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Paramagnetic Resonance and Optical Spectra of Divalent Iron in Cubic Fields. I. Theory*

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The energy level splittings of the ground state of the d^6 configuration in cubic and axial fields are given. The Zeeman splittings of the various levels are calculated for weak and strong magnetic fields. In the case of tetrahedral symmetry the effect of the perturbations of the odd parity configurations d^5p and d^5f on the ground state is estimated.

INTRODUCTION

The research reported here is a continuation of our systematic investigations on the paramagnetic resonance and optical absorption spectra of the transition group elements in cubic fields.[1]

The problem of the d^6 configuration in the crystal field of cubic symmetry is, however, of particular interest. To our knowledge the energy level scheme of divalent iron in cubic fields has not yet been treated theoretically and the optical and paramagnetic resonance spectra have not been observed experimentally. This energy level scheme is such that in an octahedral field the lowest level is an orbital triplet (Γ_5). If the perturbation of the spin-orbit interaction is taken into account the fifteen-fold degenerate level splits up into a number of levels of which a triplet is the lowest. This triplet consists of a mixture of orbital and spin wave functions. Under these circumstances the Jahn-Teller theorem[2] predicts that the complex would deform itself in order to remove this degeneracy. It was of particular importance to see whether the Jahn-Teller effect is indeed operative in the case of divalent iron.

Another part of this investigation deals with the spectrum of iron in tetrahedral symmetry. In this symmetry the orbital doublet Γ_3 is lowest. Under the combined perturbation of the cubic field and spin-orbit coupling the orbital doublet and five-fold spin degeneracy is split into a number of levels. At present there are hardly any paramagnetic resonance data of ions in tetrahedral symmetry. In the course of this investigation, stimulated by the difficulty of explaining the experimental spectra, it became clear that the problem of the energy level scheme in the tetrahedral symmetry is of considerable complexity. The reason lies in the fact that a tetrahedron has no center of symmetry. Therefore odd parity configurations can be admixed by the crystal field to the ground and some excited states.

We have estimated the effect of the admixture of the configuration d^5p and d^5f on the cubic splitting of the d^6, ^5D, ground state. The calculations presented here indicate that the effect may not be inconsiderable. It seems to us now that the estimated magnitude of this configurational mixing may have a profound effect on the magnetic properties, on the optical spectra, on the chemical bonding and on the stabilization energies of such complexes. These effects may not be limited to divalent iron but are probably equally effective in other ions located in tetrahedral symmetries.

This investigation is divided into two papers. The first paper deals with the theoretical investigations and the second with the experimental results. The theoretical section is divided under two major headings, A and B. Section A is concerned with the energy level scheme in cubic symmetries possessing a center of symmetry and section B with the energy level scheme in the tetrahedral cubic symmetry of four point charges. In view of the lengthy calculations and the large matrices this presents only a condensation of the results. The complete matrices and results are being submitted to the American Documentation Institute.

A. ENERGY LEVEL SCHEME OF d^6 IN A CUBIC FIELD POSSESSING A CENTER OF SYMMETRY

The ground state of the free ion according to Hund's rule is ^5D. The optical spectrum of Fe$^{\text{III}}$ has been carefully investigated. The whole configuration is within 60 000 cm^{-1}. The narrowest levels to ^5D ground state are the ^3P and ^3H levels removed by about 20 000 cm^{-1}. For all practical purposes, therefore, the lowest Stark levels even in a moderately strong crystal field can be considered to originate from the ^5D level. The contribution from the Stark levels originating from excited levels will contribute only slightly because of the relatively small spin-orbit interaction in iron ($\sim$100 cm^{-1}) and also because of the large separations of the excited levels. In the subsequent discussion in part A the lowest levels will be assumed to be pure Stark levels arising only from the parent ^5D state.

Group theoretical arguments tell us that the ^5D level will split into an orbital triplet ($^5\Gamma_5$ in Bethe's notation) and an orbital doublet ($^5\Gamma_3$). The spin-orbit coupling

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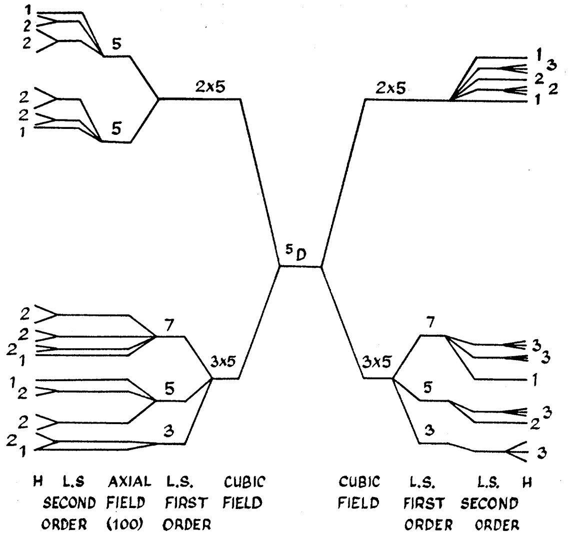

FIG. 1. Energy level scheme of the ^5D level in a cubic and axial field. The right-hand side of the figure shows the levels as split up by the cubic field and spin orbit coupling. The figure is drawn for the case of an octahedron of charges. For a tetrahedron or fluorite structure the orbital doublet is lowest. The numbers next to the levels indicate the total degeneracy. The energy of the levels is given by Eq. (4) and the order of the levels in the text is according to the order of this diagram. The left-hand side indicates the splitting of the energy levels in a relatively weak axial field.

will remove these degeneracies, i.e.,

$$D_2\times\Gamma_3=\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4+\Gamma_5,$$

and

$$D_2\times\Gamma_5=\Gamma_1+\Gamma_3+2\Gamma_4+2\Gamma_5. \tag{1}$$

We expect, therefore, a large number of levels of various degeneracies and of complex nature in which the wave function will be a mixture of orbital and spin wave functions. On quite general grounds it can be seen that in the case of the orbital doublet the calculations of the energy level scheme will have to be carried out with care. For this orbital doublet is split neither by the cubic field nor by the spin-orbit coupling acting separately. The combined effects of these perturbations will yield in the second and third order, splittings of the order of a few wave numbers.

In carrying out these calculations it is convenient to use the normalized spherical harmonic representation of the cubic potential given by

$$V^{\mathrm{I}}=V_0^{\mathrm{I}}+(7/2)D_4[Y_4^0+(70^{\frac{1}{2}}/14)(Y_4^4+Y_4^{-4})], \tag{2a}$$

and

$$V^{\mathrm{II}}=V_0^{\mathrm{II}}+(28/9)D_4[-Y_4^0+(70^{\frac{1}{2}}/14)(Y_4^4+Y_4^{-4})], \tag{2b}$$

where the first equation gives the potential for the six coordinated cubic symmetry and the second for the eight coordinated cubic symmetry. V_0 represents the constant term of the potential and D_4 is a constant. For a model of point charges at the corners of an octahedron, D_4 takes the value of $(Z_ie^2\bar{r}^4/a_i^5)(4\pi/9)^{\frac{1}{2}}$ where a_i is the distance between nearest neighbors. The expansion has been terminated at Y^4 since higher terms in Y yield zero matrix elements in the case of d electrons.

The matrix including the spin-orbit coupling perturbation is 25×25 and factors into three matrices of 6×6 and one 7×7, of which two are equivalent.

The general matrix, including the cubic field, axial field and spin-orbit effects, is given in Appendix I, Matrix I. Here Dq represents a constant factor and is a measure of the cubic field strength. A_2 represents the axial contribution and λ is the spin-orbit coupling constant in the crystal. The magnetic field H is along the symmetry axis (i.e. [1 0 0]) and $h=(e\hbar/2mc)H=\beta H$, where β is the Bohr magneton. The matrix elements have been evaluated using the appropriate Wigner coefficients of the manifold $L=$constant, i.e.,

$$c_{M,0}^{\ 2}=[3M^2-L(L+1)],$$

$$c_{M\pm4}^{\ 4}=\frac{1}{24}\cdot70^{\frac{1}{2}}\left[\frac{(L\mp M)!(L\pm M+4)!}{(L\pm M)!(L\mp M-4)!}\right]^{\frac{1}{2}}, \tag{3}$$

$$c_{M,0}^{\ 4}=\tfrac{1}{12}[35M^4-30L(L+1)M^2+25M^2$$
$$-6L(L+1)+3L^2(L+1)^2].$$

For the following it is convenient to transform matrix (I) into a scheme in which the cubic field is along the diagonal. This matrix, which will be used, is given in Appendix I, Matrix II. We shall now give results of the more important cases.

Cubic Field

Assuming $A_2=0$ and $h=0$, i.e., a pure cubic crystal field, and a zero magnetic field, the energy levels to second order and the eigenfunctions to zeroth order are given in Table I.

The right-hand side of Fig. 1 shows the energy level scheme for a cubic field, assuming $4Dq$ to be the lower level.

The effect of a magnetic field on these energy levels is calculated in two limiting cases by means of the perturbation theory.

(*a*) *Weak magnetic field* ($h\ll\lambda^2/Dq$)

λ^2/Dq is of the order of 10 cm^{-1}, and therefore $h\ll\lambda^2/Dq$ corresponds to the usual situation in the laboratory. The energy levels have been calculated (*a*) for the part not dependent on h to an accuracy of λ^2/Dq, (*b*) for the linear Zeeman effect to an accuracy of $\lambda h/Dq$, i.e., terms such as $(\lambda/Dq)^2h$ have been neglected, (*c*) for the quadratic Zeeman effect to an accuracy of $(Dq/\lambda^2)h^2$. These levels are given in Table II.

It is to be noticed that the wavefunctions are now mixed both by the spin-orbit coupling and the magnetic field.

TABLE I. Energy levels of the ground state of the d^6 configuration in a pure cubic crystal field. The energy levels are calculated to second order and the eigenfunctions to zeroth order. The numbering of the energy levels is according to the roots of Matrix II.

