PHYSICAL REVIEW B VOLUME 4, NUMBER 5 1 SEPTEMBER 1971

Theory of the Linear Electric Field Effect on the Electron-Paramagnetic-Resonance Spectra of $3d^5$ Ions in ZnS

T. Buch and A. Gelineau
Laboratoire de Luminescence II, Equipe de Recherche associé au Centre National de la Recherche Scientifique, Faculté des Sciences de Paris, Paris, France

(Received 4 February 1971)

The linear effect of an external electric field on the EPR spectra of d^5 ions in cubic crystals is described by a third-rank tensor with only one independent component. The values of this parameter are calculated from a molecular-orbital theory for Cr^+, Mn^{++}, and Fe^{+++} in ZnS (zinc blende). Very good agreement with experiment is obtained by a mechanism in which charge-transfer levels and ligand orbitals play a dominant role.

I. INTRODUCTION

First-order (linear) electric field effects in EPR spectra of transition-metal ions in crystals may in principle be observed wherever the ion site lacks a center of symmetry.[1-7] The description of these effects requires the introduction of additional terms in the spin Hamiltonian. An analysis of Kramers's invariance shows that those of the lowest order (and the only ones observed to date) are described by third-rank tensors:

$$\mathcal{H}_E = T_{ijk} S_j H_k E_i + R_{ijk} S_j S_k E_i \; . \qquad (1.1)$$

The first term may give a contribution to the gyromagnetic factor, but its effect is in general negligible, at least for ground-state orbital singlets. The second term gives a contribution to the zero-field splitting or fine structure. In fact, the second-rank tensor obtained by contraction for a given direction of the electric field, $D'_{jk} = R_{ijk} E_i$, has the same properties as the fine-structure tensor D_{jk}. The tensor R_{ijk} has the same symmetry properties[8] as the piezoelectric tensor d_{ijk}. We shall be interested in the electric field splitting of the EPR spectrum of d^5 ions in zinc blende. In this crystal, the site symmetry is tetrahedral, and the R_{ijk} tensor has only one independent component, and one has $R_{14} = R_{25} = R_{36} = R$, the other tensor components being zero.[8] In this case, the spin Hamiltonian contains the terms

$$\mathcal{H}_E = R\{E_x(S_y S_z + S_z S_y) + E_y(S_z S_x + S_x S_z) + E_z(S_x S_y + S_y S_x)\} \; . \qquad (1.2)$$

The theory is most simply (and generally) derived for the $\vec{H} \parallel \vec{E} \parallel [001]$ axis of the cubic crystal. In this case R is calculated within the lowest spin multiplet, for which $S = \frac{5}{2}$, and is given by the matrix element

$$R = \frac{i}{\sqrt{10}} \langle \tfrac{5}{2} \tfrac{5}{2} | \mathcal{H}_E | \tfrac{5}{2} \tfrac{1}{2} \rangle \; . \qquad (1.3)$$

R values have been measured[6,7,9] for Cr^+, Mn^{++}, and Fe^{3+} as substitutional impurities in ZnS (blende). The measured value for Fe^{+++} is almost 20 times that observed for the other two ions, an effect which seems inexplicable in the customary framework of the equivalent-even-field approach[3-5] in crystal-field theory.

This is not the first time such differences in the behavior of d^5 ions have been observed. Most of the properties of Mn^{++} impurities in host crystals, such as the optical spectra[10] and the gyromagnetic factor (practically equal to the free-ion value), can in fact be explained by crystal-field theory whereas the same properties of Fe^{+++} defy this approach.[11] It is the purpose of this paper to propose a coherent interpretation of all these results by means of molecular-orbital theory.

In the presence of an externally applied electric field $\vec{E}$, the physical (as opposed to the spin) Hamiltonian contains an additional term

$$V_E = e\vec{E} \cdot \textstyle\sum_i \vec{r}_i \qquad (1.4)$$

describing the interaction of the electric field with the electrons. The purpose of the theory consists in the derivation of the spin Hamiltonian (1.2) from (1.4) and the knowledge of the electronic structure of the paramagnetic center. The unpaired electrons in a transition-metal ion are "pure" d electrons in the crystal-field approach. Since the many-electron wave functions built from these electronic wave functions have even parity, an odd-parity effect, such as the linear "Stark" effect we wish to study, must occur via the odd components of the ligand field, which is able to scramble odd-parity wave functions into the ground state. In the crystal-field approach, these odd-parity functions are essentially $4p$-electron functions corresponding to excited configurations of the central ion. A perturbation calculation is able to lead to the concept of the "equivalent even field" acting within the ground-state manifold

$$V_{ee} = \frac{V_{\text{odd}} | n_{\text{odd}} \rangle \langle n_{\text{odd}} | V_E}{E_0 - E_n} \; . \qquad (1.5)$$

As we shall see, if we allow ligand functions to participate in the "complete" set of one-electron wave functions used to describe the center, their effect can dominate that of the $4p$ electrons, because frequently, the corresponding "charge-transfer" configurations, in which a ligand electron "migrates" toward the central ion, have lower energy than the $3d^{n-1}4p$ configuration. However, this possibility also depends on the relative importance of spin-orbit coupling to these charge-transfer configurations.

Molecular-orbital theory does not follow precisely the same path outlined here. The odd components of the molecular field are automatically included in the formulation of the molecular orbitals, which correspond to the symmetry of the center and thus have no even-odd characteristics from the outset. The scrambling of "odd" orbitals, $4p$ as well as ligands, is thus assured in the zero-order wave function. This makes a direct comparison between the methods somewhat difficult.

Royce and Bloembergen[1,4] have already pointed to the importance of covalent bonding for the electric field effect in Cr^{3+} in essentially ionic crystals with oxygen as a ligand. Their calculation included anisotropic spin-orbit interactions, but not the important effect of ligand spin-orbit coupling,[12] especially when dealing with heavier ligands. Our calculation shows that this coupling accounts for an important part of the effect in ZnS, because it is this effect which allows for a coupling to nonbonding charge-transfer states of t_1 symmetry to the ground state.

