left\{ \frac{\bar{s}_i \cdot \bar{s}_j}{r_{ij}^3} - 3 \frac{(\bar{s}_i \cdot \bar{r}_{ij})(\bar{s}_j \cdot \bar{r}_{ij})}{r_{ij}^5} \right\}, \quad (3)$$

where g and β are the g factor and the Bohr magneton, respectively. The term V_{axial} in (1) is the axial-symmetry component of the crystal field.

Low-energy states of the d^3 configuration in a cubic crystal field (the eigenstates of the Hamiltonian \mathcal{H}_0) necessary for the calculation are given in Fig. 1 in the strong-field coupling scheme. The ground state $t_2^3, ^4A_2$ is an orbital singlet. The crystal field, being an operator that acts only on orbital wave functions, cannot itself split the spin degeneracy of the ground state; thus the use of a spin-orbit coupling operator is necessary. For reasons of symmetry, the \mathcal{H}_{so} operator is able to mix only 4T_2 or 2T_2 excited states into the 4A_2 ground state. However, the matrix elements between the $t_2^3, ^4A_2$ ground state and $t_2^2e, ^2T_2$ excited state are zero, and only $t_2^2e, ^4T_2$ and $t_2^3, ^2T_2$ excited states are mixed into the ground state by spin-orbit coupling. Then the ground state is split by the complex action of \mathcal{H}_{so} and V_{axial} . The splitting may be calculated by perturbation theory, since the necessary condition $\mathcal{H}_{so} + V_{axial} \ll \mathcal{H}_0$ is fulfilled. The lowest order of the nonvanishing splitting of the ground state is the third order. In these third-order terms the matrix elements of \mathcal{H}_{so} are to be used twice, since only the terms proportional to the square of spin components may cause zero-field splitting, on account of the time-inversion symmetry of the Hamiltonian (1).

As pointed above, there are two directions of uniaxial stress (the direction of the tetragonal axis and of the trigonal axis) when the final crystal field is of axial symmetry. Both these cases demand a special process of calculation. We shall therefore treat the two cases separately.

Tetragonal Field (V_{tetr})

A tetragonal field having the transformation properties of the E representation of the cubic group does not

mix any of the existing excited states into the 4A_2 ground state. Thus only the diagonal matrix elements of V_{tetr} within the excited states $t_2^2e, ^4T_2$ and/or $t_2^3, ^2T_2$ take part in the third-order splitting. However, the matrix elements of V_{tetr} within the $t_2^3, ^2T_2$ states are zero. This means that only one loop exists that leads to the third-order zero-field splitting by the tetragonal field

$$\mathcal{H}_{so} \quad V_{tetr} \quad \mathcal{H}_{so} \\ t_2^3, ^4A_2 \longrightarrow t_2^2e, ^4T_2 \longrightarrow t_2^2e, ^4T_2 \longrightarrow t_2^3, ^4A_2. \quad (4)$$

The zero-field splitting is equal to $2D$, where D is the coefficient at the term $(S_x^2 - \frac{1}{3}S^2)$ in the spin Hamiltonian of the ground state. After using the loop (4), the D parameter in the case of tetragonal field is calculated:

$$D_{tetr} = \frac{4}{9} \{ \zeta^2 / [E(t_2^2e, ^4T_2)]^2 \} (\frac{3}{4}u - u'), \quad (5)$$

where $E(t_2^2e, ^4T_2)$ is the energy of the excited state, the ground state having zero energy; and u and u' are one-electron tetragonal field parameters defined as follows:

$$u = \langle e\epsilon | V_{tetr} | e\epsilon \rangle - \langle e\delta | V_{tetr} | e\delta \rangle, \quad (6)$$

$$u' = \langle t_2\xi | V_{tetr} | t_2\xi \rangle - \langle t_2\eta | V_{tetr} | t_2\eta \rangle, \quad (7)$$

in which $|e\epsilon\rangle, |e\delta\rangle$ and $|t_2\xi\rangle, |t_2\eta\rangle, |t_2\gamma\rangle$ are e and t_2 sets of d orbitals of the paramagnetic ion quantized along the tetragonal axis of the octahedron.¹⁰ The parameters u and u' represent the splitting of e and t_2 orbitals by the tetragonal crystal field.

Trigonal Field (V_{trig})

The trigonal field, transforming as the representation T_2 of the cubic group, gives nonzero matrix elements between the 4A_2 ground state and the 4T_1 excited state. The loop (4) gives, therefore, only one of the third-order contributions to the zero-field splitting in the case of trigonal field. There are some more contributions of loops, as follows:

$$V_{trig} \quad \mathcal{H}_{so} \quad \mathcal{H}_{so} \\ t_2^3, ^4A_2 \longrightarrow t_2^2e, ^4T_1 \longrightarrow t_2^2e, ^4T_2 \longrightarrow t_2^3, ^4A_2, \quad (8)$$

$$V_{trig} \quad \mathcal{H}_{so} \quad \mathcal{H}_{so} \\ t_2^3, ^4A_2 \longrightarrow t_2^2e, ^4T_1 \longrightarrow t_2^3, ^2T_2 \longrightarrow t_2^3, ^4A_2. \quad (9)$$

