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Paramagnetic and Optical Spectra of Divalent Cobalt in Cubic Crystalline Fields*

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The optical and paramagnetic resonance spectra of divalent cobalt in MgO single crystals are reported. The optical spectrum consists of stronger lines which correspond to transitions between Stark levels of the same multiplicities and weak intercombination lines. If the Slater integrals are taken as free parameters then in the intermediate coupling scheme good agreement is obtained between the observed and calculated spectrum with $Dq=960$ cm^{-1}. The Slater integrals are reduced by about 8–10% from those of the free ion. The paramagnetic resonance spectrum shows one electronic isotropic transition consisting of eight hyperfine lines at $g=4.278_5\pm0.001$ and $A=(97.7_9\pm0.2)\times10^{-4}$ cm^{-1}. The interpretation of these results shows that the orbital reduction factor $k=0.89-0.85$. Both the optical and paramagnetic results indicate covalent bonding. The effect of charge transfer is (1) to shield the nuclear charge and (2) to normalize the wave functions. Both these effects result in smaller Coulomb energy, hyperfine structure, and spin-orbit coupling constant.

No distortions of octahedral symmetry have been found to within 10^{-3} cm^{-1}. The static Jahn-Teller effect which predicts such a distortion is, therefore, very small.

I. INTRODUCTION

We have recently reported results on the paramagnetic resonance and optical spectra of Cr^{3+} and Ni^{2+} in cubic octahedral fields.[1–3] In both of these ions the lowest Stark level of the ground state F was an orbital singlet. The electron spin degeneracy is not removed even when spin-orbit coupling is taken into account. This results in only one observable electronic transition with a g factor very close to the value of that for the free-electron spin. The small deviation from this value is caused by the admixture of higher lying Stark levels by means of spin-orbit coupling to the ground state. We have also reported the surprising observation that nearly a whole configuration of d^8 in Ni^{2+} can be obtained from the optical absorption spectrum.[3]

This paper reports results on Co^{2+} in octahedral fields. This ion is of particular interest in that its lowest Stark level is an orbital triplet. Both the electronic spin and the orbital motion contribute to the magnetic moment. Noncubic crystals containing Co^{2+} show a large anisotropy in their magnetic susceptibility and in their g factors. Deviations from cubic symmetry have been attributed in part or fully to the Jahn-Teller effect.[4,5] It was hoped that by studying the spectra in which the orbital ground state is degenerate as in Co^{2+} and in Fe^{2+} some light could be shed on this effect. We have reported preliminary results on Fe^{2+} in MgO.[6,2] This paper will present a detailed discussion of the paramagnetic resonance spectrum of Co^{2+}.

A proper interpretation of the paramagnetic resonance results demands the observation and understanding of the optical spectrum. The combination of the magnetic and optical data gives us considerable insight into the nature of the crystalline field approximation.[3]

In Sec. 2 we shall discuss briefly the theory of the paramagnetic resonance spectra. We shall also deal with the behaviour of the excited levels of the configuration d^7 in cubic crystalline fields. In Sec. 3 the experimental results will be presented. We shall discuss these results in detail in Sec. 4.

II. THEORY

The theory of the paramagnetic susceptibility of Co^{2+} has been given by Schlapp and Penney.[7] This has been extended by Kambe *et al.*[8] and applied to paramagnetic resonance spectra of hydrated salts by Abragram and Pryce.[9] The latter were concerned mainly with crystals of tetragonal or trigonal symmetry. With minor modifications their theory can be applied directly to crystals with cubic symmetry with which we are concerned.

The octahedral crystalline field splits the sevenfold degenerate ^4F state into an orbital triplet (Γ_4), followed by another orbital triplet (Γ_5) and an orbital singlet (Γ_2). The next highest state in the same configuration in the free ion is the ^4P level. This level remains triply degenerate in a cubic field. It has the same group representation (Γ_4) as the ground state Stark level and, therefore, these two levels perturb each other. The separation of these levels is fairly large (about 20 000 cm^{-1}) and the interaction is correspondingly small, amounting to a few percent.

The lowest orbital triplet is fourfold spin-degenerate. If spin-orbit interaction is taken into account, this

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[1] W. Low, Phys. Rev. **105**, 807 (1957).

[2] W. Low, Ann. N. Y. Acad. Sci. (to be published).

[3] W. Low, Phys. Rev. **108**, 247 (1957), preceding paper.

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

[5] H. A. Jahn, Proc. Roy. Soc. (London) **A164**, 117 (1938).

[6] W. Low, Phys. Rev. **101**, 1827 (1956).