II. MOLECULAR MODEL OF d^5 CENTER IN ZnS (BLENDE)

Zinc blende belongs to the cubic crystal system. Each Zn atom is surrounded by 4 nearest-neighbor sulphur atoms at 2.36 Å = 4.41 a.u. The next nearest neighbors are 12 Zn atoms, whose distance to the center is only $\sqrt{\frac{8}{3}} = 1.633$ times the nearest-neighbor distance. The surroundings of a S atom are *mutatis mutandis* the same.[13] The structure of ZnS is rather ionic, but the effective charges on Zn and S are of about ± 0.85 electronic charges, indicating nevertheless appreciable covalent binding.[14]

In the model we choose, we consider the 4 nearest neighbors and the central atom engaged in molecular orbitals (MO's) formed as linear combination of metal $3d$, $4p$, and $4s$, and ligand $3s$ and $3p$ atomic orbitals. Simultaneously with chemical bonding we also consider the ligand atoms, as well as the second nearest neighboring Zn atoms with their effective charges, as point sources of a crystal electrostatic field. This crystal field is obviously not considered as a perturbation of the MO's, but is diagonalized together with the "chemical" part of the semiempirical Hartree-Fock-Roothaan[15] Hamiltonian.

Lacking any more detailed information, we assumed that the M-S distances between the impurity atom M and its neighbors are equal to the Zn-S distance in ZnS. In fact, the ionic radius of Mn^{++} is slightly greater than that of Zn^{++}, and that of Fe^{+++} is smaller. But since the self-consistent effective charge for Mn^{++} is greater than the effective charge of Zn^{++} assumed, one may estimate the effective radii to be similar. Also, for Fe^{+++} the self-consistent effective charge is less than 2+, so this ion will also be considerably larger than indicated by its formal charge.

On the other hand, the good agreement reached between calculated and observed crystal-field splittings $10Dq$, a quantity which is very sensitive to the M-S distance, seems to reinforce this choice.

The MO calculation was done by a semiempirical self-consistent method.[11] The atomic radial functions used were those of Richardson *et al.*[15,16] for the metal, and those of Watson and Freeman[17] for sulfur. The semiempirical ionization energies for a given charge configuration were obtained following the method of Basch *et al.*[18] and the off-diagonal matrix elements were obtained from Cusachs's[19] approximation. Matrix elements were corrected for ligand-ligand overlap, and for the first[20] and second neighbor crystal-field effects. It is interesting to notice in this connection that the inclusion of the second neighbor crystal-field effects proved to be essential in order to obtain correct values for $10Dq$ and the g factors.

The 50 atomic spin orbitals were combined in sets transforming as the irreducible representations of the group T_d. This decomposition yields $5T_2 + 3A_1 + 2E + T_1$ in its space part, and the problem consists in placing 37 electrons in these orbitals. We wish to point out the presence of T_1 nonbonding (pure-ligand) orbitals, whose importance was pointed out above. The diagonalization of the Hamiltonian expressed in this basis yields energies and MO coefficients which were used to compute effective charges on the $3d$, $4s$, and $4p$ orbitals of M. These three parameters were used as criteria for self-consistency.[21] The values of self-consistent charges thus obtained are listed in Table I.

The MO coefficients and energies were then used to calculate g factors and the electric-field-effect coefficients R.

TABLE I. Self-consistent charge distribution.

Met	q_{3d}	q_{4s}	q_{4p}	q_{LIG}	q_{Met}
Mn^{++}	4.78	0.7	0.09	−0.954	1.41
Fe^{+++}	5.16	0.77	0.14	−0.907	1.93
Cr^{+}	4.55	0.68	0.17	−1.04	0.60

Electrostatic repulsion splits each configuration into several terms. In view of the semiempirical character of our calculation, it did not seem justified to spend a considerable effort in any detailed calculation of these splittings. We have thus considered the excited configurations to be completely degenerate, their average energies being given by the corresponding one-electron excitation energies. This method is obviously not applicable to the ground state, however.

Thus we have obtained the energies and wave functions of the excited quartet terms of the d^5 configuration by diagonalization of the corresponding Tanabe-Sugano electrostatic matrix[22] for $^4T_1$, using the calculated $10Dq$ values together with the following values of the Racah parameters B and C (in kcm^{-1}): for Mn^{++}, $B=0.6$, $C=3.1$ (Ref. 10); for Fe^{+++}, $B=0.625$, $C=4B$ (Ref. 23); and for Cr^{+}, $B=0.7$, $C=4B$ (Ref. 22). These values are considerably smaller than the free-ion values, as is well known.

We may mention here the values of spin-orbit coupling parameters used in our subsequent calculations. These were (in kcm^{-1}) 0.26, 0.374, and 0.22 for Mn, Fe, and Cr, respectively,[11,22] and 0.40 for S. These are values interpolated between the free-ion values for different effective charge states.

III. ELECTRIC FIELD PERTURBATION

As mentioned in the Introduction, the perturbation Hamiltonian due to an externally applied electric field is

$$V_E = e\vec{E}\cdot\sum_i \vec{r}_i\ , \tag{1.4}$$

where the sum is extended over all the electrons in the center. The form of the spin Hamiltonian $\mathcal{H}_E$ indicates that we shall have to perform a perturbation calculation up to third order, using our molecular orbitals as zero-order functions and applying simultaneously the perturbation due to $\vec{E}$ and spin-orbit coupling:

$$\mathcal{H}' = \mathcal{H}_{so} + V_E\ . \tag{3.1}$$

We shall be interested in those terms of this development which may contribute to R. If $|\alpha MO\rangle$ designates the components $(M=\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2})$ of the perturbed ground-state manifold $^6A_1$, the part of a matrix element $\langle\alpha MO|\mathcal{H}'|\alpha M'O\rangle$ to be retained is

$$\langle\alpha MO|\mathcal{H}'|\alpha M'O\rangle = 2\,\mathrm{Re}\langle MO|\Bigg(\sum_{M''M'''}\sum_{jk} V_E\left|\frac{|M''j\rangle\langle M''j|}{\epsilon_0-\epsilon_j}\right|\mathcal{H}_{so}\left|\frac{|M'''k\rangle\langle M'''k|}{\epsilon_0-\epsilon_k}\right|\mathcal{H}_{so}\Bigg)|M'O\rangle$$
$$+\langle MO|\Bigg(\sum_{M''M'''}\sum_{jk}\mathcal{H}_{so}\left|\frac{|M''j\rangle\langle M''j|}{\epsilon_0-\epsilon_j}\right|V_E|M'''k\rangle\langle M'''k|\mathcal{H}_{so}\Bigg)|M'O\rangle\ . \tag{3.2}$$

Here, in general, $|Mj\rangle$ indicates a nonperturbed state, O indicating the ground state. We observe that only the second part of the right-hand member of Eq. (3.2) has the "equivalent-even-field" form of Eq. (1.5). In fact, the contribution of the first part is zero in the crystal-field approach, but not in our case. M is in each case the eigenvalue of $\hat{S}_Z$.