Having used the loops (8) and (9) and the loop similar to (4) for the trigonal field, we calculate the parameter D in this case:

$$D_{trig} = \zeta^2 \left\{ \frac{2}{9} \frac{v}{[E(t_2^2e, ^4T_2)]^2} - \frac{2\sqrt{2}}{3} \frac{v'}{E(t_2^2e, ^4T_2)E(t_2^2e, ^4T_1)} - \sqrt{2} \frac{v'}{E(t_2^3, ^2T_2)E(t_2^2e, ^4T_1)} \right\}, \quad (10)$$

¹⁰ J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, New York, 1961), p. 226.

where $E(t_2^2e, {}^4T_2)$ and $E(t_2^3, {}^2T_2)$ are the energies of the excited states, the ground state having zero energy; and v and v' are one-electron trigonal field parameters defined as follows:

$$v = \langle t_2 0 | V_{\text{trig}} | t_2 0 \rangle - \langle t_2 \epsilon | V_{\text{trig}} | t_2 \epsilon \rangle, \quad (11)$$

$$v' = \langle t_2 \epsilon | V_{\text{trig}} | e \epsilon \rangle, \quad (12)$$

in which $|t_2 0\rangle$ and $|t_2 \epsilon\rangle$, $|t_2 \epsilon\rangle$ are t_2 orbitals of the paramagnetic ion which span the representations A_1 and E of the trigonal group. They are given by the following relations:

$$\begin{aligned} |t_2 0\rangle &= \frac{1}{\sqrt{3}} \sqrt{3} (|t_2 \xi\rangle + |t_2 \eta\rangle + |t_2 \zeta\rangle), \\ |t_2 \vartheta\rangle &= \frac{1}{\sqrt{6}} \sqrt{6} (2|t_2 \xi\rangle - |t_2 \zeta\rangle - |t_2 \eta\rangle), \\ |t_2 \epsilon\rangle &= \frac{1}{\sqrt{2}} \sqrt{2} (|t_2 \xi\rangle - |t_2 \eta\rangle). \end{aligned} \quad (13)$$

3. AXIAL-FIELD SPLITTING OF $d^8(t_2^6e^2), {}^3A_2$ STATE

The calculation of the zero-field splitting of d^8 ion is essentially the same as in the case of d^3 ion. The Hamiltonian of ion in a distorted crystal field is given in (1). Low energy levels of d^8 ion in a cubic crystal field are plotted in Fig. 2. The ground state $t_2^6e^2, {}^3A_2$ is an orbital singlet. The excited states $t_2^5e^3, {}^3T_2$ and $t_2^5e^3, {}^1T_2$ are mixed into the ground state by the spin-orbit coupling.

Tetragonal Field

As in the preceding section, the tetragonal field does not mix any excited state into the ground state, so that only Pryce's mechanism is effective. The axial-field splitting D of the ground state is equal to

$$D_{\text{tet}} = \zeta^2 \left(\frac{3}{4}u - u' \right) \{ [E(t_2^5e^3, {}^3T_2)]^{-2} - [E(t_2^5e^3, {}^1T_2)]^{-2} \}, \quad (14)$$

where u and u' are the tetragonal-field parameters defined in (6) and (7).

Trigonal Field

The trigonal field gives nonzero matrix elements between the ground state and the $t_2^5e^3, {}^3T_1$ excited state. This means that some other loops leading to the third-order zero-field splitting can be found. There are two loops of that kind:

$$t_2^6e^2, {}^3A_2 \xrightarrow{V_{\text{trig}}} t_2^5e^3, {}^3T_1 \xrightarrow{\mathcal{H}_{\text{SO}}} t_2^5e^3, {}^3T_2 \xrightarrow{\mathcal{H}_{\text{SO}}} t_2^6e^2, {}^3A_2, \quad (15)$$

$$t_2^6e^2, {}^3A_2 \xrightarrow{V_{\text{trig}}} t_2^5e^3, {}^3T_1 \xrightarrow{\mathcal{H}_{\text{SO}}} t_2^5e^3, {}^1T_2 \xrightarrow{\mathcal{H}_{\text{SO}}} t_2^6e^2, {}^3A_2. \quad (16)$$

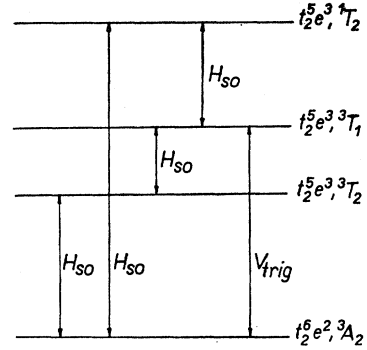


FIG. 2. Energy-level diagram for d^8 ions in the cubic crystalline field.

Summing all contributions, we get the following expression for axial-field splitting D :

$$\begin{aligned} D_{\text{trig}} &= \frac{1}{2} \zeta^2 \{ v / [E(t_2^5e^3, {}^3T_2)]^2 \\ &\quad - 3\sqrt{2} v' / E(t_2^5e^3, {}^3T_2) E(t_2^5e^3, {}^3T_1) \\ &\quad + 3\sqrt{2} v' / E(t_2^5e^3, {}^3T_1) E(t_2^5e^3, {}^1T_2) \\ &\quad - v / [E(t_2^5e^3, {}^1T_2)]^2 \}, \quad (17) \end{aligned}$$

where v and v' are trigonal-field parameters defined in (11) and (12).