[7] R. Schlapp and W. G. Penney, Phys. Rev. **42**, 666 (1932).

[8] Kambe, Koide, and Usui, Progr. Theoret. Phys. Japan **7**, 15 (1952).

[9] A. Abragram and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**, 175 (1951).

twelvefold degeneracy is in part removed. Following Abragram and Pryce,[10] it is convenient to introduce a fictitious orbital angular momentum l' which operates in the orbital triplet manifold and which has effective Lande factors $-\alpha$. Using a representation in which l_z' and S_z are diagonal, we can easily write down the fine-structure matrices.

$$\begin{array}{ccc} (\mp 1,\pm\frac{3}{2}) & (0,\pm\frac{1}{2}) & (\pm 1,\mp\frac{1}{2}) \\ \hline 3\alpha\lambda & -\sqrt{\frac{3}{2}}\alpha\lambda & 0 \\ -\sqrt{\frac{3}{2}}\alpha\lambda & 0 & -\sqrt{2}\alpha\lambda \\ 0 & -\sqrt{2}\alpha\lambda & \frac{1}{2}\alpha\lambda \end{array} \quad m=\pm\tfrac{1}{2},$$

$$\begin{array}{cc} (0,\pm\frac{3}{2}) & (\pm 1,+\frac{1}{2}) \\ \hline 0 & -\sqrt{\frac{3}{2}}\alpha\lambda \\ -\sqrt{\frac{3}{2}}\alpha\lambda & -\frac{1}{2}\alpha\lambda \end{array} \quad m=\pm\tfrac{3}{2} \tag{1}$$

$$-\tfrac{3}{2}\alpha\lambda \qquad m=\pm\tfrac{5}{2}.$$

Here $m=l_z'+S_z$. The quantity λ is the spin-orbit coupling constant of cobalt in the crystal. In the absence of any admixture of the P state, α would have the value $\frac{3}{2}$. Any admixture will reduce the value somewhat. In Abragram and Pryce's notation,[9] we write

$$\alpha=\tfrac{3}{2}\epsilon^2-\tau^2, \tag{2}$$

where ϵ and τ are defined by the coefficients of the basic orbital functions of the ground state and P state,

$$\psi=\epsilon\phi+\tau\pi, \tag{3}$$

ϕ and π being the wave functions of the $\Gamma_4(F)$ and $\Gamma_4(P)$ state in the absence of configurational interaction. The measure of this interaction can be calculated from the optical spectrum.

Solution of the matrices (1) yields the following roots: $(15/4)\lambda$ $(m=\pm\frac{1}{2})$, $(6/4)\lambda$ $(m=\pm\frac{1}{2},\pm\frac{3}{2})$, $-(9/4)\lambda$ $(m=\pm\frac{1}{2},\pm\frac{3}{2},\pm\frac{5}{2})$. As the spin-orbit coupling constant is negative the $(15/4)\lambda$ is the lowest level, and paramagnetic resonance spectra can be expected between this Kramers doublet. Figure 1 shows the splitting of the ground state by means of the spin-orbit interaction. The wavefunction of the doublet can be written as

$$|\tfrac{1}{2}\rangle=\frac{1}{\sqrt{2}}|-1,\tfrac{3}{2}\rangle-\frac{1}{\sqrt{3}}|0,\tfrac{1}{2}\rangle_1+\frac{1}{\sqrt{6}}|1,-\tfrac{1}{2}\rangle,$$

$$|-\tfrac{1}{2}\rangle=\frac{1}{\sqrt{2}}|1,-\tfrac{3}{2}\rangle-\frac{1}{\sqrt{3}}|0,-\tfrac{1}{2}\rangle+\frac{1}{\sqrt{6}}|-1,\tfrac{1}{2}\rangle. \tag{4}$$

The splitting factors $g_{\shortparallel}$ is equal to $g_{\perp}$ for pure cubic fields. The splitting factor can be easily calculated to first order:

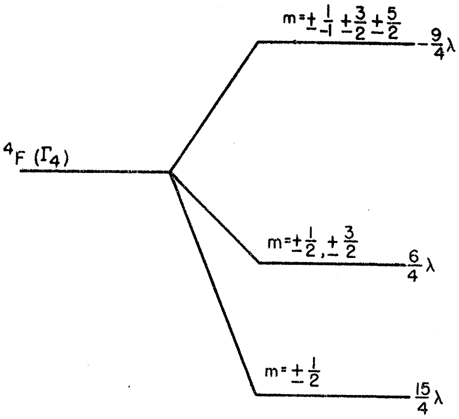

FIG. 1. Fine-structure splitting of the ground state Stark level of Co^{2+} under the action of the combined octahedral crystalline field and spin-orbit interaction. $m=l_z+S_z$ and is the spin coupling constant in the crystal.