Energy levels	Wave function
$\left.\begin{array}{r}E_{13}=\\E_{19}=\\E_{25}=\end{array}\right\}4Dq+3\lambda+(9/25)(\lambda^2/Dq)$	$\Psi_{13}=(3/20)^{\frac{1}{2}}[(-2-1)+(2-1)+2(-1-2)]+(1/10)^{\frac{1}{2}}(1,0)$ $\Psi_{19}=(3/10)^{\frac{1}{2}}[(-1-1)+(11)]+(1/5)^{\frac{1}{2}}[(-20)+(20)]$ $\Psi_{25}=(3/20)^{\frac{1}{2}}[(21)+(-21)+2(12)]+(1/10)^{\frac{1}{2}}[(-10)]$
$\left.\begin{array}{r}E_{12}=\\E_{7}=\\E_{24}=\end{array}\right\}4Dq+\lambda+\frac{3}{5}(\lambda^2/Dq)$	$\Psi_{12}=(1/12)^{\frac{1}{2}}[-(-2-1)-(2-1)+2(-1-2)]-(1/2)^{\frac{1}{2}}(1,0)$ $\Psi_{7}=(1/6)^{\frac{1}{2}}[-(-2-2)-(2-2)-(-22)-(22)+(1-1)+(-11)]$ $\Psi_{24}=(1/12)^{\frac{1}{2}}[-(21)-(-21)+2(12)]-(1/2)^{\frac{1}{2}}(-10)$
$\left.\begin{array}{r}E_{5}=\\E_{18}=\end{array}\right\}4Dq+\lambda+(6/5)(\lambda^2/Dq)$	$\Psi_{5}=(1/6)^{\frac{1}{2}}[(-2-2)+(2-2)+(-22)+(22)+(1-1)+(-11)]$ $\Psi_{18}=(1/2)^{\frac{1}{2}}[(-1-1)-(11)]$
$\left.\begin{array}{r}E_{10}=\\E_{17}=\\E_{22}=\end{array}\right\}4Dq-2\lambda+(6/25)(\lambda^2/Dq)$	$\Psi_{10}=(1/40)^{\frac{1}{2}}[5(-12)+2(-2-1)+2(2-1)-\frac{1}{2}(-1-2)]-(3/20)^{\frac{1}{2}}(+10)$ $\Psi_{17}=(1/5)^{\frac{1}{2}}[(-1-1)+(11)]+(3/10)^{\frac{1}{2}}[(-20)+(20)]$ $\Psi_{22}=(1/40)^{\frac{1}{2}}[5(1-2)+2(21)+2(-21)-\frac{1}{2}(12)]-(3/20)^{\frac{1}{2}}(-10)$
$\left.\begin{array}{r}E_{4}=\\E_{11}=\\E_{23}=\end{array}\right\}4Dq-2\lambda+(6/5)(\lambda^2/Dq)$	$\Psi_{4}=(1/12)^{\frac{1}{2}}[(-2-2)+(2-2)-(-22)-(22)-2(1-1)+2(-11)]$ $\Psi_{11}=(1/24)^{\frac{1}{2}}[3(-12)-2(-2-1)-2(2-1)+(-1-2)]+\frac{1}{2}(10)$ $\Psi_{23}=(1/24)^{\frac{1}{2}}[3(1-2)-2(21)-2(-21)+(12)]+\frac{1}{2}(-10)$
$E_6=4Dq-2\lambda+(12/5)(\lambda^2/Dq)$	$\Psi_{6}=(1/12)^{\frac{1}{2}}[(-2-2)+(2-2)-(-22)-(22)+2(1-1)-2(-11)]$
$E_3=-6Dq-(12/5)(\lambda^2/Dq)$	$\Psi_{3}=(1/8)^{\frac{1}{2}}[-(-2-2)+(2-2)+(-22)-(22)+2(00)]$
$\left.\begin{array}{r}E_{9}=\\E_{2}=\\E_{21}=\end{array}\right\}-6Dq-(9/5)(\lambda^2/Dq)$	$\Psi_{9}=(1/8)^{\frac{1}{2}}[-(-2-1)+(2-1)]+(3/4)^{\frac{1}{2}}(01)$ $\Psi_{2}=\frac{1}{2}[(-2-2)-(2-2)+(-22)-(22)]$ $\Psi_{21}=(1/8)^{\frac{1}{2}}[-(21)+(-21)]+(3/4)^{\frac{1}{2}}(0-1)$
$\left.\begin{array}{r}E_{1}=\\E_{14}=\end{array}\right\}-6Dq-(6/5)(\lambda^2/Dq)$	$\Psi_{1}=(1/8)^{\frac{1}{2}}[(-2-2)-(2-2)-(-22)+(22)+2(00)]$ $\Psi_{14}=\frac{1}{2}[(-20)-(20)+(0-2)-(02)]$
$\left.\begin{array}{r}E_{8}=\\E_{15}=\\E_{20}=\end{array}\right\}-6Dq-\frac{3}{5}(\lambda^2/Dq)$	$\Psi_{8}=(3/8)^{\frac{1}{2}}[(-2-1)-(2-1)]+\frac{1}{2}(01)$ $\Psi_{15}=(1/2)^{\frac{1}{2}}[(0-2)+(02)]$ $\Psi_{20}=(3/8)^{\frac{1}{2}}[(21)-(-21)]+\frac{1}{2}(0\text{-}1)$
$E_{16}=-6Dq,$	$\Psi_{16}=\frac{1}{2}[(-20)-(20)-(0-2)+(02)]$

TABLE II. The energy levels of the ground state of the d_6 configuration in a cubic field in a weak magnetic field ($h\ll\lambda^2/Dq$). The energy levels have been calculated (*a*) for the part not dependent on h to an accuracy of λ^2/Dq, (*b*) for the linear Zeeman effect to an accuracy of $\lambda h/Dq$, i.e., terms such as $(\lambda^2/Dq)h$ have been neglected, (*c*) for the quadratic Zeeman effect to an accuracy of $(Dq/\lambda^2)h^2$.

E_1	$-6Dq-(6/5)(\lambda^2/Dq)$		$+(40/3)(Dqh^2/\lambda^2)$
E_2	$-6Dq-(9/5)(\lambda^2/Dq)$		
E_3	$-6Dq-(12/5)(\lambda^2/Dq)$		$-(40/3)(Dqh^2/\lambda^2)$
E_4	$4Dq-2\lambda+(6/5)(\lambda^2/Dq)$		$-(10/3)(Dqh^2/\lambda^2)$
E_5	$4Dq+\lambda+(6/5)(\lambda^2/Dq)$		$+15(Dqh^2/\lambda^2)$
E_6	$4Dq-2\lambda+(12/5)(\lambda^2/Dq)$		$+(10/3)(Dqh^2/\lambda^2)$
E_7	$4Dq+\lambda+\frac{3}{5}(\lambda^2/Dq)$		$-15(Dqh^2/\lambda^2)$
E_8	$-6Dq-\frac{3}{5}(\lambda^2/Dq)$	$-h+\frac{3}{5}(\lambda h/Dq)$	$+\frac{5}{2}Dqh^2/\lambda^2$
E_9	$-6Dq-(9/5)(\lambda^2/Dq)$	$+h+\frac{1}{5}(\lambda h/Dq)$	$-\frac{5}{2}Dqh^2/\lambda^2$
E_{10}	$4Dq-2\lambda+(6/25)(\lambda^2/Dq)$	$+\frac{3}{2}h-(6/25)(\lambda h/Dq)$	$-(125/32)(Dqh^2/\lambda^2)$
E_{11}	$4Dq-2\lambda+(6/5)(\lambda^2/Dq)$	$+\frac{1}{2}h-\frac{2}{5}(\lambda h/Dq)$	$+(125/32)(Dqh^2/\lambda^2)$
E_{12}	$4Dq+\lambda+\frac{3}{5}(\lambda^2/Dq)$	$-\frac{3}{2}h+\frac{1}{5}(\lambda h/Dq)$	
E_{13}	$4Dq+3\lambda+(9/25)(\lambda^2/Dq)$	$-\frac{7}{2}h-(9/25)(\lambda h/Dq)$	
E_{14}	$-6Dq-(6/5)(\lambda^2/Dq)$		$-(40/3)(Dqh^2/\lambda^2)$
E_{15}	$-6Dq-\frac{3}{5}(\lambda^2/Dq)$		
E_{16}	$-6Dq$		$+(40/3)(Dqh^2/\lambda^2)$
E_{17}	$4Dq-2\lambda+(6/25)(\lambda^2/Dq)$		
E_{18}	$4Dq+\lambda+(6/5)(\lambda^2/Dq)$		
E_{19}	$4Dq+3\lambda+(9/25)(\lambda^2/Dq)$		
E_{20}	$-6Dq-\frac{3}{5}(\lambda^2/Dq)$	$+h-\frac{3}{5}(\lambda h/Dq)$	$+\frac{5}{2}(Dqh^2/\lambda^2)$
E_{21}	$-6Dq-(9/5)(\lambda^2/Dq)$	$-h-\frac{1}{5}(\lambda h/Dq)$	$-\frac{5}{2}(Dqh^2/\lambda^2)$
E_{22}	$4Dq-2\lambda+(6/25)(\lambda^2/Dq)$	$-\frac{3}{2}h+(6/25)(\lambda h/Dq)$	$-(125/32)(Dqh^2/\lambda^2)$
E_{23}	$4Dq-2\lambda+(6/5)(\lambda^2/Dq)$	$-\frac{1}{2}h+\frac{2}{5}(\lambda h/Dq)$	$+(125/32)(Dqh^2/\lambda^2)$
E_{24}	$4Dq+\lambda+\frac{3}{5}(\lambda^2/Dq)$	$+\frac{3}{2}h-\frac{1}{5}(\lambda h/Dq)$	
E_{25}	$4Dq+3\lambda+(9/25)(\lambda^2/Dq)$	$+\frac{7}{2}h+(9/25)(\lambda h/Dq)$	

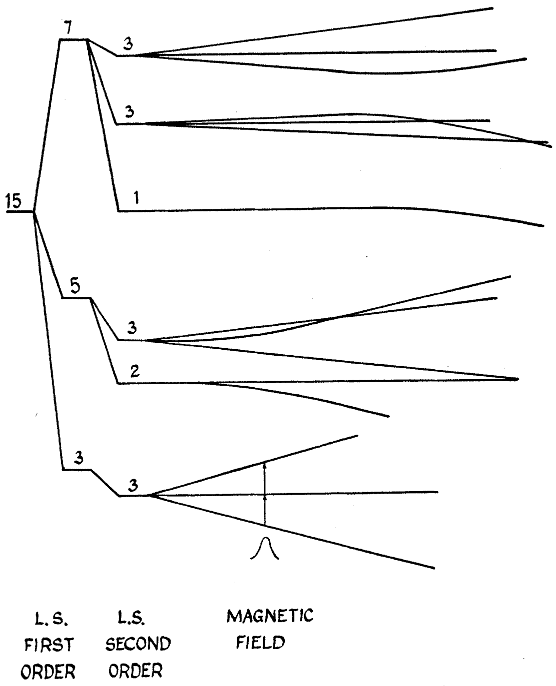

FIG. 2. Energy level scheme of the orbital triplet in weak and strong magnetic fields. The energy levels are given by Eqs. (5) and (8). The order, using the notation of Eq. (5) is 13, 19, 25 for the lowest triplet; 5, 18; 12, 7, 24 for the following doublet and triplet; 6; 11, 4, 23; 10, 17, 22 for the singlet, triplet, and highest triplet.