4. CONTRIBUTION OF IONIC CRYSTAL FIELD TO THE VALUES OF THE AXIAL-FIELD PARAMETERS

The low-symmetry component of the crystal field in the strain-induced cubic crystals may be conveniently expressed in the form

$$V = \sum_{\Gamma, \gamma} C_{\gamma}(\Gamma) V_{\gamma}(\Gamma) e_{\gamma}(\Gamma), \quad (18)$$

where $e_{\gamma}(\Gamma)$ are the strain-tensor components, having the transformation properties of the γ subvector of Γ cubic-group representation. Only those strain components which have E and T_2 symmetry take part in the case of axial distortions. They may be expressed as linear combinations of the usual six strain components¹¹ in the following way:

$$\begin{aligned} e_{\vartheta}(E) &= 2e_{zz} + e_{xx} + e_{yy}, \\ e_{\epsilon}(E) &= e_{xx} - e_{yy}, \\ e_{\xi}(T_2) &= e_{yz}, \quad e_{\eta}(T_2) = e_{zx}, \quad e_{\zeta}(T_2) = e_{xy}. \end{aligned} \quad (19)$$

$V_{\gamma}(\Gamma)$ in (18) is a function of electron coordinates which has the same transformation properties as $e_{\gamma}(\Gamma)$, and $C_{\gamma}(\Gamma)$ is a constant. If $V_{\gamma}(\Gamma)$ is expanded in a power series in the electron coordinates, it may further be written as

$$C_{\gamma}(\Gamma) V_{\gamma}(\Gamma) = \sum_n C_{n\gamma}(\Gamma) V_{n\gamma}(\Gamma), \quad (20)$$

where $C_{n\gamma}(\Gamma)$ are constants, and $V_{n\gamma}(\Gamma)$ are normalized

¹¹ C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1959), 2nd ed., Chap. 4, p. 86.

cubic harmonics¹² with the T_2 symmetry, multiplied by r^n . When the crystal field is acting on d electrons, n in (20) runs over 2 and 4. The values of the coefficients $C_{n\gamma}(\Gamma)$ can be obtained by using the point-charge model and summing the electrostatic field coming from the positive and negative charges at all the lattice points. Such a calculation had been done by Kanamori¹³ for the MgO crystal, and Schawlow *et al.*⁸ have used it for determining the $C_{n\gamma}(\Gamma)$.

We now use the crystal-field expansion (18) and (19) to determine the axial-field parameters of tetragonal and trigonal field. In the case of tetragonal distortion the only nonvanishing term in (18) is that with the $e_\vartheta(E)$ strain component. For the application of a tetragonal field to $3d$ Hartree-Fock wave functions of the free paramagnetic ion, we get the tetragonal-field parameters defined in (6) and (7) as follows:

$$u_{\text{ion}} = \langle e || V_n(E) || e \rangle C_{n\vartheta}(E) e_\vartheta(E), \quad (21)$$

$$u_{\text{ion}}' = \frac{1}{2}\sqrt{3} \langle t_2 || V_n(E) || t_2 \rangle C_{n\vartheta}(E) e_\vartheta(E). \quad (22)$$

The double-barred matrices¹⁴ have the following values:

$$\begin{aligned} \langle e || V_n(E) || e \rangle &= -2 \langle e\vartheta || V_{n\vartheta}(E) || e\vartheta \rangle \\ &= -(2\sqrt{5})/(7\sqrt{\pi}) \langle r^2 \rangle, \quad \text{for } n=2 \\ &= -(3\sqrt{5})/(7\sqrt{3\pi}) \langle r^4 \rangle, \quad \text{for } n=4, \end{aligned} \quad (23)$$

$$\begin{aligned} \langle t_2 || V_n(E) || t_2 \rangle &= \sqrt{3} \langle t_2\zeta || V_{n\vartheta}(E) || t_2\zeta \rangle \\ &= -(\sqrt{15})/(7\sqrt{\pi}) \langle r^2 \rangle, \quad \text{for } n=2 \\ &= (2\sqrt{5})/(7\sqrt{\pi}) \langle r^4 \rangle, \quad \text{for } n=4, \end{aligned} \quad (24)$$

$$\langle r^n \rangle = \int_0^\infty r^n R_{3d}^2(r) r^2 dr,$$

where $R_{3d}(r)$ is the Hartree-Fock radial wave function of the $3d$ orbital of the paramagnetic ion.