$$\begin{aligned} g_{\shortparallel}&=2\langle\tfrac{1}{2}|L_z+2S_z|\tfrac{1}{2}\rangle,\\ (g_S)_{\shortparallel}&=(6/2)+(2/3)-(2/6)=10/3,\\ (g_L)_{\shortparallel}&=2\alpha(\tfrac{1}{2}-\tfrac{1}{6})=\tfrac{2}{3}\alpha. \end{aligned} \tag{5}$$

If α is $\frac{3}{2}$ then $(g_L)_{\shortparallel}=1$, and the total splitting factor to first order is 4.333.

In the second order the spin-orbit coupling mixes in a slight amount of the Γ_5 state to the ground state. This can be seen from the Table I in which the direct product of $D_{\frac{3}{2}}\times\Gamma_i$ is tabulated. The second-order contribution is $-(15/2)\lambda/\Delta$, where Δ is the separation between the two triplet states. This neglects in second order the contribution of the admixture of the P state, which would amount only to a very slight correction to the already small quantity of the second order.

The total splitting factor, to second order, is then

$$g=g_{\shortparallel}=g_{\perp}=10/3+(2/3)k\alpha-(15/2)\lambda/\Delta. \tag{6}$$

We introduce here with Stevens[11] an additional factor k, called the orbital reduction factor in anticipation of results to be presented later. When $k=1$ the ion is perfectly ionic and there is no distortion of the d atomic wave functions. If there is some covalent bonding present, some electron transfer to the surrounding ligands, k will be smaller than one.

Cobaltous ions show an extended hyperfine structure in their paramagnetic resonance spectra. This structure arises from three sources in general: $(A_L+A_S$

TABLE I. Direct product representations $D_{\frac{3}{2}}\times\Gamma_i$ and $D_{\frac{1}{2}}\times\Gamma_i$.

$D_{\frac{3}{2}}\times\Gamma_1=\Gamma_8$	$D_{\frac{1}{2}}\times\Gamma_1=\Gamma_6$
$D_{\frac{3}{2}}\times\Gamma_2=\Gamma_8$	$D_{\frac{1}{2}}\times\Gamma_2=\Gamma_7$
$D_{\frac{3}{2}}\times\Gamma_3=\Gamma_6+\Gamma_7+\Gamma_8$	$D_{\frac{1}{2}}\times\Gamma_3=\Gamma_8$
$D_{\frac{3}{2}}\times\Gamma_4=\Gamma_6+\Gamma_7+2\Gamma_8$	$D_{\frac{1}{2}}\times\Gamma_4=\Gamma_6+\Gamma_8$
$D_{\frac{3}{2}}\times\Gamma_5=\Gamma_6+\Gamma_7+2\Gamma_8$	$D_{\frac{1}{2}}\times\Gamma_5=\Gamma_7+\Gamma_8$

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[10] A. Abragram and H. M. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[11] W. K. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

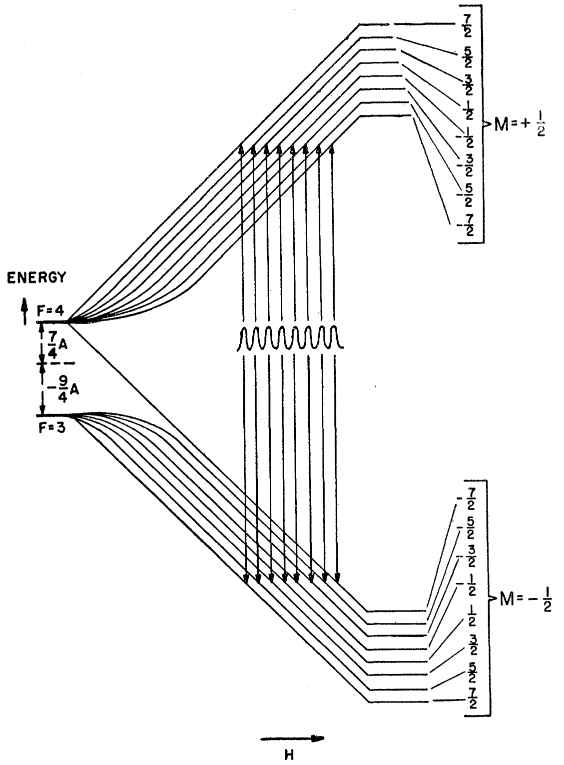

FIG. 2. The hyperfine structure splitting in weak and strong magnetic fields.