Following Eq. (1.3) it will suffice to calculate one matrix element (3.2), that for which $M=\frac{5}{2}$, $M'=\frac{1}{2}$. V_E is independent of spin, and the selection rule for M is $\Delta M=0$, ±1. The spin-orbit coupling Hamiltonian is

$$\mathcal{H}_{so}=\sum_i\sum_\alpha\zeta_\alpha\vec{l}_i^{\,\alpha}\,\vec{S}_i=\sum_i\vec{\tau}_i\cdot\vec{S}_i=\vec{\tau}\cdot\vec{S}\ , \tag{3.3}$$

where α indicates summation over all atoms, i indicates the electrons, and $\vec{l}_i^{\,\alpha}$ is the angular momentum of electron i relative to the nucleus α.[12] We write $\vec{\tau}_i=\sum_\alpha\zeta_\alpha\vec{l}_i^{\,\alpha}$, and omit for simplicity the summation over the electrons; we have

$$\langle\alpha\tfrac{5}{2}0|\mathcal{H}'|\alpha\tfrac{1}{2}0\rangle=\sum_{jk}\big[\tfrac{1}{2}\,\mathrm{Re}\langle\tfrac{5}{2}0|V_E|\tfrac{5}{2}j\rangle\langle\tfrac{5}{2}j|\tau_-S_+|\tfrac{3}{2}k\rangle$$
$$\times\langle\tfrac{3}{2}k|\tau_-S_+|\tfrac{1}{2}0\rangle+\tfrac{1}{4}\langle\tfrac{5}{2}0|\tau_-S_+|\tfrac{3}{2}j\rangle\langle\tfrac{3}{2}j|V_E|\tfrac{3}{2}k\rangle$$
$$\times\langle\tfrac{3}{2}k|\tau_-S_+|\tfrac{1}{2}0\rangle\big][(\epsilon_0-\epsilon_j)(\epsilon_0-\epsilon_k)]^{-1}\ , \tag{3.4}$$

where j, k represent the excited states.

The symmetry of the cluster is T_d. In this group, the ground state transforms as A_1, $\vec{\tau}$ belongs to T_1, and the pertinent part of V_E is T_2. The excited states to be considered in (3.4) must thus be T_1 for the second part, and T_1 or T_2 for the first. The spin multiplicity in each case can be 6 or 4. We have thus excited states of type $^4T_1$, $^4T_2$, $^6T_1$, and $^6T_2$ to consider. In the ground-state configuration d^5, the only sextet is the ground state $^6A_1$, and only the second part of (3.4) contributes. For contributions from within d^5 we have thus only the three quartets $^4T_1$ to consider. However, for the excited configurations all the possibilities mentioned exist, thus providing us with a very large number of excited states whose energies are furthermore unknown to be considered, as we pointed out above. This situation makes it preferable to abandon the symmetry and multiplicity classification of states altogether, even at the cost of the powerful methods of tensor operator theory.[24] We work therefore directly in a representation in which $\hat{S}_Z$ and the configurations are considered to be diagonal.

We shall work exclusively within a strong-field representation appropriate to our MO scheme. We are interested in the excited states originating in the following configurations.

(1) The ground manifold d^5, denoted $A^M(M=5)$ whose strong-field configurations are $4t_2^3\,2e^2$, $4t_2^4\,2e$, $4t_2^2\,2e^3$.

(2) Excited manifolds, where one electron of the complete shells t_1^6, $1e^2$, or nt_2^6 $(n=1,\ 2,\ 3)$ is excited up to a level $4t_2$ or $2e$. It is useless to list all these configurations; examples are $t_1^5\,4t_2^4\,2e^2$ and $3t_2^5\,4t_2^3\,2e^3$. As usual, we neglect to write down the complete shells. These configurations are denoted generally $A^{M+1}X^{N-1}$.

Each configuration is described by a number of Slater determinants, which can be easily derived from the ground-state determinantal wave vector. The manner in which this is done, and the notation used, is described in Appendix A.

For what follows, it will be convenient to consider separately the two parts of Eq. (3.4). Each part contains V_E one time and $\mathcal{H}_{so}$ two times. In the second part, V_E is the second factor; we call this part H. In the first part, it is the first factor; we call this D.

In each part, D or H, two excited states contribute as intermediate states. We distinguish three cases: (1) Both excited states belong to excited manifolds; (2) both excited states belong to the ground manifold; (3) one excited state belongs to each, the ground and excited manifolds.

Use of the results of Appendix A allows us to show that D_1, the contribution to D from case 1 above, is zero. Similarly, one finds that H_2 is zero. D_2 is the only contribution from a crystal-field approach. Case 3 contributes to both D and H.

Once the reduction to one-electron matrix elements is performed, we find the following expressions for H_1:

$$H_1=\frac{1}{2\sqrt{10}}\sum_X\sum_{ijx}\left[(\epsilon_X-\epsilon_i)(\epsilon_X-\epsilon_j)\right]^{-1}\times\langle x|\hat{Z}|i\rangle\langle i|\hat{\tau}_-|j\rangle\langle j|\hat{\tau}_-|x\rangle\,,\qquad(3.5)$$

where X denotes all complete shells, $x\in X$, $i,\ j\in A$, and $\hat{Z}$ is the Z components of the one-electron dipole moment, and $\hat{\tau}_-$ the one-electron orbital operator defined in Eq. (3.3).