In the case of trigonal distortion, only those strain components with T_2 symmetry are nonzero and they are of equal magnitude. We define the following linear combination of strain components

$$e(T_2) = e_\xi(T_2) + e_\eta(T_2) + e_\zeta(T_2),$$

under the condition

$$e_\xi(T_2) = e_\eta(T_2) = e_\zeta(T_2). \quad (25)$$

Using the crystal field defined in (18) with nonvanishing strain components (25) only and Hartree-Fock solutions for one-electron $3d$ orbitals of the paramagnetic ion, we get the following trigonal-field parameters

according to (11) and (12):

$$v_{\text{ion}} = \sqrt{\frac{3}{2}} \langle t_2 || V_n(T_2) || t_2 \rangle C_n(T_2) e(T_2), \quad (26)$$

$$v_{\text{ion}}' = \sqrt{\frac{1}{2}} \langle t_2 || V_n(T_2) || e \rangle C_n(T_2) e(T_2), \quad (27)$$

where

$$C_n(T_2) = C_{n\xi}(T_2) = C_{n\eta}(T_2) = C_{n\zeta}(T_2),$$

and double-barred matrices¹⁴ have the following values:

$$\begin{aligned} \langle t_2 || V_n(T_2) || t_2 \rangle &= \sqrt{6} \langle t_2\eta || V_{n\xi}(T_2) || t_2\xi \rangle \\ &= (3\sqrt{10})/(14\sqrt{\pi}) \langle r^2 \rangle, \quad \text{for } n=2 \end{aligned} \quad (28)$$

$$= (\sqrt{30})/(7\sqrt{\pi}) \langle r^4 \rangle, \quad \text{for } n=4, \quad (29)$$

$$\begin{aligned} \langle t_2 || V_n(T_2) || e \rangle &= \sqrt{3} \langle t_2\xi || V_{n\xi}(T_2) || e\vartheta \rangle \\ &= -(\sqrt{15})/(7\sqrt{\pi}) \langle r^2 \rangle, \quad \text{for } n=2 \end{aligned} \quad (30)$$

$$= (3\sqrt{5})/(14\sqrt{\pi}) \langle r^4 \rangle, \quad \text{for } n=4. \quad (31)$$

5. COVALENT CONTRIBUTIONS TO THE CRYSTAL-FIELD PARAMETERS

According to the generally accepted mechanism of covalency of the paramagnetic-ion complex, the electron-occupied ligand orbitals are mixed into the $3d$ orbitals of the paramagnetic ion by the one-electron self-consistent Hamiltonian of the complex¹⁵. Then the cubic-field splitting of d orbitals into the sets of e and t_2 orbitals, calculated up to the second order, is given by

$$\Delta_{\text{cov}} = \sum_i E_i^{-1} |\langle e | h | l_i e \rangle|^2 - \sum_k E_k^{-1} |\langle t_2 | h | l_k t_2 \rangle|^2, \quad (32)$$

where h is the one-electron self-consistent Hamiltonian of the complex, and $|l_i e\rangle$ and $|l_k t_2\rangle$ are linear combinations of ligand orbitals having the same transformation properties as the paramagnetic ion orbitals e and t_2 , being orthogonalized to these orbitals. E_i (E_k) is the energy difference between the e (t_2) orbital and the appropriate ligand orbital. Now the e and t_2 states are split by the action of the self-consistent Hamiltonian of the axially distorted octahedral complex. The orbitals of split states span the representations of the tetragonal or trigonal subgroups of the cubic group. In the case of tetragonal distortion, the e orbitals span A_1 and B_1 representations and the t_2 orbitals span

¹² H. A. Bethe, Ann. Physik **3**, 133 (1929).

¹³ J. Kanamori, Progr. Theoret. Phys. (Kyoto) **17**, 197 (1956).

¹⁴ Y. Tanabe and H. Kamimura, J. Phys. Soc. Japan **13**, 394 (1958).

¹⁵ R. G. Shulman and S. Sugano, Phys. Rev. **130**, 506 (1963); K. Knox, R. G. Shulman, and S. Sugano, *ibid.* **130**, 512 (1963); S. Sugano and R. G. Shulman, *ibid.*, **130**, 517 (1963); R. E. Watson and A. J. Freeman, *ibid.*, **134**, A1526 (1964); F. Šimánek and Z. Sroubek, Phys. Status Solidi **4**, 251 (1964).

B_2 and E representations of the tetragonal subgroup. Then the axial-field parameters defined in (6) and (7), up to the second order, are given by

$$u_{\text{cov}} = \sum_i E_i^{-1} |\langle e\epsilon(A_1) | h_{\text{tet}} | l_i(A_1) \rangle|^2 - \sum_k E_k^{-1} |\langle e\vartheta(B_1) | h_{\text{tet}} | l_k(B_1) \rangle|^2, \quad (33)$$

$$u_{\text{cov}}' = \sum_i E_i^{-1} |\langle t_2^* \zeta(B_2) | h_{\text{tet}} | l_i(B_2) \rangle|^2 - \sum_k E_k^{-1} |\langle t_2^* \xi(E) | h_{\text{tet}} | l_i(E) \rangle|^2, \quad (34)$$

where $l_i(\Gamma)$ are linear combinations of ligand orbitals which span the Γ representation of tetragonal subgroup and h_{tet} is self-consistent Hamiltonian of tetragonally distorted octahedral complex.