If the ground state is the orbital triplet, i.e., in octahedral symmetry, (Dq negative), the lowest state is a triplet and the g factor given by

$$g=\tfrac{7}{2}+(9/25)(\lambda/Dq). \tag{4}$$

If the symmetry is eight coordinated, the lowest level will be a singlet and will show no Zeeman splitting. The next level is a triplet with a g factor of about

$$g=1+\tfrac{1}{5}(\lambda/Dq) \tag{5}$$

in which Dq is now positive (λ is negative).

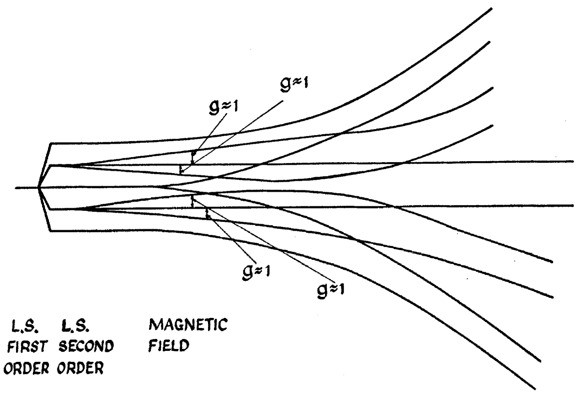

FIG. 3. Energy level scheme of the orbital doublet in weak and strong magnetic field. The energy levels are given by Eqs. (5) and (8).

The right-hand side of Fig. 1 indicates the effect of a weak magnetic field.

(*b*) *Intermediate magnetic fields* ($\lambda^2/Dq \ll h \ll \lambda$)

The energy levels as shown by perturbation calculations are given in Table III. The energy levels for weak and intermediate fields are shown in Fig. 2 and Fig. 3.

Axial Field

There are two axial fields to be considered. One in which the axial field is along one of the cubic axis. The energy levels of this case can easily be obtained from Matrix II since A_2 is along the diagonal. The case in which the axial field b_2 is along the [111] direction is a little more complicated. In this case the axis of quantization is the [111] direction and the cubic matrix has to be transformed to this direction. The cubic matrix is diagonalized and a perturbation theory is applied. Two cases are considered.

TABLE III. The energy levels of the ground state of the d^6 configuration is a cubic field in intermediate magnetic fields. ($\lambda^2/Dq \ll h \ll \lambda$).

$$\begin{aligned}
E_1&=-6Dq-(9/5)(\lambda^2/Dq)+4h\\
E_2&=-6Dq-(9/5)(\lambda^2/Dq)\\
E_3&=-6Dq-(9/5)(\lambda^2/Dq)-4h\\
E_4&=4Dq-2\lambda+(9/5)(\lambda^2/Dq)-2h\\
E_5&=4Dq+\lambda+(9/10)(\lambda^2/Dq)+3h\\
E_6&=4Dq-2\lambda+(9/5)(\lambda^2/Dq)+2h\\
E_7&=4Dq+\lambda+(9/10)(\lambda^2/Dq)-3h\\
E_8&=-6Dq-\tfrac{3}{2}(\lambda^2/Dq)-2h\\
E_9&=-6Dq-(9/10)(\lambda^2/Dq)-2h\\
E_{10}&=4Dq-2\lambda+(21/25)(\lambda^2/Dq)-h\\
E_{11}&=4Dq-2\lambda+\tfrac{3}{5}(\lambda^2/Dq)+3h\\
E_{12}&=4Dq+\lambda+\tfrac{3}{5}(\lambda^2/Dq)-\tfrac{3}{2}h\\
E_{13}&=4Dq+3\lambda+(9/25)(\lambda^2/Dq)-\tfrac{7}{2}h\\
E_{14}&=-6Dq-\tfrac{3}{5}(\lambda^2/Dq)-4h\\
E_{15}&=-6Dq-\tfrac{3}{5}(\lambda^2/Dq)\\
E_{16}&=-6Dq-\tfrac{3}{5}(\lambda^2/Dq)+4h\\
E_{17}&=4Dq-2\lambda+(6/25)(\lambda^2/Dq)\\
E_{18}&=4Dq+\lambda+(6/5)(\lambda^2/Dq)\\
E_{19}&=4Dq+3\lambda+(9/25)(\lambda^2/Dq)\\
E_{20}&=-6Dq-(9/10)(\lambda^2/Dq)+2h\\
E_{21}&=-6Dq-\tfrac{3}{2}(\lambda^2/Dq)-2h\\
E_{22}&=4Dq-2\lambda+\tfrac{3}{5}(\lambda^2/Dq)-3h\\
E_{23}&=4Dq-2\lambda+(21/25)(\lambda^2/Dq)+h\\
E_{24}&=4Dq+\lambda+\tfrac{3}{5}(\lambda^2/Dq)+\tfrac{3}{2}h\\
E_{25}&=4Dq+3\lambda+(9/25)(\lambda^2/Dq)+\tfrac{7}{2}h
\end{aligned}$$

(*a*) *Axial field compared with the spin orbit coupling* ($b_2 \gg \lambda\,\mathbf{L}\cdot\mathbf{S}$)

The energy levels are given in Table IV [neglecting terms of the order of λ^2/Dq or $(\lambda^2/Dq)\cdot(\lambda/b_2)$].

TABLE IV. Energy levels of the ground state of the d^6 configuration in a cubic and axial field. The axial field is strong compared with the spin-orbit coupling and both are larger than the magnetic perturbation. ($Dq \gg b_2 \gg \lambda L\cdot S \gg h$). Terms of the order λ^2/Dq or $\lambda^2/Dq\cdot\lambda/b_2$ are neglected.

		Admixture of the order of λ/b_2 by
$E_1=-6Dq+\frac{4}{5}(\lambda b_2/Dq)-\frac{1}{5}(b_2^2/Dq)-4h$	$\Phi_1=(1/3)^{\frac{1}{2}}(2-2)+(2/3)^{\frac{1}{2}}(-1-2)$	Φ_4
$E_2=-6Dq+\frac{4}{5}(\lambda b_2/Dq)-\frac{1}{5}(b_2^2/Dq)+4h$	$\Phi_2=(1/3)^{\frac{1}{2}}(-22)-(2/3)^{\frac{1}{2}}(1\ 2)$	Φ_3
$E_3=-6Dq-\frac{2}{5}(\lambda b_2/Dq)-\frac{1}{5}(b_2^2/Dq)$	$\Phi_3=(1/6)^{\frac{1}{2}}(2\ 1)+(1/3)^{\frac{1}{2}}(-11)+(1/6)^{\frac{1}{2}}(-2-1)-(1/3)^{\frac{1}{2}}(1-1)$	Φ_2, Φ_4
$E_4=-6Dq-\frac{2}{5}(\lambda b_2/Dq)-\frac{1}{5}(b_2^2/Dq)$	$\Phi_4=(1/6)^{\frac{1}{2}}(-2-1)-(1/3)^{\frac{1}{2}}(1-1)-(1/6)^{\frac{1}{2}}(2\ 1)-(1/3)^{\frac{1}{2}}(-1\ 1)$	Φ_1, Φ_3
$E_5=4Dq+b_2-2\lambda-\frac{4}{5}(\lambda b_2/Dq)+\frac{1}{5}(b_2^2/Dq)+3h$	$\Phi_5=(2/3)^{\frac{1}{2}}(-2\ 2)+(1/3)^{\frac{1}{2}}(+1+2)$	
$E_6=4Dq+b_2-2\lambda-\frac{4}{5}(\lambda b_2/Dq)+\frac{1}{5}(b_2^2/Dq)-3h$	$\Phi_6=-(2/3)^{\frac{1}{2}}(2-2)+(1/3)^{\frac{1}{2}}(-1-2)$	
$E_7=4Dq+b_2+\lambda+\frac{2}{5}(\lambda b_2/Dq)+\frac{1}{5}(b_2^2/Dq)$	$\Phi_7=(1/3)^{\frac{1}{2}}(-2-1)+(1/6)^{\frac{1}{2}}(1-1)-(1/3)^{\frac{1}{2}}(2\ 1)+(1/6)^{\frac{1}{2}}(-1\ 1)$	Φ_9
$E_8=4Dq+b_2+\lambda+\frac{2}{5}(\lambda b_2/Dq)+\frac{1}{5}(b_2^2/Dq)$	$\Phi_8=-(1/3)^{\frac{1}{2}}(2\ 1)+(1/6)^{\frac{1}{2}}(-11)-(1/3)^{\frac{1}{2}}(-2-1)-(1/6)^{\frac{1}{2}}(1-1)$	
$E_9=4Dq-2b_2$	$\Phi_9=(0\ 0)$	Φ_7
$E_{10}=-6Dq-\frac{4}{5}(\lambda b_2/Dq)-\frac{1}{5}(b_2^2/Dq)+4h$	$\Phi_{10}=(1/3)^{\frac{1}{2}}(2\ 2)+(2/3)^{\frac{1}{2}}(-1\ 2)$	Φ_{11}
$E_{11}=-6Dq-\frac{1}{5}(b_2^2/Dq)$	$\Phi_{11}=(1/3)^{\frac{1}{2}}(-2\ 0)-(2/3)^{\frac{1}{2}}(1\ 0)$	Φ_{10}, Φ_{12}
$E_{12}=-6Dq+\frac{2}{5}(\lambda b_2/Dq)-\frac{1}{5}(b_2^2/Dq)-2h$	$\Phi_{12}=(1/3)^{\frac{1}{2}}(2-1)+(2/3)^{\frac{1}{2}}(-1-1)$	Φ_{11}
$E_{13}=4Dq-2b_2-4h$	$\Phi_{13}=(0-2)$	Φ_{15}
$E_{14}=4Dq+b_2+\frac{1}{5}(b_2^2/Dq)-h$	$\Phi_{14}=(2/3)^{\frac{1}{2}}(-2\ 0)+(1/3)^{\frac{1}{2}}(1\ 0)$	Φ_{16}
$E_{15}=4Dq+b_2-\lambda-\frac{2}{5}(\lambda b_2/Dq)+\frac{1}{5}(b_2^2/Dq)-h$	$\Phi_{15}=(2/3)^{\frac{1}{2}}(2-1)+(1/3)^{\frac{1}{2}}(-1-1)$	Φ_{13}
$E_{16}=4Dq-2b_2+2h$	$\Phi_{16}=(0\ 1)$	Φ_{14}, Φ_{17}
$E_{17}=4Dq+b_2+2\lambda+\frac{4}{5}(\lambda b_2/Dq)+\frac{1}{5}(b_2^2/Dq)+5h$	$\Phi_{17}=-(2/3)^{\frac{1}{2}}(2\ 2)+(1/3)^{\frac{1}{2}}(-1\ 2)$	Φ_{16}
$E_{18}=-6Dq-\frac{4}{5}(\lambda b_2/Dq)-\frac{1}{5}(b_2^2/Dq)-4h$	$\Phi_{18}=(1/3)^{\frac{1}{2}}(-2-2)-(2/3)^{\frac{1}{2}}(1-2)$	Φ_{19}
$E_{19}=-6Dq-\frac{1}{5}b_2^2/Dq$	$\Phi_{19}=(1/3)^{\frac{1}{2}}(2\ 0)+(2/3)^{\frac{1}{2}}(-1\ 0)$	Φ_{18}, Φ_{20}
$E_{20}=-6Dq+\frac{2}{5}(\lambda b_2/Dq)-\frac{1}{5}(b_2^2/Dq)+2h$	$\Phi_{20}=(1/3)^{\frac{1}{2}}(-2\ 1)-(2/3)^{\frac{1}{2}}(1\ 1)$	Φ_{19}
$E_{21}=4Dq-2b_2+4h$	$\Phi_{21}=(0\ 2)$	Φ_{23}
$E_{22}=4Dq+b_2+\frac{1}{5}(b_2^2/Dq)+h$	$\Phi_{22}=-(2/3)^{\frac{1}{2}}(2\ 0)+(1/3)^{\frac{1}{2}}(-1\ 0)$	Φ_{24}
$E_{23}=4Dq+b_2-\lambda-\frac{1}{5}(\lambda b_2/Dq)+\frac{1}{5}(b_2^2/Dq)+h$	$\Phi_{23}=(2/3)^{\frac{1}{2}}(-2\ 1)+(1/3)^{\frac{1}{2}}(1\ 1)$	Φ_{21}
$E_{24}=4Dq-2b_2-2h$	$\Phi_{24}=(0\ -1)$	Φ_{22}, Φ_{25}
$E_{25}=4Dq+b_2+2\lambda+\frac{4}{5}(\lambda b_2/Dq)+\frac{1}{5}(b_2^2/Dq)-5h$	$\Phi_{25}=(2/3)^{\frac{1}{2}}(-2-2)+(1/3)^{\frac{1}{2}}(1-2)$	Φ_{24}