As mentioned above, we retain the symmetry representation for the quartet states of the ground manifold. Each term ${}^4_\alpha T_1(\alpha=1,\ 2,\ 3)$ is a linear combination of the states ${}^4_iT_1$ originating in the configurations $t_2^3e^2$ $({}^4_1T_1)$, t_2^4e $({}^4_2T_1)$, and $t_2^2e^3$ $({}^4_3T_1)$. They are

$$|{}^4_\alpha T_1Mk\rangle=\textstyle\sum_i a_i^\alpha|{}^4_iT\,Mk\rangle\,,\qquad(3.6)$$

where $k=x,\ y,\ z$. The coefficients a_i^α are those obtained by diagonalization of the electrostatic energy. Each $|{}^4_iT\,Mk\rangle$ in turn is a linear combination of Slater determinants; for example,

$$|{}^4_iT_1\tfrac{3}{2}\,x\rangle=\sum_{jk}C^i_{jk}|\bar{j}\,[k]\rangle$$

in the notation of Appendix A. One obtains an expression for D_2 in terms of monoelectronic matrix elements of $\hat{Z}$ and $\hat{\tau}$, of the form

$$D_2=\frac{1}{2\sqrt{10}}\sum_{\alpha\beta}\frac{Z_{\alpha\beta}\,\mathcal{S}_\alpha\mathcal{S}_\beta}{E(\alpha)E(\beta)}\,,\quad\alpha,\ \beta=1,\ 2,\ 3,$$

$$E(\alpha)=\epsilon({}^4_\alpha T_1)-\epsilon({}^6A_1)\qquad(3.7)$$

where the matrix elements

$$\mathcal{S}_\alpha=\langle{}^6A_1\tfrac{5}{2}|\tau_-S_+|{}^4_\alpha T_1\tfrac{3}{2}\,x\rangle\qquad(3.8)$$

and

$$Z_{\alpha\beta}=\langle{}^4_\alpha T_1\tfrac{3}{2}\,y|\hat{Z}|{}^4_\beta T_1\tfrac{3}{2}\,x\rangle$$

are given in Appendix B in terms of the reduced one-electron matrix elements. The corresponding expansions of D_3 and H_3 are

$$D_3=\tfrac{1}{2}\sum_{\alpha=1}^{3}\sum_{i=1}^{3}\sum_X\sum_{x\in X}\sum_{jk}\left[E(\alpha)(\epsilon_X-\epsilon_j)\right]^{-1}\times\langle x|\hat{\tau}|j\rangle\langle k|\hat{Z}|x\rangle\,C^i_{jk}\,a_i^\alpha\,\zeta_\alpha\,,$$

$$H_3=\tfrac{1}{2}\sum_{\alpha=1}^{3}\sum_{i=1}^{3}\sum_X\sum_{x\in X}\sum_{jk}\left[E(\alpha)(\epsilon_x-\epsilon_j)\right]^{-1}\times\langle x|\tilde{Z}|j\rangle\langle k|\hat{\tau}_-|x\rangle\,C^i_{jk}\,a_i^\alpha\,\zeta_\alpha\,.\qquad(3.9)$$

At this point, symmetry arguments and the Wigner-Eckhart theorem may be introduced to perform the sums over the components of the different configurations (sums over x, i, and j in above expressions). One finds thus the final expressions

$$H_1=\frac{1}{2\sqrt{10}}\left\{\frac{\sqrt{2}ASB}{[\epsilon(t_1)-\epsilon(4t_2)]^2}-\frac{2ALM+\sqrt{2}CBL}{[\epsilon(t_1)-\epsilon(4t_2)][\epsilon(t_1)-\epsilon(2e)]}+\frac{2(\sqrt{\tfrac{3}{2}})J_1SL_1}{[\epsilon(1e)-\epsilon(4t_2)]^2}+2\sqrt{2}\sum_{n\neq4}\left[\frac{F_nSS_n}{[\epsilon(nt_2)-\epsilon(4t_2)]^2}-\frac{1}{2}\,\frac{F_nLL_n}{[\epsilon(nT_2)-\epsilon(4t_2)][\epsilon(nt_2)-\epsilon(2e)]}\right]\right\},$$

$$D_3+H_3=\frac{i}{2\sqrt{10}}\sum_{\alpha=1}^{3}\frac{\mathcal{S}_\alpha}{E(\alpha)}\quad\frac{8\sqrt{2}\,ABa_1^\alpha-(AM-4\sqrt{2}\,BC)a_2^\alpha}{\epsilon(t_1)-\epsilon(4t_2)}-\frac{1}{\sqrt{2}}\,\frac{(BC-8\sqrt{2}\,AM)a_3^\alpha}{\epsilon(t_1)-\epsilon(2e)}+\frac{(\sqrt{6})L_1J_1a_1^\alpha}{\epsilon(1e)-\epsilon(4t_2)}$$

$$+\sum_{n\neq 4}\left[\frac{8\sqrt{2}\,F_n S_n a_1^{\alpha}+(\sqrt{\tfrac{3}{2}})\,G_n S_n a_2^{\alpha}}{\epsilon(nt_2)-\epsilon(4t_2)}-\frac{[8\sqrt{2}\,L_n F_n+(\sqrt{\tfrac{3}{2}})\,G_n S_n]\,a_3^{\alpha}}{\epsilon(nt_2)-\epsilon(2e)}\right]\Bigg\}\;. \tag{3.10}$$

The letters A, S, B, etc. in these expressions indicate the reduced matrix elements of $\hat{Z}$ and of $\hat{\tau}_-$ which are given in Appendix B.

The calculation of the reduced matrix elements of the orbital operator $\hat{\tau}$ is described in Ref. 11. In this work we used the same choice of the local coordinate system as described in that reference. We might notice, again, that the ligand spin-orbit coupling terms are the only ones to allow the important influence of the t_1 manifold in the electric field effect. The calculation of the reduced matrix elements of the dipole moment is somewhat lengthly but offers no special difficulty. A vector-coupling technique leads to integrals which are calculated by the same technique as overlaps and other two-center integrals.