In the case of trigonal distortion the e orbitals span the E representation and t_2 orbitals span the A_1 and E representations of the trigonal subgroup. Then the trigonal-field parameters defined in (11) and (12) are given by

$$v_{\text{cov}} = \sum_i E_i^{-1} |\langle t_2^0(A_1) | h_{\text{trig}} | l_i(A_1) \rangle|^2 - \sum_k E_k^{-1} |\langle t_2^0(E) | h_{\text{trig}} | l_i(E) \rangle|^2, \quad (35)$$

$$v_{\text{cov}}' = \sum_i E_i^{-1} \langle e\epsilon(E) | h_{\text{trig}} | l_i(E) \rangle \times \langle l_i(E) | h_{\text{trig}} | t_{2g}(E) \rangle. \quad (36)$$

To simplify the expressions for the crystal-field parameters, we introduce the matrix elements of the self-consistent Hamiltonian between the paramagnetic-ion wave functions and wave functions of one ligand ion. These matrix elements we shall call one-bond integrals. In the octahedral complex there are two types of one-bond integrals, that between σ functions and that between π functions. Using the p and s functions of the ligand ion, we have the following three one-bond integrals:

$$\begin{aligned} H_{\sigma^p} &= \langle d\sigma | h | p\sigma \rangle, \\ H_{\sigma^s} &= \langle d\sigma | h | s \rangle, \\ H_{\pi} &= \langle d\pi | h | p\pi \rangle, \end{aligned} \quad (37)$$

where $d\sigma$ and $d\pi$ are the σ and π $3d$ orbitals of the paramagnetic ion, $p\sigma$ and $p\pi$ are the σ and π $2p$ orbitals of the ligand ion, and s is the $2s$ function of the ligand ion. Now the covalent contributions to the crystal-field parameters Δ , u , u' , v , and v' can be written in terms of the one bond-integrals (37). To compute Δ it is possible to neglect the distortion of the complex, giving

$$\Delta_{\text{cov}} = 3 \sum_{i=s,p} (|H_{\sigma^i}|^2/E_{i\sigma}) - 4(|H_{\pi}|^2/E_{\pi}). \quad (38)$$

The u , u' , v , and v' parameters may be calculated from the geometry of the distorted complex. In the case of tetragonal distortion, the distances between paramagnetic ion and ligand ions are changed, and the

angles between bonds are preserved. After the detailed calculation we obtain the following results:

$$u_{\text{cov}} = - \sum (12H_{\sigma^i}/E_{i\sigma}) (dH_{\sigma^i}/de_{zz}) e_{zz}, \quad (39)$$

$$u_{\text{cov}}' = -(12H_{\pi}/E_{\pi}) (dH_{\pi}/de_{zz}) e_{zz}. \quad (40)$$

In the case of the trigonal distortion, the angles between bonds are changed, the distances between ligands and paramagnetic ion being preserved. After the detailed calculation we obtain the following expressions for the trigonal-field parameters:

$$v_{\text{cov}} = (4 |H_{\pi}|^2/E_{\pi}) e_{zz}, \quad (41)$$

$$v_{\text{cov}}' = - \sum_{i=p,s} (3\sqrt{2} |H_{\sigma^i}|^2/E_{i\sigma}) e_{zz}. \quad (42)$$

6. THE CONTRIBUTION OF ANISOTROPIC SPIN-SPIN COUPLING TO THE ZERO-FIELD SPLITTING

The distortions of wave functions by the low-symmetry component of the crystalline field make the spin-spin coupling anisotropic. The more important mechanism that distorts the wave functions is the covalency effect. In order to take account of the effect of this distortion, we adopt the molecular-orbital (MO) model to describe the one-electron d functions. The Hamiltonian of the spin-spin interaction H_{ss} is given in (3). This Hamiltonian can be expanded in a power series in the coordinates of electrons i and j .¹⁶ If we keep only those members which give nonvanishing matrix elements between d -electron wave functions, we can write

$$\begin{aligned} V_{12} &= 8\pi \left[\frac{1}{4} (s_{+i}s_{-j} + s_{-i}s_{+j}) - s_{zi}s_{zj} \right] \\ &\times \{ (1/\sqrt{5}r_{<}^3) Y_0^0(i) Y_2^0(j) \\ &+ (r_{>}^3/r_{<}^5) [\frac{1}{3}\sqrt{3} (Y_2^2(i) Y_4^{-2}(j) + Y_2^{-2}(i) Y_4^2(j)) \\ &+ \sqrt{\frac{3}{5}} (Y_2^1(i) Y_4^{-1}(j) + Y_2^{-1}(i) Y_4^1(j)) \\ &+ \frac{2}{5}\sqrt{5} Y_2^0(i) Y_4^0(j)] \}, \end{aligned} \quad (43)$$

where s_{+i} , s_{-i} are the ladder spin operators of electron i ; $r_{>}$ and $r_{<}$ are the greater and the smaller radius vectors of electrons i and j ; and $Y_l^m(i)$ are spherical harmonics of the coordinates of electron i .

Using the MO approach with linear combinations of atomic orbitals (LCAO), we can write three t_2 antibonding molecular orbitals in the following form:

$$\psi(t_2\alpha) = N_{\alpha} (|t_2\alpha\rangle - \lambda_{i\alpha} |l_2\alpha\rangle), \quad (44)$$

where $|t_2\alpha\rangle$ refer to the t_2 wave functions of the paramagnetic ion, $|l_2\alpha\rangle$ are linear combinations of ligand orbitals, and N_{α} are normalization factors. Now the 4A_2 ground-state wave functions are three antisymmetric electron wave functions given by the Slater determinants constructed from the molecular orbitals

¹⁶ R. E. Watson and M. Blume, Phys. Rev. **139**, A1209 (1965).