(*b*) *The axial field is weak compared with the spin-orbit coupling:* $[\lambda(\mathbf{L}\cdot\mathbf{S})>b_2]$

These energy levels are given in Table V.

The various cases are illustrated in Figures 1, 4, and 5. The left-hand side of Fig. 1 indicates the level scheme in which the axial field (along [100]) is weaker than the first order $\mathbf{L}\cdot\mathbf{S}$ perturbation, but stronger than the second order correction. Figure 4 gives the case in which the axial field is stronger than the first order spin-orbit perturbation. Figure 5 indicates the very weak field case for the Γ_3 level in which the axial field is weaker than the second order $L\,S$ perturbation. It is to be noticed that in these very weak fields the lowest doublet has a $g_{\parallel}\sim 2$, $g_{\perp}=0$ along the [100] direction.

B. INFLUENCE OF CONFIGURATION INTERACTION (d^5p) ON THE ENERGY LEVELS OF d^6 IN A TETRAHEDRAL FIELD

The crystal field potential of a tetrahedron differs from that given in Eq. (2) in that it contains odd spherical harmonics. The potential expressed in cartesian coordinates, assuming a point charge model, is given to sixth order in (r/b) by

$$V=\frac{Ze}{b}\left[4+\frac{20}{3^{\frac{1}{2}}}\frac{xyz}{b^3}-\frac{35}{9}\left(\frac{x^4+y^4+z^4-\frac{3}{5}r^4}{b^4}\right)\left(1+12\frac{r^2}{b^2}\right)+\frac{308}{9}\left(\frac{x^6+y^6+z^6-(3/7)\,r^6}{b^6}\right)\right]. \qquad (6)$$

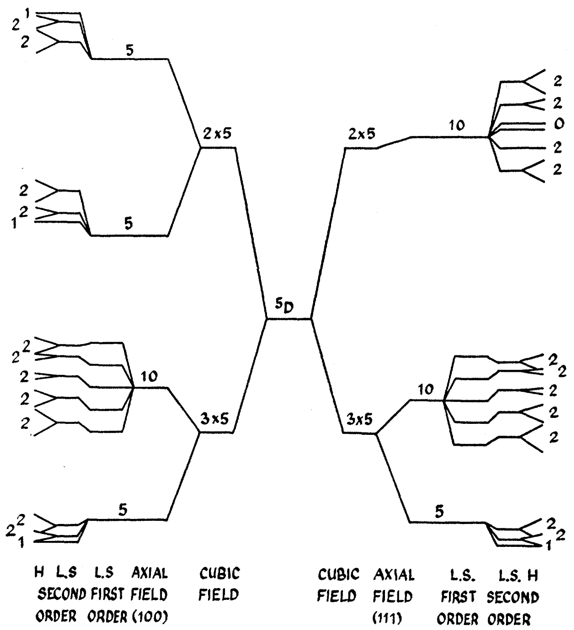

FIG. 4. Energy level scheme in a very strong cubic field, and axial field stronger than the spin orbit interaction in an external magnetic field. The right-hand side shows the splitting in the trigonal case. The g factor of the lowest levels is approximately 0, 4, and 8 for the singlet, and two doublets. The g factor of the lowest doublet of the Γ_3 state is approximately 8. The right-hand side shows the splitting for the tetragonal case (axial field along the [100] direction).

TABLE V. Energy levels of the ground state of the d^6 configuration in a cubic and axial field. The axial field is weak compared with the spin-orbit coupling ($Dq \gg \lambda L \cdot S \gg b_2 \gg h$).

$$E_1 = -6Dq - (1/45)(b_2^2/Dq)$$
$$E_2 = -6Dq - (12/5)(\lambda^2/Dq) - (17/45)(b_2^2/Dq)$$
$$E_3 = -6Dq - \tfrac{3}{5}(\lambda^2/Dq) - (1/45)(b_2^2/Dq) + \tfrac{2}{5}(\lambda b_2/Dq)$$
$$E_4 = -6Dq - (9/5)(\lambda^2/Dq) - (17/45)(b_2^2/Dq) + \tfrac{2}{5}(\lambda b_2/Dq)$$
$$E_5 = 4Dq - 2\lambda + b_2 + (6/5)(\lambda^2/Dq) + \tfrac{1}{5}(b_2^2/Dq) - \tfrac{4}{5}(\lambda b_2/Dq) + 3h$$
$$E_6 = 4Dq - 2\lambda + b_2 + (6/5)(\lambda^2/Dq) + \tfrac{1}{5}(b_2^2/Dq) - \tfrac{4}{5}(\lambda b_2/Dq) - 3h$$
$$E_7 = 4Dq - 2\lambda - \tfrac{4}{5}b_2 + (36/25)(\lambda^2/Dq) + (2/25)(b_2^2/Dq) + (16/25)(\lambda b_2/Dq) - (54/125)(b_2^2/\lambda)$$
$$E_8 = 4Dq + \lambda + b_2 + \tfrac{3}{5}(\lambda^2/Dq) + \tfrac{1}{5}(b_2^2/Dq) + \tfrac{2}{5}(\lambda b_2/Dq)$$
$$E_9 = 4Dq + 3\lambda - \tfrac{1}{5}b_2 + (9/25)(\lambda^2/Dq) + (3/25)(b_2^2/Dq) - (6/25)(\lambda b_2/Dq) + (54/125)(b_2^2/\lambda)$$
$$E_{10} = -6Dq - \tfrac{3}{5}(\lambda^2/Dq) + \tfrac{1}{10}(b_2^2/Dq) - \tfrac{1}{5}(\lambda b_2/Dq) + h$$
$$E_{11} = -6Dq - (6/5)(\lambda^2/Dq) - \tfrac{1}{5}(b_2^2/Dq)$$
$$E_{12} = -6Dq - (9/5)(\lambda^2/Dq) - \tfrac{1}{2}(b_2^2/Dq) - \tfrac{1}{5}(\lambda b_2/Dq) + h$$
$$E_{13} = 4Dq + \lambda - b_2 - 3h + \tfrac{2}{3}\, b_2^2/\lambda$$
$$E_{14} = 4Dq - 2\lambda - \tfrac{3}{5}b_2 + h - (208/375)(b_2^2/\lambda)$$
$$E_{15} = 4Dq - 2\lambda - 2h - \tfrac{2}{3}b_2^2/\lambda$$
$$E_{16} = 4Dq + \lambda + \tfrac{1}{2}b_2 + \tfrac{3}{2}h + (1/24)(b_2^2/\lambda)$$
$$E_{17} = 4Dq + 3\lambda + \tfrac{1}{10}b_2 + \tfrac{7}{2}h + (513/1000)(b_2^2/\lambda)$$
$$E_{18} = -6Dq - \tfrac{3}{5}\lambda^2/Dq + \tfrac{1}{10}b_2^2/Dq - \tfrac{1}{5}\lambda b_2/Dq - h$$
$$E_{19} = -6Dq - (6/5)\lambda^2/Dq - \tfrac{1}{5}b_2^2/Dq$$
$$E_{20} = -6Dq - (9/5)\lambda^2/Dq - \tfrac{1}{2}b_2^2/Dq - \tfrac{1}{5}\lambda b_2/Dq - h$$
$$E_{21} = 4Dq + \lambda - b_2 + 3h + \tfrac{2}{3}b_2^2/\lambda$$
$$E_{22} = 4Dq - 2\lambda - \tfrac{3}{5}b_2 - h - (208/375)(b_2^2/\lambda)$$
$$E_{23} = 4Dq - 2\lambda + 2h - \tfrac{2}{3}b_2^2/\lambda$$
$$E_{24} = 4Dq + \lambda + \tfrac{1}{2}b_2 - \tfrac{3}{2}h + (1/24)b_2^2/\lambda$$
$$E_{25} = 4Dq + 3\lambda + \tfrac{1}{10}b_2 - \tfrac{7}{2}h + (513/1000)b_2^2/\lambda$$

Here b is the distance between adjacent ions.

Expressing this in normalized spherical harmonics, this can be written

$$\begin{aligned} V = (Ze/b)\{&4 + (20/3)(2\pi/35)^{\frac{1}{2}}(r/b)^3(Y_3^2 + Y_3^{-2}) \\ &- (\tfrac{1}{2})(4\pi/9)^{\frac{1}{2}}(r/b)^4[(28/9)Y_4^0 - (2/9)(70)^{\frac{1}{2}} \\ &\times (Y_4^4 + Y_4^{-4})][1 + 12(r/b)^2] + (\tfrac{1}{2})(4\pi/13)^{\frac{1}{2}} \\ &\times (r/b)^6[(16/9)Y_6^0 + (8/9)(14)^{\frac{1}{2}} \\ &\times (Y_6^4 + Y_6^{-4})]\}. \end{aligned} \tag{6a}$$

For d electrons, the potential, therefore, consists of two terms: U^3 odd in spherical harmonics and U^4 even in spherical harmonics. U^4 has the same form as the potentials given in Eq. (2b) except for a factor of $\frac{1}{2}$. As long as we calculate matrix elements of the type $\langle d|V|d\rangle$ the odd part of the potential will not contribute since on replacing x, y, z by $-x$, $-y$, $-z$, the potential $V \rightarrow -V$, but $\int \Psi_d \Psi_d d\tau$ does not change sign. The energy level scheme is then given as calculated in (A). However, if one considers an odd configuration such as d^5p or d^5f the matrix elements $(d|U^3|p)$ and $(d|U^3|f)$ will differ from zero.[3] It is the purpose of this section to estimate this perturbation.