IV. EFFECTIVE ELECTRIC FIELD AND PIEZOELECTRIC EFFECT

An electric field acting upon a molecular cluster may have two effects: It polarizes the electrons of the cluster—this is the effect we have calculated in detail in Sec. III. Besides, it may act on the ions themselves, distorting the cluster and producing thus an additional effect.

Also, measurements are done in such a way that an electric tension is applied to a sample placed in the microwave cavity of an EPR spectrometer. Results of such measurements are given in terms of the externally applied field which, due to the dielectric polarization of the sample, is widely different from the electric field locally affecting the cluster and electrons. When comparing theory and experiment it is therefore necessary to estimate the relation between local and external field.

The effective field may be expressed by the Lorenz-Lorentz equation

$$E=E_{\text{ext}}\,\frac{\epsilon+2}{3}\;, \tag{4.1}$$

where E is the microscopic field, and ϵ the dc dielectric constant of the crystal, which for ZnS is 8. This expression is valid when the field due to the surrounding ions is zero. This condition leads us to a consideration of ionic polarization of the crystal. The displacement of the ions under the effect of an external electric field is given phenomenologically by the piezoelectric property of ZnS. This is due to the fact[8] that an applied field with components E^i_{ext} produces a deformation described by the strain tensor ϵ_{jk}, and is related to E^i_{ext} by the third-rank piezoelectric tensor d_{ijk}:

$$\epsilon_{jk}=\textstyle\sum_i d_{ijk}\,E^i_{\text{ext}}\;. \tag{4.2}$$

If $\mathcal{H}$ is the electronic energy of the system, for the linear effect of E,

$$\mathcal{H}(E)=\mathcal{H}(O)+\frac{d\mathcal{H}}{dE_i}\,E_i\;,$$

but

$$\frac{d\mathcal{H}}{dE_i}=\frac{\partial\mathcal{H}}{\partial E_i}+\sum_{jk}\frac{\partial\mathcal{H}}{\partial\epsilon_{jk}}\,\frac{\partial\epsilon_{jk}}{\partial E_i}=\frac{\partial\mathcal{H}}{\partial E_i}+\sum_{jk}d_{ijk}\,\frac{\partial\mathcal{H}}{\partial\epsilon_{jk}}\;. \tag{4.3}$$

The total linear effect is thus decomposed into a primary effect (electronic polarization) and a secondary effect (ionic polarization).

As we already mentioned, the tensor d_{ijk} has the same symmetry properties as the tensor R_{ijk}. For a cubic crystal of the hemihedral class $\bar{4}3m$ it has only one independent component, whose value[25] is $d=3.2\times10^{-12}$ MKSA. For a field applied in the [001] direction, the corresponding deformation is a shearing strain ϵ_{12}, whose value for an applied field of 10^6 V/m is 3.2×10^{-6}. This displacement of the atoms surrounding the paramagnetic ion produces an additional electric field which is equivalent to that of a set of dipoles of dipole moment $u\cong1.6\times10^{-34}$ MKSA at the site of each of the nearest neighbors, and pointing in the directions [110], [$\bar{1}\bar{1}$0], [1$\bar{1}$0], and [$\bar{1}$10], respectively, the first two outward, the last two inward with respect to the central ion.

The field of one such dipole moment at the center of the cluster is ϵ times the direct charge effect of the undisplaced ion, and amounts to about 5% of the primary (electronic) effect. The superposition of the different dipoles representing the displacement of the neighbors reduces this effect still further. We thus conclude that the secondary effect is negligible, and also that the microscopic field is correctly expressed by the Lorenz-Lorentz equation (4.1).

V. RESULTS AND DISCUSSION

Table II gives the most important results of our calculations in comparison with the measured values.

The general agreement is satisfactory. A detailed physical analysis of the results is, however, rather difficult, as is frequently the case for molecular-orbital calculations when a comparison with the results of crystal-field theory is desired.

In an ionic model, the equivalent even field is determined by the energy of the odd excited states, which are the $4p$ states of the central ion. But as mentioned in the Introduction, in a molecular approach, there are also odd ligand states to be considered. But the condition for their participation

TABLE II. Comparison of calculated parameters with experiment.

	R_{expt} (10^4 cm^{-1}/kV/mm)	R_{theor} (10^4 cm^{-1}/kV/mm)	10 Dq expt (kcm^{-1})	10Dq theor	Δg expt	Δg theor
Mn	0.09	0.115	5.0	4.8	−0.0001	+0.0003
Fe	1.40	1.74	3.4	6.1	0.016	0.017
Cr	0.08	0.10		7.1	−0.0028	−0.0014

is, as we have seen, their spin-orbit coupling to the central atom.

The spin-orbit matrix elements are of the same order of magnitude for all three d^5 ions, the values being somewhat larger for Fe^{+++} than for other ions. The introduction of ligand spin-orbit coupling means that the spin-orbit coupling matrix elements involving the antibonding orbitals are about 10% larger than the free-ions values, instead of being lowered by "orbital reduction." The spin-orbit coupling effect on the nonbonding orbitals is significant although smaller than that involving the metal orbitals.

The energy of the strong-field ground configuration $4t_2^3 2e^2$ relative to the excited states depends on the antibonding orbitals $4t_2$ and $2e$; but in these relatively ionic complexes it also depends on the electrostatic shift of the ligand orbitals. The more covalent the bonding, the more antibonding become the one-electron levels $4t_2$ and $2e$, being lifted towards higher energies. A comparison of the results for the three d^5 ions shows that Fe^{+++} is somewhat more covalent than Mn^{++} or Cr^+. But in these strongly ionic clusters, this effect is overpowered by the electrostatic effects of the differing effective charges, so that the ground state of Fe^{+++} lies in fact lower and, therefore, closer to the nonbonding or weakly bonding orbitals $3t_2$ and t_1, which have essentially ligand $p\pi$ character.