TABLE I. The values of various constants for V^{2+} , Cr^{3+} , and Ni^{2+} ions needed in the calculations. ζ is the reduced one-electron spin-orbit coupling parameter, B is the linear combination of radial integrals over the interelectronic distance in Racah's notation, $\Delta=10Dq$ is the splitting of the d -electron level in the cubic crystalline field, $\langle r^2 \rangle$ and $\langle r^4 \rangle$ are the radial integrals defined in (24), and M_0 and M_2 are the radial integrals defined in (46).

	ζ (cm^{-1})	B (cm^{-1})	Δ (cm^{-1})	$\langle r^2 \rangle$ (a.u.)	$\langle r^4 \rangle$ (a.u.)	M_0 (cm^{-1})	M_2 (cm^{-1})
V^{2+}	120	755	14 000	2.063	9.425	0.915	0.499
Cr^{3+}	200	918	18 000	1.446	4.340	1.41	0.776
Ni^{2+}	500	1030	8 600	1.127	3.017	2.375	1.295

(44). The ground-state levels were calculated by using the spin-spin interaction operator in the form (43) and the above-mentioned determinant wave functions. The one-center integrals between ligand wave functions and the two-center integrals between ligand and paramagnetic-ion wave functions were omitted. This approximation does not affect the results too much in the case of small covalency. After the detailed calculation we obtained the following contributions to the parameter D in the case of the tetragonal as well as of the trigonal distortion:

(i) Tetragonal distortion:

$$D_{\text{tet}} = -(1/7)N_{\xi}^2(N_{\xi}^2 - N_{\zeta}^2)(M_0 - 4M_2), \quad (45)$$

where M_n are radial parameters

$$M_n = \frac{1}{2}(\xi^2\beta^2) \int_0^{\infty} \int_0^{\infty} \frac{r_1^{>n}}{r_1^{<n+3}} R_{3d}^2(i) R_{3d}^2(j) r_1 r_2 dr_1 dr_2, \quad (46)$$

$R_{3d}(r_i)$ in (46) are Hartree-Fock radial wave functions of $3d$ electrons. N_{α} in (45) are normalization constants defined by Eq. (44). The admixture of ligand orbitals in the antibonding molecular orbitals was calculated and the normalization constants were determined. By the same procedure as used in the preceding section, the normalization constants N_{α} can be written in terms of one-bond integrals. Then the parameter D_{tet} is given by

$$D_{\text{tet}} = \frac{1}{7}^2 (M_0 - 4M_2) (H_{\pi}/E_{\pi}^2) (dH_{\pi}/de_{zz}) e_{zz}. \quad (47)$$

(ii) In the case of the trigonal distortion the contribution to the parameter D is

$$D_{\text{trig}} = (1/7)N_{\epsilon}^2(N_{\epsilon}^2 - N_0^2)(M_0 - (8/7)M_2), \quad (48)$$

where M_0 and M_2 are again radial parameters (46). D_{trig} calculated in terms of the one bond integrals is

$$D_{\text{trig}} = \frac{4}{7}(M_0 - \frac{8}{7}M_2) (H_{\pi}^2/E_{\pi}^2) e_{zz}. \quad (49)$$

Finally we must note that the contribution to the zero-field splitting of the 3A_2 state of the d^3 configuration is equal to zero when calculated in the framework of this approximation.

7. COMPARISON WITH EXPERIMENT

The zero-field splitting in strained cubic crystals is usually expressed in terms of parameters G_{11} and G_{44} , called the spin-lattice coefficients.² The axial-field splittings in the cases of the tetragonal and trigonal distortions are in simple linear relations to these spin-lattice coefficients. The parameters D_{tet} and D_{trig} are given by

$$D_{\text{tet}} = \frac{3}{4}G_{11}e_{\theta}(E) \quad (50)$$

and

$$D_{\text{trig}} = G_{44}[e_{\xi}(T_2) + e_{\eta}(T_2) + e_{\zeta}(T_2)], \quad (51)$$

under the condition $e_{\xi}(T_2) = e_{\eta}(T_2) = e_{\zeta}(T_2)$.

The magnitudes of G_{11} and G_{44} for the V^{2+} , Cr^{3+} and Ni^{2+} ions have been measured by electron spin resonance.¹³ We have estimated the numerical values of G_{11} and G_{44} given by the three mechanisms introduced in the preceding sections. For that purpose a number of empirical constants were used. The energies of excited states were determined according to the calculations of Tanabe and Sugano¹⁷ for known values of Δ and B . The value of the spin-orbit constant ζ in a crystal may be reduced to as little as 80% of the free-ion value. The values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ were calculated using Watson's analytical Hartree-Fock wave functions for free ions.¹⁸ The values of all parameters mentioned are shown in Table I. The value of the lattice constant of MgO is 3.97 atomic units (a.u.).