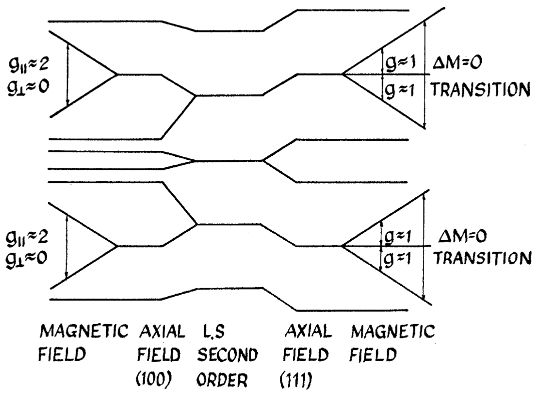

FIG. 5. Energy levels in an external magnetic field for the case where the axial field is weaker than the first and second order spin-orbit interaction perturbation. Only the levels of the Γ_3 state are shown.

There are two ways to approach the problem. One way is to construct the strong crystal field wave functions describing the e and t_2 energy levels. The "corrected" wave functions will be a linear combination of the strong field functions of the d, p, and f electrons. For example the t_2 functions will have the form

$$\Phi(t_2) = \Psi_0(t_2) + a\Psi(4p_i) + b\Psi(4f_i)$$

where a and b will be a measure of the admixture. These wave functions can then be used to calculate the energy separation of the Γ_3 and Γ_5 levels. Another method, used here, is to consider the effect on the ground state of the various excited levels of the two higher configurations. This scheme is more suitable for the weak field case which is that usually found in tetrahedral symmetries.

We shall make the following simplifying assumptions:

1. A point charge model is assumed and the overlap of the charge distributions between the ion and the

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[3] Because of the triangle condition and parity only the d^5p and d^5f configuration interact with d^6 through U^3.

surroundings is neglected. The effect of the covalent bonding can later be taken into account by constructing the appropriate linear combination of atomic orbitals.

2. We shall assume that energy difference between the excited configurations and the ground state is the same as in the free ion. This will certainly not be correct since the constant part of the potential differs in the excited configuration from that of the d^6 configuration. Further because of the overlap of the wave function on the adjacent ions the spectrum resembles probably more the Coulomb energy of Mn^{2+} and the corresponding Coulomb energy will be smaller. In view of the absence of experimental data in a crystal we shall assume the energy difference between the centers of gravity of the excited configurations and the ground state to be about 100 000 and 150 000 cm^{-1}, respectively. Since in all probability the separation in a crystal is smaller this will give a lower limit in the perturbation.

3. It is found experimentally that the crystal field splittings in tetrahedral symmetry are small compared with the term separation. We shall neglect the Stark splittings, caused by the U^4 or U^3 terms of the excited levels (and similarly that caused by $\Sigma\, e^2/r_{ij}$). These splittings will effect only in second order our calculations of the separation of the Γ_3 and Γ_5 levels. The fine structure splitting of the ground state levels (caused by spin orbit interaction) will however be effected indirectly by this splitting. The main effect of the d^5p configuration on this fine structure separation of the gound state is by terms of the form

$$\frac{(d^6|U^3|d^5p)(d^5p|\mathbf{L}\cdot\mathbf{S}|d^5p)(d^5p|U^3|d^6)}{(E_{d^5p}-E_{d^6})^2}.$$

The effect of the fine structure splitting of the excited states (split mainly by U^4) on the fine structure of the ground state is given by terms of the form

$$\frac{(d^6|U^3|d^5p)(d^5p|\mathbf{L}\cdot\mathbf{S}|d^5p)(d^5p|U^4|d^5p)(d^5p|U^3|d^6)}{(E_{d^5p}-E_{d^6})^3}$$

and similar terms for d^5f. Since this is a third order calculation this is to be considered small.

It is to be noticed that the magnitude of the splitting of $(d^5p|U^4|d^5p)$ may differ considerably since the magnitude of the crystal field potential is different in an excited configuration.

4. We shall neglect the interaction of the configuration such as d^5np with d^5nf with $n=5, 6\cdots$. This interaction yields the same matrix elements as the interaction with d^54p and d^54f, only the radial integrals and the energy level separations being different. The only effect of these configurations is, therefore, to change the effective value of the radial integrals. Since the effect of these higher configurations is small and since the radial integrals can at best be only estimated we shall neglect the effect of these configurations.

5. We have also neglected the effect of the configuration interactions such as d^54s, induced by electron correlation term $\Sigma\, e^2/r_{ij}$ on the separation of the Γ_3 and Γ_5 levels. It is felt that this mixing may be smaller than the perturbation caused by the odd part of the potential.

We shall follow the notation and methods of Racah.[4] We indicate here the calculation for the perturbation by the $3d^54p$ configuration. The calculations for the $3d^54f$ configuration follow the same lines. According to the Wigner-Eckart theorem the matrix elements to be calculated may be written:

$$\begin{aligned}(3d^6\,{}^5DM|U_q^3|3d^5\,4p\,{}^5LM')&\\ =(-1)^{2+M}(3d^6\,{}^5D\|U^3\|3d^5\,4p\,{}^5LV(2L3;-MM'q)&\\ =[(-1)^{3-q+2+M}/\sqrt{7}](3d^6\,{}^5D\|U^3\|3d^5\,4p\,{}^5L)&\\ \times(2L-MM')|(2L3-q).& \quad (7)\end{aligned}$$

The transformation from the l scheme to the L scheme is given by Racah [II, Eq. (44b)] and is

$$\begin{aligned}(3d^5\,L'd\,{}^5D\|U^3\|3d^5\,L'p\,{}^5L)&\\ =(-1)^{L'+3-2-1}(3d^5\,3d\|U^3\|3d^5\,4p)&\\ \times[2(2l+1)(2L+1)]^{\frac{1}{2}}W(221L;L'3)& \quad (8)\end{aligned}$$

where L' is the orbital angular momentum of the d^5 configuration, $W(221L;L'3)$ the Racah coefficient.

The wavefunction of the level ${}^5D$ of the configuration d^6 is a linear combination of the functions $3d^5L'd$ with different L' of the d^5 configuration. The coefficients of these functions, called fractional parentage, are not tabulated. They can, however, easily be obtained from the equation [Racah III, Eq. (19)]

$$\begin{aligned}[d^5(S'L')dSL[\![d^6\,SL]&\\ =(-1)^{S+S'+L+L'-2-\frac{1}{2}}\left[\frac{(4+1)(2S'+1)(2L'+1)}{6(2S+1)(2L+1)}\right]^{\frac{1}{2}}&\\ \times[d^4(SL)dS'L'[\![d^5S'L'].& \quad (9)\end{aligned}$$

Here $L=2$, $S=2$ and the values of L' are $L'=0$ $(S'=\frac{5}{2})$, $L'=1$ $(S'=\frac{3}{2})$, $L'=2$ $(S'=\frac{3}{2})$, $L'=3$ $(S'=\frac{3}{2})$, $L'=4$ $(S'=\frac{3}{2})$. The fractional parentage coefficients of d^4d are given by Racah. The calculated fractional parentage coefficients are given in Table VI.

We shall assume that for each term in the $3d^54p$ there corresponds one parent, i.e., to each L of a given level corresponds a definite L'.

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[4] G. Racah, Phys. Rev. **61**, 186 (1942), I; **62**, 438 (1942), II; **63**, 367 (1943), III.

TABLE VI. The effect of the perturbation by the d^5p configuration on the Γ_3 and Γ_5 levels.

Term	Coefficient of fractional parentage $[d^6\,{}^5D[\![d^5(L'')dD]$	Racah coefficients $W(221L,L''3)$	Normalization $[(2L'+1)(2L+1)/(2K+1)]^{\frac12}$ $=[(5/7)(2L+1)]^{\frac12}$	Perturbation of the Γ_3 level in units of $\lvert(3d\|U^3\lvert4p)\rvert^2/E(L)$	Perturbation of the Γ_5 level in units of $(3d\|U^3\|4p)^2/E(L)$
${}^5P({}^6S)$	$(1/5)^{\frac12}$	$(1/15)^{\frac12}$	$(15/7)^{\frac12}$	0	$\frac15(1/15)(15/7)(10/21)$
${}^5P({}^4P)$	$-(\frac1{10})^{\frac12}$	$\frac13(\frac15)^{\frac12}$	$(15/7)^{\frac12}$	0	$\frac1{10}(1/45)(15/7)(10/21)$
${}^5P({}^4D)$	$(\frac16)^{\frac12}$	$\frac15(1/21)^{\frac12}$	$(15/7)^{\frac12}$	0	$\frac16(1/525)(15/7)(10/21)$
${}^5D({}^4P)$	$-(\frac1{10})^{\frac12}$	$\frac15(\frac23)^{\frac12}$	$(25/7)^{\frac12}$	$\frac1{10}(2/75)(25/7)1$	0
${}^5D({}^4D)$	$(\frac16)^{\frac12}$	$\frac15(2/7)^{\frac12}$	$(25/7)^{\frac12}$	$\frac16(2/175)(25/7)1$	0
${}^5D({}^4F)$	$-(7/30)^{\frac12}$	1/35	$(25/7)^{\frac12}$	$(7/30)(1/1225)(25/7)1$	0
${}^5F({}^4D)$	$(\frac16)^{\frac12}$	$(2/35)(6)^{\frac12}$	$(5)^{\frac12}$	0	$\frac16(24/1215)(5)\frac23$
${}^5F({}^4F)$	$-(7/30)^{\frac12}$	$(1/7)(\frac3{10})^{\frac12}$	$(5)^{\frac12}$	0	$(7/30)(3/490)(5)\frac23$
${}^5F({}^4G)$	$(\frac3{10})^{\frac12}$	$(1/21)(\frac1{10})^{\frac12}$	$(5)^{\frac12}$	0	$\frac3{10}(1/4410)(5)\frac23$
${}^5G({}^4F)$	$-(7/30)^{\frac12}$	$(1/7)(\frac56)^{\frac12}$	$3(5/7)^{\frac12}$	$(7/30)(5/294)(45/7)(8/15)$	$(7/30)(5/294)(45/7)(14/45)$
${}^5G({}^4G)$	$(\frac3{10})^{\frac12}$	$\frac13(1/42)^{\frac12}$	$3(5/7)^{\frac12}$	$\frac3{10}(1/378)(45/7)(8/15)$	$\frac3{10}(1/378)(45/7)(14/15)$
${}^5H({}^4G)$	$(\frac3{10})^{\frac12}$	$\frac13(1/7)^{\frac12}$	$(55/7)^{\frac12}$	$\frac3{10}(1/63)(55/7)(21/55)$	$\frac3{10}(1/63)(55/7)(68/105)$

The matrix elements then are:

$$\begin{aligned}&(3d^6\,{}^5DM|U_q^3|3d^5\,4p\,{}^5L(L'')M')\\&\quad=(d^6\,{}^5D[\![d^5(L'')d\,{}^5D)(-1)^{2+M}(-1)^{L''+3-2-L}\\&\qquad\times(3d\|U^3\|4p)[(2L+1)5]^{\frac12}W(221L;L''3)\\&\qquad\quad\times[(-1)^{L-q}/\sqrt7](L2M'-M|L23-q).\qquad(10)\end{aligned}$$

We need in addition the various Racah coefficients. These can be calculated according to the formulas given by Rose,[5] or as tabulated by Biedenharn.[6] We list these in Table VI.