The partial results given in Table III show that it is just these nearly nonbonding $3t_2$ and t_1 states which completely dominate over all others in the determination of the magnitude of R, furnishing more than 70% of the total of the form of the "crossed" contribution H_3+D_3. One might thus consider a simplified covalent model, which should greatly aid to the understanding of the magnetic properties of these ions without recurring to the complications and clumsiness of a complete MO calculation. In such a model, two energy parameters would describe the essential properties of the ion: the customary cubic crystal-field splitting parameters $10Dq$, and a new parameter characterizing the energy difference between the ligand orbitals $p\pi$ and the average of the split $3d$ functions of the central ion. This new parameter should be correlated with the deepness of the impurity ground-state level relative to the valence band of the host crystal.[26]

In the limit in which nonbonding interaction is neglected, one finds the situation described by Royce and Bloembergen,[1,4] which is, however, completely unable to account for the experimental facts, especially the large difference in both Δg and R, on going from Cr^+ and Mn^{++} to Fe^{+++}.

ACKNOWLEDGMENTS

We wish to thank C. Marti and R. Parrot for helpful discussions.

APPENDIX A: NOMENCLATURE AND CALCULATION OF MATRIX ELEMENTS BETWEEN DETERMINANTAL STATE FUNCTIONS

We shall use the following notation (all determinantal functions are assumed to be normalized):

$|\,\rangle = |A^M X^N\rangle = |\xi\eta\zeta\theta\epsilon\,,\ X^N\rangle, \quad X^N = t_1^6 3t_2^6 1e^4$, etc.

$|(\bar{j})\rangle = \bar{j}$ replaces j (spin inversion) in $|\,\rangle$. For example,

$$|(\bar{\eta})\rangle = |\xi\bar{\eta}\zeta\theta\epsilon\,,\ X^N\rangle\,.$$

$|\bar{j}\,\rangle = \bar{j}$ is added at the last place in $|\,\rangle$. For example,

$$|\bar{\eta}\rangle = |\xi\eta\zeta\theta\epsilon\bar{\eta}\rangle = -\,|\xi\eta\bar{\eta}\zeta\theta\epsilon\rangle\,.$$

$|[\bar{x}]\rangle = \bar{x}$ is missing in the complete shell X^N. For example,

$|\bar{\xi},\ [\bar{y}]\rangle = |\xi\bar{\xi}\eta\zeta\theta\epsilon,\ x\bar{x}yz\bar{z}\rangle$ if $X^N = x\bar{x}y\bar{y}z\bar{z}$.

The spin projection quantum number is kept for state specification. We thus have

$$|A^M X^N \tfrac{5}{2}\rangle = |\,\rangle\,, \quad |A^{M+1} X^{N-1} \tfrac{5}{2}\rangle_{ix} = (-1)^{M-i}\,|\bar{i}\,[\bar{x}]\rangle\,,$$

$$|A^M X^N \tfrac{3}{2}\rangle = \frac{1}{\sqrt{M}} \sum_j |(\bar{j})\rangle\,,$$

$$|A^{M+1} X^{N-1} \tfrac{3}{2}\rangle_{ix} = (-1)^{M-i}\,|\bar{i}\,[x]\rangle\,,$$

$$|A^M X^N \tfrac{1}{2}\rangle = \frac{1}{[\frac{1}{2}M(M-1)]^{1/2}} \sum_{j\neq k} |(\bar{j})(\bar{k})\rangle\,,$$

$$|A^{M+1} X^{N-1} \tfrac{3}{2}\rangle_{ijx} = (-1)^{M-i}\,|\bar{i}(\bar{j})[\bar{x}]\rangle\,.$$

The matrix elements of a one-electron operator $F=\sum f$ which we shall need are as follows {we write $[\,|A^{M+1}X^{N-1}\tfrac{5}{2}\rangle_{jn}]^\dagger = {}_{jn}\langle A^{M+1}X^{N-1}\tfrac{5}{2}|$, etc.}:

TABLE III. Contribution of different levels to R_{theor}.

(10^{-4}cm^{-1}/kV/mm)	R_{theor}	H_1	D_2	H_3+D_3	Contribution of t_1+3t_2
Mn	0.116	0.007	−0.003	0.11	0.10
Fe	1.74	0.15	0.100	1.68	1.21
Cr	0.10	0.002	−0.007	0.105	0.07

$$\langle A^M X^N \tfrac{5}{2}|F|A^{M+1} X^{N-1} \tfrac{5}{2}\rangle_{jx} = \langle |F\{(-1)^{M-j}|\bar{j}\,[\bar{x}]\rangle = (-1)^{M-j}\langle \bar{x}|f|\bar{j}\rangle , \tag{A1}$$

$$\langle A^M X^N \tfrac{5}{2}|F|A^{M+1} X^{N-1} \tfrac{3}{2}\rangle_{jx} = (-1)^{M-j}\langle |F|\bar{j}\,[x]\rangle = -(-1)^{M-j}\langle x|f|\bar{j}\rangle , \tag{A2}$$

$$\langle A^M X^N \tfrac{5}{2}|F|A^{M+1} X^{N-1} \tfrac{3}{2}\rangle_{jkx} = (-1)^{M-j}\langle |F|\bar{j}\,(\bar{k})[\bar{x}]\rangle = (-1)^{M-i}\langle \bar{x}k|f|\bar{j}\,\bar{k}\rangle = 0 , \tag{A3}$$

$${}_{jx}\langle A^{M+1} X^{N-1} \tfrac{5}{2}|F|A^{M+1} Y^{N'-1} \tfrac{3}{2}\rangle_{ky} = (-1)^{j+k}\langle \bar{j}\,[\bar{x}]|F|\bar{k}[y]\rangle = \delta_{jk}\langle y|f|\bar{x}\rangle , \tag{A4}$$

$$\begin{aligned}{}_{jx}\langle A^{M+1} X^{N-1} \tfrac{5}{2}|F|A^{M+1} Y^{N'-1} \tfrac{3}{2}\rangle_{kly} &= (-1)^{j+k}\langle \bar{j}\,[\bar{x}]|F|\bar{k}(\bar{l})[\bar{y}]\rangle \\ &= \delta_{xy}[\delta_{jk}\langle l|f|\bar{l}\rangle + (-1)^{j+k}\delta_{jl}\langle j|f|\bar{k}\rangle] ,\end{aligned} \tag{A5}$$