The estimation of covalent contribution to the axial-field parameters u , u' , v , and v' was performed by fitting to the value of Δ_{cov} . Since there is good reason to suppose that the only essential parts of Δ are the ionic and the covalent parts, we combine the observed value of Δ with that calculated by using the point-charge model to obtain the value of Δ_{cov} . Besides, we assume that the values of the transfer integrals are proportional to the appropriate overlap integrals with one constant of proportionality in the range of distortions induced by experimentally available pressures. To determine the derivatives of the overlap integrals, it is necessary to know their values at two distances close to one another. Because the difference between these two distances is small compared to their magnitudes,

TABLE II. The values of the overlap integrals and their derivatives between d orbitals of a Mn^{2+} ion and p orbitals of a F^{-} ion at the internuclear distance 3.97 a.u. for the normal as well as the expanded wave functions of the Mn^{2+} ion.

w	$10^2 \langle d \sigma \rangle$	$-10^2 \frac{d \langle d \sigma \rangle}{de_{zz}}$	$10^2 \langle d \pi \rangle$	$-10^2 \frac{d \langle d \pi \rangle}{de_{zz}}$
0.85	9.345	16.9	6.135	20.7
0.90	8.605	17.1	5.455	18.8
1.00	7.124	17.5	4.094	15.0

¹⁷ Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 9, 753 (1954).

¹⁸ R. E. Watson, MIT Solid-State and Molecular Theory Group, Technical Report No. 12, 1959 (unpublished).

TABLE III. The contributions to the spin-lattice strain coefficients G_{11} and G_{44} (tetragonal and trigonal field splitting) for V^{2+} , Cr^{3+} , and Ni^{2+} ions in MgO crystals due to the three mechanisms discussed in the paper. In the last row are the experimental values measured by EPR (Refs. 1 and 2).

	V^{2+}		Cr^{3+}		Ni^{2+}	
	G_{11} (cm $^{-1}$)	G_{44} (cm $^{-1}$)	G_{11} (cm $^{-1}$)	G_{44} (cm $^{-1}$)	G_{11} (cm $^{-1}$)	G_{44} (cm $^{-1}$)
Ionic	0.51	2.16	0.40	2.64	15	49
Covalency	-0.07	0.97	0.13	2.32	28	9
Spin-spin. Anisotropy	0.12	0.00	0.08	0.00
Sum	0.56	3.13	0.61	4.96	43	58
Experiment	0.42	3.0	0.6	4.2	57	36

the integrals must be calculated very exactly. The tables of overlap integrals between p and d orbitals published by Jaffé *et al.*¹⁹ have a very coarse interval, so that the derivatives cannot be estimated with satisfactory exactness. Therefore we have used a table of overlap integrals between Mn^{2+} and F^- ions published by Marshall and Stuart.²⁰ This table is calculated quite exactly and has a sufficiently fine interval. Further, this table also covers overlap integrals between radially-expanded wave functions, which are necessary for our calculations. This radial expansion of wave functions is represented by a simple scaling of 10% with appropriate renormalization. Using this table, we derived values of overlap integrals for scaling parameter $w=0.85$ by linear extrapolation. The $3d$ wave functions of the Ni^{2+} ion are more radially contracted than those of the Mn^{2+} ion, but in contrast the $2p$ wave functions of O^{2-} ion are more expanded than those of F^- ion. Expecting these opposing effects on the size of integrals to cancel, we may use the integrals calculated by Marshall and Stuart with the scaling factor $w=1$ for Ni^{2+} ion in an oxygen complex. For integrals of Cr^{3+} and V^{2+} ions, the wave functions of which are more expanded than that of Ni^{2+} , we use the values of the integrals with the scaling factor $w=0.9$ and 0.85 , respectively. The values of the overlap integrals and their derivatives for the distance between nuclei 3.91 a.u. are given in Table II. The estimated numerical contributions to the parameters G_{11} and G_{44} are shown in Table III together with the experimental values. The constant of proportionality between transfer and overlap integrals, needed only in the calculation of the contribution of anisotropic spin-spin coupling, is estimated to equal 4. The values of the radial parameters M_0 and M_2 defined in (44) for V^{2+} and Cr^{3+} ions have been calculated by Blume and Watson²¹ and are shown in Table I.

8. DISCUSSION

As is evident from Table III, the agreement between the calculated and the observed values is relatively

¹⁹ H. H. Jaffé and G. O. Daak, J. Chem. Phys. **21**, 966 (1953); H. H. Jaffé, *ibid.* **21**, 258 (1953).

²⁰ W. Marshall and R. Stuart, Phys. Rev. **123**, 2048 (1961).

²¹ M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **271**, 565 (1963).