The configuration d^5p has the following quintuplet energy levels: ${}^5P$, ${}^5G$, ${}^5H$, ${}^5F$, ${}^5D$, and ${}^5S$ (see Table VI).

TABLE VII. The effect of the perturbation by the d^5f configuration on the Γ_3 and Γ_5 levels.

Term	Coefficient of fractional parentage	Racah coefficient	Normalization	Shift of Γ_3 level	Shift of Γ_5 level
${}^5P({}^4D)$	$(\frac16)^{\frac12}$	$(2/35)(6)^{\frac12}$	$(15/7)^{\frac12}$	0	$\frac16(24/1225)(15/7)(10/21)$
${}^5P({}^4F)$	$-(7/30)^{\frac12}$	$(1/7)(\frac3{10})^{\frac12}$	$(15/7)^{\frac12}$	0	$(7/30)(3/490)(15/7)(10/21)$
${}^5P({}^4G)$	$(\frac3{10})^{\frac12}$	$(1/21)(\frac1{10})^{\frac12}$	$(15/7)^{\frac12}$	0	$\frac3{10}(1/4410)(15/7)(10/21)$
${}^5D({}^4P)$	$-(\frac1{10})^{\frac12}$	$-\frac15(3/7)^{\frac12}$	$(5/7)^{\frac12}$	$\frac1{10}(3/175)(25/7)1$	0
${}^5D({}^4D)$	$(\frac16)^{\frac12}$	$(1/70)(6)^{\frac12}$	$(5/7)^{\frac12}$	$\frac16(6/4900)(25/7)1$	0
${}^5D({}^4F)$	$-(7/30)^{\frac12}$	$(\frac1{10})^{\frac12}$	$(5/7)^{\frac12}$	$(7/30)\frac1{10}(25/7)1$	0
${}^5D({}^4G)$	$(\frac3{10})^{\frac12}$	$(1/14)(\frac13)^{\frac12}$	$(5/7)^{\frac12}$	$\frac3{10}(1/588)(25/7)1$	0
${}^5F({}^6S)$	$(\frac15)^{\frac12}$	$(1/35)^{\frac12}$	$(5)^{\frac12}$	0	$\frac15(1/35)(5)\frac23$
${}^5F({}^4P)$	$-(\frac1{10})^{\frac12}$	$-\frac12(1/70)^{\frac12}$	$(5)^{\frac12}$	0	$\frac1{10}(1/280)(5)\frac23$
${}^5F({}^4D)$	$(\frac16)^{\frac12}$	$-(11/420)(6)^{\frac12}$	$(5)^{\frac12}$	0	$\frac16[726/(420)^2](5)\frac23$
${}^5F({}^4F)$	$-(7/30)^{\frac12}$	$(2/7)(1/15)^{\frac12}$	$(5)^{\frac12}$	0	$(7/30)(4/735)(5)\frac23$
${}^5F({}^4G)$	$(\frac3{10})^{\frac12}$	$(1/21)(11/4)^{\frac12}$	$(5)^{\frac12}$	0	$\frac3{10}(11/1764)(5)\frac23$
${}^5G({}^4P)$	$-(\frac1{10})^{\frac12}$	$\frac16(5/14)^{\frac12}$	$3(5/7)^{\frac12}$	$\frac1{10}(5/504)(45/7)(8/15)$	$\frac1{10}(5/504)(45/7)(14/45)$
${}^5G({}^4D)$	$(\frac16)^{\frac12}$	$-(1/14)(\frac32)^{\frac12}$	$3(5/7)^{\frac12}$	$\frac16(3/282)(45/7)(8/15)$	$\frac16(3/382)(45/7)(14/15)$
${}^5G({}^4F)$	$-(7/30)^{\frac12}$	0	$3(5/7)^{\frac12}$	0	0
${}^5G({}^4G)$	$(\frac3{10})^{\frac12}$	$(1/21)(11/3)^{\frac12}$	$3(5/7)^{\frac12}$	$\frac3{10}(11/1323)(45/7)(8/15)$	$\frac3{10}(11/1323)(45/7)(14/45)$
${}^5H({}^4D)$	$(\frac16)^{\frac12}$	$(1/7)(\frac16)^{\frac12}$	$(55/7)^{\frac12}$	$\frac16(1/294)(55/7)(21/55)$	$\frac16(1/294)(55/7)(68/165)$
${}^5H({}^4F)$	$-(7/30)^{\frac12}$	$-(1/14)(5/3)^{\frac12}$	$(55/7)^{\frac12}$	$(7/30)(5/588)(55/7)(21/55)$	$(7/30)(5/588)(55/7)(68/165)$
${}^5H({}^4G)$	$(\frac3{10})^{\frac12}$	$(1/42)(13)^{\frac12}$	$(55/7)^{\frac12}$	$\frac3{10}(13/1764)(55/7)(21/55)$	$\frac3{10}(13/1764)(55/7)(68/165)$

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[5] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).
[6] L. C. Biedenharn, Oak Ridge National Laboratory Report ORNL 1098 (unpublished).

The ${}^5S$ level does not perturb the ${}^5D$ level since the triangular condition Δ (D, S, 3) does not hold. Hence we have to calculate the effect of the other 5 levels, i.e.

$$(DM|U_q{}^3|LM')=\text{const}\times(L2M'-M|L23-q),\ q=\pm 2.$$

The appropriate Wigner coefficients are given in Table IV[4] in Condon and Shortley[7]:

From Eq. (10) the various matrices can be obtained. These matrices have $5(2L'+1)$ columns and lines. The matrices are evaluated by perturbation theory. Tables VI and VII summarize these calculations. The perturbations on the energy levels are given by

$$\begin{aligned}
{}^5P\text{ level}\quad & \Gamma_3=-6\,Dq,\\
& \Gamma_5\sim 4\,Dq-\frac{10}{21}\frac{\alpha^2}{E(P)},\\
{}^5D\text{ level}\quad & \Gamma_3\sim -6\,Dq-\frac{\alpha^2}{E(D)},\\
& \Gamma_5=4\,Dq,\\
{}^5F\text{ level}\quad & \Gamma_3=-6\,Dq,\\
& \Gamma_5\sim 4\,Dq-\frac{2}{3}\frac{\alpha^2}{E(F)},\\
{}^5G\text{ level}\quad & \Gamma_3\sim -6\,Dq-\frac{8}{15}\frac{\alpha^2}{E(G)},\\
& \Gamma_5\sim -4\,Dq-\frac{14}{45}\frac{\alpha^2}{E(G)},\\
{}^5H\text{ level}\quad & \Gamma_3\sim -6\,Dq-\frac{21}{55}\frac{\alpha^2}{E(H)},\\
& \Gamma_5\sim -4\,Dq-\frac{68}{165}\frac{\alpha^2}{E(H)},
\end{aligned}$$

where

$$\alpha=[d^6\,{}^5D]\!]d^5(L'')dD](3d\|U^3\|4p)W(221L;L''3)\times[(5/7)(2L+1)]^{\frac{1}{2}}(-1)^{1+L''}\qquad(12)$$

and similarly for the $d^5\,{}^4f$ configuration.

Assuming now that

$$E(P)\sim E(G)\sim E(F)\sim E(D)\sim E(H)\sim E_{d^5p}-E_{d^6}$$

we find the sums of column 5 and column 6 in Table VI to be 23/294 and 671/1751. The difference between these two sums is approximately $0.31[(d\|U^3\|p)^2/(E_{d^5p}-E_{d^6})]$. Similarly the sums of columns 5 and 6 in Table VII are 0.123 for the Γ_3 level and 0.0629 for the Γ_5 level and the relative separation has therefore increased by about $0.06[(d\|U^3\|f)^2/(E_{d^5f}-E_{d^6}]$.

The extent of the effect of this perturbation will depend critically on the knowledge of the radial integrals. These integrals are of course not known in the solid. One need to know the nature of the wave function including the overlap on the surroundings. An estimate of these integrals can be obtained by comparing it with the integral of $(d\|U^4\|d)$ which can be obtained from the experimentally observed spectra.

Consider ratio

$$\frac{(d\|U^3\|p)}{(d\|U^4\|d)}=\frac{\gamma(d\|Y_3\|p)\cdot I_1}{\delta(d\|Y_4\|d)\cdot I_2},\qquad(13)$$

where

$$I_1=\int R(3d)(r^3/b^4)R(4p)r^2dr,$$

$$I_2=\int R(3d)(r^4/b^5)R(3d)r^2dr,$$

and

$$\gamma=(20/3)(2\pi/35)^{\frac{1}{2}}Z_pe^2,$$

$$\delta=-(1/2)(4\pi/9)^{\frac{1}{2}}(28/9)Z_de^2.$$

The angular part in (18) can be calculated from

$$(l_i\|Y_1\|l_f)=(l_i\,1\,0\,0|l_i\,1\,l_f\,0)\frac{(2l_i+1)(2l+1)}{4\pi(2l_f+1)},\qquad(14)$$

and therefore

$$\frac{(d\|U^3\|p)}{(d\|U^4\|d)}=\frac{-10}{7}\left(\frac{5}{2}\right)^{\frac{1}{2}}\frac{Z_p}{Z_d}\frac{I_1}{I_2}.$$

Using hydrogenic wave function and taking $Z_p=2$–3, $Z_d=5$–6, and taking the distance between zinc and the sulfide ion to be about 2.3 A, one can evaluate these two integrals. It is found that the exact choice of these parameters is not very important in the evaluation of I_1/I_2. I_1 is only slightly smaller than I_2 (I_1 is about $-0.8\,I_2$).[8] The ratio (13) is therefore of the order of one. In Appendix II it is shown that $(d\|U^4\|d)=10(70)^{\frac{1}{2}}Dq$. Taking $Dq\sim 330$ cm^{-1} one finds $(d\|U^3\|p)$ of the order

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[7] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).