$${}_{jx}\langle A^{M+1} X^{N-1} \tfrac{3}{2}|F|A^{M+1} Y^{N'-1} \tfrac{3}{2}\rangle_{ky} = (-1)^{j+k}\langle \bar{j}\,[x]|F|\bar{k}[y]\rangle = \delta_{jk}\langle y|f|x\rangle + (-1)^{j+k}\delta_{xy}\langle \bar{j}|f|\bar{k}\rangle , \tag{A6}$$

$${}_{jx}\langle A^{M+1} X^{N-1} \tfrac{3}{2}|F|A^{M+1} Y^{N'-1} \tfrac{3}{2}\rangle_{kly} = (-1)^{j+k}\langle \bar{j}\,[x]|F|\bar{k}\,(\bar{l})[\bar{y}]\rangle = \delta_{jk}\langle l\bar{y}|f|\bar{l}\,x\rangle = 0 , \tag{A7}$$

$$\begin{aligned}{}_{jx}\langle A^{M+1} X^{N-1} \tfrac{3}{2}|F|A^{M}\tfrac{1}{2}\rangle &= (-1)^{M-j}\frac{1}{[\frac{1}{2}M(M-1)]^{1/2}}\sum_{k\neq l}\langle \bar{j}\,[x]|F|(\bar{k})(\bar{l})\rangle \\ &= (-1)^{M-j}\frac{2}{[\frac{1}{2}M(M-1)]^{1/2}}\sum\langle j\,l|f|\bar{l}\,x\rangle = 0 ,\end{aligned} \tag{A8}$$

$$\begin{aligned}{}_{jky}\langle A^{M+1} X^{N-1} \tfrac{3}{2}|F|A^{M}\tfrac{1}{2}\rangle &= \frac{(-1)^{M-j}}{[\frac{1}{2}M(M-1)]^{1/2}}\sum_{il}\langle \bar{j}(\bar{k})[\bar{x}]|F|(\bar{i})(\bar{l})\rangle \\ &= \frac{(-1)^{M-j}}{[\frac{1}{2}M(M-1)]^{1/2}}\sum_{il}[\delta_{ki}\delta_{jl} + \delta_{kl}\delta_{ji}]\langle j|f|\bar{x}\rangle = \frac{(-1)^{M-j}}{[\frac{1}{2}M(M-1)]^{1/2}}\langle j|f|\bar{x}\rangle .\end{aligned} \tag{A9}$$

The quartet states $^4T_1$ of d^5 are combinations of determinants of type $|\bar{i}[j]\rangle$. For these,

$${}_{ix}\langle A^{M+1} X^{N-1} \tfrac{5}{2}|F|\bar{j}[\bar{k}]\rangle = (-1)^{M-i}\langle \bar{i}\,[\bar{x}]|F|\bar{j}\,[k]\rangle = (-1)^{M-i}\delta_{ij}\langle k|f|\bar{x}\rangle , \tag{A10}$$

$${}_{ix}\langle A^{M+1} X^{N-1} \tfrac{3}{2}|F|\bar{j}[k]\rangle = -(-1)^{M-i}\langle \bar{i}[x]|F|\bar{j}\,[k]\rangle = -(-1)^{M-i}\delta_{ij}\langle k|f|x\rangle , \tag{A11}$$

$${}_{ijx}\langle A^{M+1} X^{N-1} \tfrac{3}{2}|F|\bar{k}[l]\rangle = (-1)^{M-i}\langle \bar{i}\,(\bar{j})[\bar{x}]|F|\bar{k}[l]\rangle = 0 . \tag{A12}$$

With these results, an expression such as that for H_1 [Eq. (3.8)] reads

$$\begin{aligned}H_1 = \tfrac{1}{2}\sum_{\substack{X\\Y}}\sum_{\substack{x\in X\\y\in X}}\sum_{ijk\in A}(\epsilon_X\epsilon'_X)^{-1}\langle A^M X^N \tfrac{5}{2}|\mathcal{H}_E|A^{M+1}X^{N-1}\tfrac{5}{2}\rangle_{ix} \\ \times\langle A^{M+1}X^{N-1}\tfrac{5}{2}|\tau_- S_+|A^{M+1}Y^{N'-1}\tfrac{3}{2}\rangle_{iky}\langle A^{M+1}Y^{N'-1}\tfrac{3}{2}|\tau_- S_+|A^M X^N\tfrac{1}{2}\rangle .\end{aligned}$$

This is the product of elements (A1), (A5), and (A9); (A5) forces $X=Y$. We write ϵ_X, ϵ'_X for the energies, to differentiate excitation to $4t_2$ and $2e$. One finds thus the equation (3.5).

Similarly H_3 is a product of matrix elements given by (A1), (A10), and (3.8), and D_3 of (A2), (A11), and (3.8).

APPENDIX B: REDUCED MATRIX ELEMENTS AND QUARTET FUNCTIONS $Z_{\alpha\beta}$ AND $\mathcal{S}_\alpha$

In terms of the quartet state coefficients a_i^α, the functions $Z_{\alpha\beta}$ and $\mathcal{S}_\alpha$ are given by

$$\mathcal{S}_\alpha = -a_1^\alpha S + (a_2^\alpha - a_3^\alpha)(-\tfrac{1}{2}\sqrt{3})L , \tag{B1}$$

$$\begin{aligned}Z_{\alpha\beta} &= \tfrac{1}{2}J(a_1^\alpha a_2^\beta + a_2^\alpha a_1^\beta + a_1^\alpha a_3^\beta + a_3^\alpha a_1^\beta) \\ &\quad + \frac{1}{2\sqrt{2}}F(a_2^\alpha a_2^\beta - a_3^\alpha a_3^\beta) \\ &= Z_{\beta\alpha} .\end{aligned} \tag{B2}$$

The notation and values of the reduced matrix elements in Eq. (3.10) are the following:

$$S_n = \langle 4t_2\|\hat{\tau}\|nt_2\rangle = i\sqrt{2}\left\{C_d^4 C_d^n \zeta_d - C_p^4 C_p^n \zeta_p + \zeta_L \times\left[\frac{1}{\sqrt{2}}(C_\sigma^4 C_\pi^n + C_\pi^4 C_\sigma^n) + \frac{C_\pi^4 C_\pi^n}{2}\right]\right\} ,$$

TABLE IV. Numerical values of reduced matrix elements of the electric dipole moment and of the spin-orbit interaction.