good. We must stress that the purpose of this paper is not an exact calculation of the zero-field splitting, but only an approximate estimation of the contributions of individual mechanisms and their trend for different ions in comparison with the experimental values. This purpose was, as it seems to us, sufficiently fulfilled. It is evident from the results that the main mechanisms giving contributions to the zero-field splitting are the ionic and the covalent crystal fields with the spin-orbit interaction. The effect of the anisotropic spin-spin coupling within the ground state due to covalency effects is small for d^3 ions, and it vanishes for d^8 ions. We may assume, however, that the effects of this mechanism should be more important for the ions containing more unpaired electrons in a shell, as in the d^5 configuration. From Table III it is evident that for d^3 ions the experimental values of G_{44} are greater than those of G_{11} , whereas for d^8 ions the values of G_{44} are smaller than those of G_{11} . The calculated ionic contributions have the same trend for d^3 ions and d^8 ions (they are greater for G_{44} than for G_{11}); this means that they worsen the agreement with experiment for d^8 ions. But the covalency contributions improve the agreement with experiment both for d^3 and for d^8 ions. What is the reason for the covalency mechanism's having a trend for d^3 ions opposite to that for d^8 ions, even though the ionic mechanism has the same trend for both configurations? In the expressions (5) and (14), two tetragonal-field parameters u and u' contribute to the zero-field splitting. The covalent contributions to these two parameters have the same sign, and their magnitudes are close to the ratio $\frac{3}{4} \approx u'/u$, so that the contribution to the zero-field splitting is nearly cancelled. This cancellation is more effective for ions with more expanded wave functions, like Cr^{3+} and V^{2+} , and less effective for the more contracted Ni^{2+} ion wave functions. That is the reason why d^3 ions have a greater covalent contribution to the tetragonal-field splitting than d^8 ions. In the contributions to trigonal-field splittings (parameter G_{44}) no similar cancellation takes place. Thus the d^8 ions, having more contracted wave functions and smaller transfer integrals, have smaller covalent contributions to G_{44} value than d^3 ions.

To verify the results of our calculation, it should be suitable to perform the measurements of zero-field splitting of d^3 and d^8 ions on stressed nonoxide cubic

crystals. The fluoride cubic crystals with perovskite structure seem to be advantageous for that purpose. It is evident that both ionic and covalent contributions to the zero-field splitting are smaller in fluorides than in oxides. But from our calculations it appears that the covalent contribution to the ratio G_{11}/G_{44} should be different for fluorides than for oxides. From the considerations given above, the ratio G_{11}/G_{44} should be greater for fluorides than for oxides because of more contracted fluorine $2p$ wave functions.

Note added in proof. Recently the values of G_{11} and G_{44} for Cr^{3+} and Ni^{2+} in MgO were computed by Tucker^{22,23} using the point-charge model. These values differ greatly from the point-charge contributions estimated in this paper for the following reasons: (i) Tucker's values are obtained from a fit to the experimental value of the cubic field splitting²²; thus they

²² E. B. Tucker, Proc. IEEE, **53**, 1547 (1965).

²³ E. B. Tucker, Phys. Rev. **143**, 264 (1966).

are three or four times greater than the values computed from the first principles. (ii) The expression for G_{44} used by Tucker is smaller by a factor of 3 than in our expressions (10) or (17), in which the terms caused by the excited states t_2^3 , 2T_2 or $t_2^5e^3$, 1T_2 are truncated and near-neighbor model is used. (iii) The effect of further neighbors is not negligible, and some terms differ by as much as 50% when Kanamori sums are used instead of the near-neighbor model. (iv) The effect of the excited states t_2^3 , 2T_2 and/or $t_2^5e^3$, 1T_2 was not considered in Altshuler *et al.*'s²⁴ expression for G_{44} used by Tucker, though their effect is substantial.

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²⁴ S. A. Altshuler, B. I. Kochalzev, and A. M. Leushin, Usp. Fiz. Nauk **75**, 459 (1961) [English transl.: Soviet Phys.—Usp. **4**, 880 (1962)].

Quantum Theory of an Optical Maser.* I. General Theory

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A quantum statistical analysis of an optical maser is presented in generalization of the recent semiclassical theory of Lamb. Equations of motion for the density matrix of the quantized electromagnetic field are derived. These equations describe the irreversible dynamics of the laser radiation in all regions of operation (above, below, and at threshold). Nonlinearities play an essential role in this problem. The diagonal equations of motion for the radiation are found to have an apparent physical interpretation. At steady state, these equations may be solved via detailed-balance considerations to yield the photon statistical distribution $\rho_{n,n}$. The resulting distribution has a variance which is significantly larger than that for coherent light. The off-diagonal elements of the radiation density matrix describe the effects of phase diffusion in general and provide the spectral profile $|E(\omega)|^2$ as a special case. A detailed discussion of the physics involved in this paper is given in the concluding sections. The theory of the laser adds another example to the short list of solved problems in irreversible quantum statistical mechanics.

I. INTRODUCTION

THE theory of an optical maser due to Lamb¹ treats the atoms quantum-mechanically while considering the radiation as a classical electromagnetic field. This theory has provided a basis for understanding a wide range of observed laser phenomena and has been extensively tested by Javan and Szöke,² Fork and

Pollack,³ and others. Extensions of the theory to allow for the presence of a magnetic field^{4,5} or cavity anisotropy⁶ have been made by several authors, and there is no doubt that remarkable fits are being obtained with experimental data. The ring laser has been analyzed by Aronowitz,⁷ and by Gyorfyy and Lamb,⁸ again in good agreement with observations. Various forms of modulation can be discussed, as in the work of Harris.⁹ The buildup in time of oscillations from a

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⁵ M. Sargent, III, W. E. Lamb, Jr., and R. L. Fork (to be published).

⁶ W. M. Doyle and M. B. White, Phys. Rev. **147**, 359 (1966).

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⁸ B. L. Gyorfyy and W. E. Lamb, Jr. (to be published).

⁹ S. E. Harris and R. Targ, Appl. Phys. Letters **5**, 202 (1964); S. E. Harris and O. P. McDuff, *ibid.* **5**, 205 (1964).