[8] Ligand integrals have recently been tabulated by C. J. Ballhausen and E. M. Ancmon, Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd. **31**, No. 9 (1958).

of 28 000 cm^{-1}. The relative depression of the Γ_3 and Γ_5 levels is therefore $0.3(28\,000)^2/10^5 \sim 2000$ cm^{-1}. The evaluation of the radial integral may be smaller possibly by 50% but on the other hand it is very likely that the relative separation between the two configurations in the tetrahedral symmetry may be only of the order of 5×10^4 cm^{-1}.

The radial integral of $\int R(3d)(r^3/b^4)R(4f)r^2dr$ can be evaluated similarly. Using hydrogen wave functions this radial integral is only a little larger than that of I_1. (It is about 1.3–1.5 I_1 depending on the effective charges used). The relative shift is therefore about (using the maximum valve of 1.5 I_1) $0.06(42\,000)^2/1.5(10)^5 \sim 700$ cm^{-1} or about one third of that of the $3d^54p$ configuration. The total shift (note that the two shifts have opposite signs, the d^54p perturbation shifts the Γ_5 level more than the Γ_3 level and the d^54f does the opposite) is therefore about 2000−700 or about 1300 cm^{-1}. These relative shifts will only be increased by means of the $3d^5np$ and $3d^5nf$ ($n=5\cdots$) configurations.

This shift of 1300 cm^{-1} is relatively large compared with the observed separation of about 3300 cm^{-1}. If these calculations should prove to be correct then the effective Dq value is larger than 330 cm^{-1} and the effect of the perturbation of the excited states even larger. However, because of the many approximations it is not at all certain that the perturbation may not be considerably smaller or even larger. However, if the perturbation is as large as estimated then the perturbation carried out above breaks down. Indeed one might expect other perturbations of the type

$$\frac{|(3d^6|U^3|3d^54p)|^2|(3d^54p|U^3|3d^54d)|^2}{(E_{3d^54p}-E_{3d^6})(E_{3d^54d}-E_{3d^6})(2)}$$

since $3d^54p$ and $3d^54d$ will interact through U^3 as well. These kind of successive perturbations (in which the off-diagonal elements are nearly as large as the diagonal elements) make the calculations unmanageable. The situation will of course be even worse in trivalent ions in tetrahedral fields since the crystal field (Dq) is usually much larger.

EXPERIMENTAL EVIDENCE

There are very few measured spectra of the iron group in the tetrahedral symmetry. One of these ions Fe^{2+} in ZnS is discussed in the following paper. It may be pertinent to remark here that if the configuration interaction is as large as outlined above it will have a considerable effect on the individual levels of the Γ_3 state. This is because these levels are very closely spaced of the order of a few cm^{-1} only. It is very likely that had we worked in a complete cubic field representation of the excited d^5p configuration and considered the perturbation of each excited Stark level, we would have found that the relative spacing of the close-lying levels would have changed drastically and possibly even the relative order of the levels might have been changed. Indeed this is one of the possible explanations of the g factor and the optical spectrum in ZnS, assuming it to arise from divalent iron.

The other more conclusive evidence is from the optical spectrum of divalent cobalt in spinels[9] (the paramagnetic resonance spectrum has been measured as well and indicates the spectrum is nearly isotropic). Crystal field theory predicts that the cobalt, which sits in the tetrahedral site, would have an orbital singlet as a ground state, and the next orbital triplets would be removed by about 10 Dq and 18 $Dq-\Delta$ where Δ is a small perturbation by the near P level. Weak field calculations yield also a ratio of 10:18. In cubic fields such as CaF$_2$ this ratio is obeyed fairly well in the case of Co^{2+}. Mrs. R. Stahl-Brada's data on this crystal indicate that the ratio of 10:18 is not obeyed, indeed the Γ_4 level is much higher than 18 Dq (by about 1300 cm^{-1}). Similarly the relative spacing of the fine structure of the various levels as well as the absolute spacing do not agree with those calculated from a pure cubic field of a d^3 configuration.

We are now actively engaged in investigating a number of other ions in tetrahedral symmetry.

Implications

If the above conjectures prove to be correct this will have a number of important implications. First of all it will prove to be difficult to calculate and correlate consistently the optical spectra since these calculations for all the levels will become very lengthy and laborious and in view of the many uncertainties unrewarding. Second these admixtures may have some effect on the intensities of the absorption lines. It is well known that intensities of the absorption lines in tetrahedral symmetry are stronger by a factor of about 20–100 than in the octahedral configuration. The admixture of the odd configuration will increase the intensities and it is possible that the increase can be as much as one hundred. Third these perturbations may effect both the Jahn-Teller instabilities as well as cation distributions amongst octahedral and tetrahedral sites in spinels.[9]

ACKNOWLEDGMENT

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[9] R. Stahl-Brada and W. Low (to be published).

APPENDIX I

Matrix I

General Matrix of the ground state of d^6 including cubic field Dq, axial field along the 1 0 0 direction A_2, spin orbit coupling λ, and external magnetic field $\beta H(L+2S)=h(L+2S)$.

$$\begin{array}{cccccccc}
M_L & -2 & 2 & -2 & 2 & 1 & 0 & -1 \\
M_S & -2 & -2 & 2 & 2 & -1 & 0 & 1 \\
 & -Dq+4\lambda+2A_2-6h & 5Dq & & & & & \\
 & 5Dq & -Dq-4\lambda+2A_2-2h & & & 2\lambda & & \\
 & & & -Dq-4\lambda+2A_2+2h & 5Dq & & & 2\lambda \\
 & & & 5Dq & -Dq+4\lambda+2A_2+6h & & & \\
 & & 2\lambda & & & 4Dq-\lambda-A_2-h & 3\lambda & \\
 & & & & & 3\lambda & -6Dq-2A_2 & 3\lambda \\
 & & & 2\lambda & & & 3\lambda & 4Dq-\lambda-A_2+h
\end{array}$$

$$\begin{array}{ccccccc}
M_L & -2 & 2 & -1 & 1 & 0 & -1 \\
M_S & -1 & -1 & -2 & 0 & 1 & 2 \\
 & -Dq+2\lambda+2A_2-4h & 5Dq & 2\lambda & & & \\
 & 5Dq & -Dq-2\lambda+2A_2 & & 6^{\frac{1}{2}}\lambda & & \\
 & 2\lambda & & 4Dq+2\lambda-A_2-5h & & & \\
 & & 6^{\frac{1}{2}}\lambda & & 4Dq-A_2+h & 3\lambda & \\
 & & & & 3\lambda & -6Dq-2A_2+2h & 6^{\frac{1}{2}}\lambda \\
 & & & & & 6^{\frac{1}{2}}\lambda & 4Dq-2\lambda-A_2+3h
\end{array}$$

$$\begin{array}{ccccccc}
M_L & -2 & 2 & -1 & 0 & 1 & 0 \\
M_S & 0 & 0 & -1 & -2 & 1 & 2 \\
 & -Dq+2A_2-2h & 5Dq & 6^{\frac{1}{2}}\lambda & & & \\
 & 5Dq & -Dq+2A_2+2h & & & 6^{\frac{1}{2}}\lambda & \\
 & 6^{\frac{1}{2}}\lambda & & 4Dq+\lambda-A_2-3h & 6^{\frac{1}{2}}\lambda & & \\
 & & & 6^{\frac{1}{2}}\lambda & -6Dq-2A_2-4h & & \\
 & & 6^{\frac{1}{2}}\lambda & & & 4Dq+\lambda-A_2+3h & 6^{\frac{1}{2}}\lambda \\
 & & & & & 6^{\frac{1}{2}}\lambda & -6Dq-2A_2+4h
\end{array}$$

$$\begin{array}{ccccccc}
M_L & 2 & -2 & 1 & -1 & 0 & 1 \\
M_S & 1 & 1 & 2 & 0 & -1 & -2 \\
 & -Dq+2\lambda+2A_2+4h & 5Dq & 2\lambda & & & \\
 & 5Dq & -Dq-2\lambda+2A_2 & & 6^{\frac{1}{2}}\lambda & & \\
 & 2\lambda & & 4Dq+2\lambda-A_2+5h & & & \\
 & & 6^{\frac{1}{2}}\lambda & & 4Dq-A_2-h & 3\lambda & \\
 & & & & 3\lambda & -6Dq-2A_2-2h & 6^{\frac{1}{2}}\lambda \\
 & & & & & 6^{\frac{1}{2}}\lambda & 4Dq-2\lambda-A_2-3h
\end{array}$$

Matrix II

This is Matrix I transformed so that the cubic field is along the diagonal. The wave functions Ψ are given in the text by Eq. (4).

$$\begin{array}{ccccccc}
\psi_1 & \psi_2 & \psi_3 & \psi_4 & \psi_5 & \psi_6 & \psi_7 \\
-6Dq+2A_2 & -2(2)^{\frac{1}{2}}h & & -(2/3)^{\frac{1}{2}}h & 2(3)^{\frac{1}{2}}\lambda & & 2(3)^{-\frac{1}{2}}h \\
-2(2)^{\frac{1}{2}}h & -6Dq+2A_2 & 2(2)^{\frac{1}{2}}h & 2(3)^{\frac{1}{2}}\lambda & -2(2/3)^{\frac{1}{2}}h & -2(3)^{-\frac{1}{2}}h & -(6)^{\frac{1}{2}}\lambda \\
 & 2(2)^{\frac{1}{2}}h & -6Dq-2A_2 & 2(3)^{\frac{1}{2}}h & & -2(6)^{\frac{1}{2}}\lambda & -2(3)^{-\frac{1}{2}}h \\
-(2/3)^{\frac{1}{2}}h & 2(3)^{\frac{1}{2}}\lambda & (2/3)^{\frac{1}{2}}h & 4Dq-2\lambda+2A_2 & -2^{\frac{1}{2}}h & -2h & \\
2(3)^{\frac{1}{2}}\lambda & -2(2/3)^{\frac{1}{2}}h & & -(2)^{\frac{1}{2}}h & 4Dq+\lambda+2A_2 & & 3h \\
 & -2(3)^{-\frac{1}{2}}h & -2(6)^{\frac{1}{2}}\lambda & -2h & & 4Dq-2\lambda+2A_2 & (2)^{\frac{1}{2}}h \\
2(3)^{-\frac{1}{2}}h & -(6)^{\frac{1}{2}}\lambda & -2(3)^{-\frac{1}{2}}h & & 3h & (2)^{\frac{1}{2}}h & 4Dq+\lambda-A_2
\end{array}$$