	Cr^+	Mn^{++}	Fe^{+++}
		(a.u.)	
A	−1.1422	−0.5966	−0.5128
C	0.3911	0.5410	1.1390
F_1	−0.2288	−0.1793	−0.1339
F_2	0.1886	0.1858	0.1895
F_3	−0.1270	−0.0548	−0.0234
F_4	−0.1200	−0.0644	−0.0460
F_5	0.0871	0.1075	0.0597
G_1	0.2810	−0.6299	−0.5467
G_2	0.0464	0.0392	0.1056
G_3	−0.6851	−0.6457	−1.0971
G_4	0.4828	0.3447	0.4485
G_5	−0.1062	−0.0028	−0.2356
J_1	−1.1627	−0.7627	−0.6204
J_2	0.1951	0.1453	0.3055
		(kcm^{-1})	
$-(\sqrt{-1})\times S_1$	0.0144	−0.0120	−0.0107
S_2	−0.0777	−0.0511	−0.0291
S_3	−0.0797	−0.0618	−0.0459
S_4	0.2515	0.2617	0.3983
S_5	0.0807	0.0616	0.0531
B	0.0053	0.0104	0.0151
L_1	0.0197	0.0567	0.2800
L_2	0.4553	0.4817	0.6915
M	−0.0664	−0.0727	−0.1343

$$|nt_2\rangle = C_d^n(3d) + C_p^n(4p) + C_s^n(3s_L) + C_\sigma^n(3p_{L\sigma}) + C_\pi^n(3p_{L\pi}),$$

$$n = 1, 2, 3, 4, 5$$

$$B = \langle 4t_2 \| \hat{\tau} \| t_1 \rangle = -\frac{i}{\sqrt{3}}\, \zeta_L \left(C_\sigma^4 - \frac{C_\pi^4}{\sqrt{2}} \right),$$

$$L_m = \langle 4t_2 \| \hat{\tau} \| me \rangle = -\frac{2i}{\sqrt{6}} \left[-\sqrt{6}\, C_d'^m C_d^4 \zeta_d + \tfrac{1}{2} \zeta_L C_\pi'^m \right.$$

$$\left. \times \left(C_\sigma^4 - \frac{C_\pi^4}{\sqrt{2}} \right) \right] \quad (m = 1, 2),$$

$$|me\rangle = C_d'^m(3d) + C_\pi'^m(3p_{L\pi}),$$

$$M = \langle 2e \| \hat{\tau} \| t_1 \rangle = \frac{i}{\sqrt{2}}\, C_\pi'^2 \zeta_L .$$

In the text we have written $S_4 = S$ and $L_2 = L$.

Dipole-moment reduced matrix elements are as follows:

$$A = \langle t_1 \| \hat{Z} \| 4t_2 \rangle,$$

$$C = \langle t_1 \| \hat{Z} \| 2e \rangle,$$

$$F_n = \langle nt_2 \| \hat{Z} \| 4t_2 \rangle, \quad F = F_4$$

$$G_n = \langle nt_2 \| \hat{Z} \| 2e \rangle,$$

$$J_m = \langle me \| \hat{Z} \| 4t_2 \rangle, \quad J = J_2 = -\tfrac{1}{2}(\sqrt{6})\, G_4 .$$

The values of these matrix elements for Cr^+, Mn^{++}, and Fe^{+++} are given in Table IV.

---

[1] N. Bloembergen and E. B. Royce, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem*, edited by W. Low (Academic, New York, 1963), p. 607.

[2] G. W. Ludwig and F. S. Ham, in Ref. 1, p. 620.

[3] J. O. Artman and J. C. Murphy, in Ref. 1, p. 634.

[4] E. B. Royce and N. Bloembergen, Phys. Rev. 131, 1912 (1963).

[5] A. Kiel and W. B. Mims, Phys. Rev. 153, 257 (1966).

[6] C. Marti, R. Parrot, and G. Roger, J. Phys. Chem. Solids 31, 257 (1970).

[7] B. Lambert, C. Marti, and R. Parrot, J. Luminescence 3, 21 (1970).

[8] J. F. Nye, *Propriêtês Physiques des Cristaux* (Dunod Cie, Paris, 1961).

[9] R. Parrot, G. Tronche, and C. Marti, Compt. Rend. 269, 321 (1969).

[10] D. Curie and J. S. Prener, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967).

[11] L. D. Kandel, M. C. G. Passeggi, and T. Buch, J. Phys. Chem. Solids 30, 321 (1969).

[12] A. A. Misetich and T. Buch, J. Chem. Phys. 41, 2524 (1964).

[13] W. L. Roth, in Ref. 10.

[14] K. Kunc, M. Balkanski, and N. Nusimovici, Phys. Status Solidi 41, 491 (1970).

[15] G. C. J. Roothaan, Rev. Mod. Phys. 32, 179 (1961).

[16] J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, J. Chem. Phys. 38, 796 (1963).

[17] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 521 (1961).

[18] H. Basch, A. Viste, and H. B. Gray, Theoret. Chim. Acta. 3, 485 (1965).

[19] L. C. Cusachs, J. Chem. Phys. 43, 5157 (1965).

[20] D. D. Radke and R. F. Fenske, J. Am. Chem. Soc. 89, 2297 (1967).

[21] L. D. Kandel, M. C. Passeggi, and T. Buch (unpublished).

[22] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge U.P., Cambridge, England, 1964).

[23] C. K. Jørgensen, *Absorption Spectra and Chemical Binding in Complexes* (Pergamon, Oxford, 1962).

[24] J. S. Griffith, *Irreducible Tensors for Molecular Symmetry Groups* (Prentice-Hall, London, 1962).

[25] K. S. Knol, Konink. Inst. Amsterdam 35, 99 (1932).

[26] T. Buch (unpublished).