$$\begin{array}{cccccc}
\psi_8 & \psi_9 & \psi_{10} & \psi_{11} & \psi_{12} & \psi_{13} \\
-6Dq+2A_2+h & +3^{\frac{1}{2}}h & 2(3/5)^{\frac{1}{2}}\lambda-(3/5)^{\frac{1}{2}}h & h & 2^{-\frac{1}{2}}h & 6\cdot 10^{-\frac{1}{2}}\lambda-3\cdot 10^{-\frac{1}{2}}h \\
+3^{\frac{1}{2}}h & -6Dq-2A_2+h & 5^{-\frac{1}{2}}h & 2\cdot 3^{\frac{1}{2}}\lambda-3^{-\frac{1}{2}}h & -6^{\frac{1}{2}}\lambda-6^{-\frac{1}{2}}h & (3/10)^{\frac{1}{2}}h \\
2(3/5)^{\frac{1}{2}}\lambda-(3/5)^{\frac{1}{2}}h & 5^{-\frac{1}{2}}h & 4Dq-2\lambda-A_2+(3/2)h & (15^{\frac{1}{2}}/2)h & (6/5)^{\frac{1}{2}}h & \\
h & 2\cdot 3^{\frac{1}{2}}\lambda-3^{-\frac{1}{2}}h & (15^{\frac{1}{2}}/2)h & 4Dq-2\lambda+2A_2+(1/2)h & -2^{\frac{1}{2}}h & \\
2^{-\frac{1}{2}}h & -6^{\frac{1}{2}}\lambda-6^{-\frac{1}{2}}h & (6/5)^{\frac{1}{2}}h & -2^{\frac{1}{2}}h & 4Dq+\lambda-A_2-(3/2)h & -(9/2)5^{-\frac{1}{2}}h \\
6\cdot 10^{-\frac{1}{2}}\lambda-3\cdot 10^{-\frac{1}{2}}h & (3/10)^{\frac{1}{2}}h & & & -(9/2)5^{-\frac{1}{2}}h & 4Dq+3\lambda-A_2-(7/2)h
\end{array}$$

$$\begin{array}{cccccc}
\psi_{14} & \psi_{15} & \psi_{16} & \psi_{17} & \psi_{18} & \psi_{19} \\
-6Dq+2A_2 & -2\cdot 2^{\frac{1}{2}}h & & (6/5)^{\frac{1}{2}}h & 2\cdot 3^{\frac{1}{2}}\lambda & -2\cdot 5^{-\frac{1}{2}}h \\
-2\cdot 2^{\frac{1}{2}}h & -6Dq-2A_2 & 2.2^{\frac{1}{2}}h & 2\cdot(3/5)^{\frac{1}{2}}\lambda & & 3(2/5)^{\frac{1}{2}}\lambda \\
 & 2\cdot 2^{\frac{1}{2}}h & -6Dq-2A_2 & (6/5)^{\frac{1}{2}}h & & -2\cdot 5^{-\frac{1}{2}}h \\
(6/5)^{\frac{1}{2}}h & 2(3/5)^{\frac{1}{2}}\lambda & (6/5)^{\frac{1}{2}}h & 4Dq-2\lambda-A_2 & -3(2/5)^{\frac{1}{2}}h & \\
2\cdot 3^{\frac{1}{2}}\lambda & & & -3(2/5)^{\frac{1}{2}}h & 4Dq+\lambda-A_2 & -3(3/5)^{\frac{1}{2}}h \\
-2\cdot 5^{-\frac{1}{2}}h & 3(2/5)^{\frac{1}{2}}\lambda & -2\cdot 5^{-\frac{1}{2}}h & & -3(3/5)^{\frac{1}{2}}h & 4Dq+3\lambda+2A_2
\end{array}$$

$$\begin{array}{cccccc}
\psi_{20} & \psi_{21} & \psi_{22} & \psi_{23} & \psi_{24} & \psi_{25} \\
-6Dq+2A_2+h & -3^{\frac{1}{2}}h & 2(3/5)^{\frac{1}{2}}+(3/5)^{\frac{1}{2}}h & -h & -(2)^{-\frac{1}{2}}h & 6\cdot 10^{-\frac{1}{2}}\lambda+3\cdot 10^{-\frac{1}{2}}h \\
-3^{\frac{1}{2}}h & -6Dq-2A_2-h & -5^{-\frac{1}{2}}h & 2\cdot 3^{\frac{1}{2}}\lambda+3^{-\frac{1}{2}}h & -6^{\frac{1}{2}}\lambda+6^{-\frac{1}{2}}h & -(3/10)^{\frac{1}{2}}h \\
2(3/5)^{\frac{1}{2}}\lambda+(3/5)^{\frac{1}{2}}h & -5^{-\frac{1}{2}}h & 4Dq-2\lambda-A_2-(3/2)h & -(15/4)^{\frac{1}{2}}h & -(6/5)^{\frac{1}{2}}h & \\
-h & 2\cdot 3^{\frac{1}{2}}\lambda+3^{-\frac{1}{2}}h & -(15/4)^{\frac{1}{2}}h & 4Dq-2\lambda+2A_2+(1/2)h & 2^{\frac{1}{2}}h & \\
-(2)^{-\frac{1}{2}}h & -6^{\frac{1}{2}}\lambda+6^{-\frac{1}{2}}h & -(6/5)^{\frac{1}{2}}h & 2^{\frac{1}{2}}h & 4Dq+\lambda-A_2+(3/2)h & (9/2)\cdot 5^{-\frac{1}{2}}h \\
6\times 10^{-\frac{1}{2}}\lambda+3\times 10^{-\frac{1}{2}}h & -(3/10)^{\frac{1}{2}}h & & & (9/2)\cdot 5^{-\frac{1}{2}}h & 4Dq+3\lambda-A_2+)7/)2
\end{array}$$

APPENDIX II

We want to prove that $(d\|U^4\|d)=10\ Dq(70)^{\frac{1}{2}}$. According to Racah (III):

$$\begin{aligned}(d^6\,{}^5DM\|U_q^4|d^6\,{}^5dM')\\ =\Sigma_{L'}(d^6\,{}^5D\llbracket d^5L'd\,{}^5D)(L'd\,{}^5DM|U_q^4|L'd\,{}^5DM')\\ \times(d^5L'd\,{}^5D\rrbracket d^6\,{}^5D).\quad(1)\end{aligned}$$

According to the Eckart-Wigner theorem the dependence on M and M' can be written

$$\begin{aligned}(L'd\,{}^5DM|U_q^4|L'd\,{}^5DM')\\ =(-1)^{D+M}(L'd\,{}^5D\|U^{(4)}\|L'd\,{}^5D)\\ \times[(-1)^{D-q}/(2.4+1)^{\frac{1}{2}}](DDM'-M|DD4-q).\quad(2)\end{aligned}$$

U^4 operates on d but not on L':

$$\begin{aligned}(L'd\,{}^5D\|U^4\|L'd\,{}^5D)=(-1)^{L'+4-d-D}[(2l+1)(2l+1)]^{\frac{1}{2}}\\ \times W(dDdD;L'4)(d\|U^4\|d).\quad(3)\end{aligned}$$

Substituting Eqs. (3) and (2) into (1) we get

$$\begin{aligned}(d^6\,{}^5DM|U_q^4|d^6\,{}^5DM')\\ =(-1)^{M-q}(5/3)(d\|U^4\|d)(22M'-M|224-q)\\ \times\Sigma_{L'}(-1)^{L'}(d^6\,{}^5D\llbracket d^5L'd\,{}^5D)W(2222;L'4)\\ \times(d^5L'd\,{}^5D\rrbracket d^6\,{}^5D).\quad(4)\end{aligned}$$

The sum is

$$\begin{aligned}\sum_{L=0}^{4}(-1)^{L'}(d^6\,{}^5D\llbracket d^5L'd\,{}^5D)W(2222;L'4)\\ \times(d^5L'd\,{}^5D\rrbracket d^6\,{}^5D)=3/50.\end{aligned}$$

Hence

$$\begin{aligned}(d^6\,{}^5D0|U_0^4|d^6\,{}^5D0)\\ =(-1)^{0-0}(5/3)(d\|U^4\|d)(220-0|224-0)(3/50)\\ =\tfrac{1}{10}(d\|U^4\|d)(36/70)^{\frac{1}{2}}.\quad(5)\end{aligned}$$

But this matrix element is according to the usual calculation $+6\ Dq$, therefore

$$(d\|U^4\|d)=10\ Dq(70)^{\frac{1}{2}}.$$

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Paramagnetic Resonance and Optical Spectra of Divalent Iron in Cubic Fields. II. Experimental Results*

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The paramagnetic resonance absorption of Fe^{2+} in MgO is observed at $g=3.428$ and 6.86. The optical absorption line is found at 10 000 cm^{-1}. The paramagnetic resonance spectrum indicates considerable covalent bonding. The origin of the line at 6.86 is discussed.

In tetrahedral ZnS a paramagnetic line is found at $g=2.25$ and optical absorption at 3 μ and 0.7 μ. Possible explanations of this spectrum are discussed.

A short discussion of the optical absorption spectra of trivalent iron in MgO is presented.

INTRODUCTION

In the preceding paper[1] we have calculated in detail the energy level scheme of the ^5D level in an octahedral and tetrahedral crystal symmetry. This paper will be divided into two main sections, (A) The paramagnetic and optical spectra of Fe^{2+} in MgO and (B) The paramagnetic and optical spectra in tetrahedral sphalerite (ZnS). Section (C) will deal with a number of additional observations on these crystals. In Secs. (A) and (B) it is shown that the spectra in MgO can be understood along the lines developed in (I), but that a definitive interpretation of the spectra in ZnS is at present still lacking.

A. THE PARAMAGNETIC AND OPTICAL SPECTRA OF Fe^{2+} IN THE OCTAHEDRAL CRYSTAL SYMMETRY OF MgO

Magnesium oxide has a face-centered cubic structure. Each magnesium ion is surrounded by six equidistant oxygen ions. In this octahedral crystal field the ground state is an orbital triplet (Γ_5). This triplet which is fivefold spin degenerate splits into a number of levels by spin-orbit interaction of which a triplet is the lowest. As shown in (I), this triplet gives rise to a first order Zeeman splitting in an external magnetic field. Transitions among these levels are permitted. Since the other levels are fairly close it is expected that the spin-lattice relaxation time will be short. Indeed it proved necessary to cool the crystal to liquid helium temperature in order to detect any resonance. At 4°K only the lowest triplet is populated to a significant degree. (The next level is removed by about $2\lambda\sim150$–$200\ cm^{-1}$ or 200–280°K.) One will not expect, therefore, to observe resonance from the higher levels.

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[1] W. Low and M. Weger, preceding paper [Phys. Rev. **118**, 1119 (1960)], (to be referred to as I).