$+A_{SK})S_z \cdot I_z$, where A_L is the contribution from the orbital moment, A_S the contribution from the spin moment, and A_{SK} is the contribution of unpaired s electrons which may be present because of configuration interaction of $3s\,d^7\,4s$ with $3s^2\,d^7$. Following Abragram and Pryce's notation,[9] $A_L = Pg_L$ and $A_{SK} = -\frac{1}{2}kPg_S$, where $P = 2_\gamma\beta\beta_N\langle 1/r^3\rangle_{\text{Av}}$, γ is the gyromagnetic ratio and β, β_N are the Bohr and nuclear magnetons, respectively. The contribution A_S is negligible in the case of cubic fields. P is of course not known but Abragram and Pryce estimate its value from experimental results of the paramagnetic resonance spectra on cobalt fluosilicate and cobalt ammonium sulfate to be $P = 0.0225 \pm 0.0005$ cm^{-1}. Unfortunately, in the cubic field we have only one experimental parameter A but two unknown quantities P and k. In Fig. 2 the hyperfine splitting of the ground state doublet is shown for low and high fields.

From Eq. (6) it is seen that the g factor and in turn the hyperfine structure depend on the amount of admixture of the P state to the ground state. We have, therefore, investigated the optical spectrum in detail.

The configuration $3d^7$ yields the following states for the free ion: ^4F, ^4P, ^2P, ^2D, ^2G, ^2H, ^2F. Experimentally all but the ^2P and ^2F level have been determined for the free ion.[12] The ^2P level has the same electrostatic energy as the ^2H level, and we take it to be approximately 22 000 cm^{-1}. The ^2F level we estimate to be about 35 000 cm^{-1} above the ^4F level. At any rate it turns out that our results are fairly insensitive to the exact choice of the ^2F level. Finkelstein and Van Vleck[13] have calculated the matrix elements for d^3. The same matrix elements are applicable here except with the reversed sign of Dq, where Dq is a parameter which measures the crystal field strength.

We have calculated these matrix elements as a function of Dq, and the resulting energy levels are shown in Fig. 3. As it is well known,[14] there are two ^2D terms in this configuration. These two terms are well separated in d^7. Unfortunately the second D term has not been observed spectroscopically. We estimate that it is about 59 000 cm^{-1} above the ^4F level. We then calculate the unperturbed D levels to be at 29 000 and 52 000 cm^{-1}, respectively, and the matrix element $\langle {}^2D_a|E|{}^2D_b\rangle = 13\,300$ cm^{-1}. In Fig. 3 we show only the first of the ^2D levels. The other one is so high that it cannot be observed in a crystal.

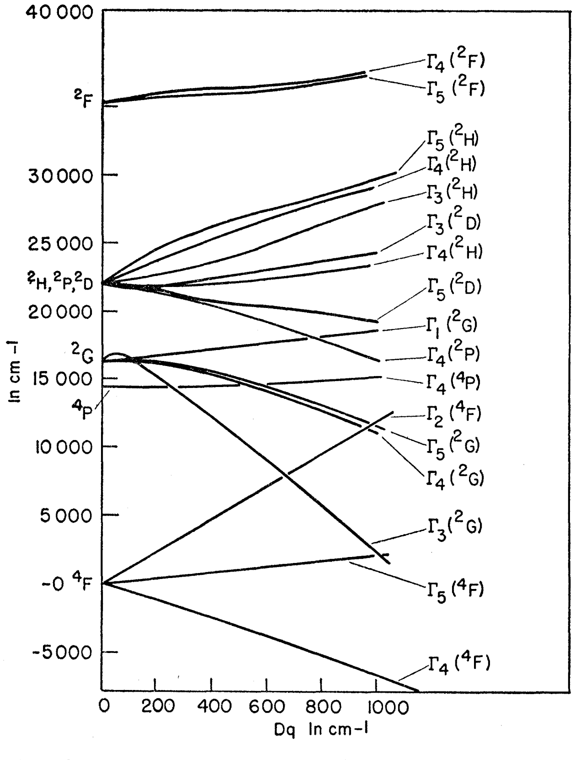

FIG. 3. Energy level diagram of Co^{2+} as a function of cubic field strength Dq in octahedral symmetry. The energy values of the ^4P, ^2D, ^2H, ^2G at $Dq=0$ are those of the free ion. The values of ^2P and ^2F are estimated electrostatic energies without the Trees correction.

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[12] C. E. Moore, *Atomic Energy Levels*, U. S. National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1952), Vol. 2. The value of the ^2D level is marked with a question mark in this circular. We shall use it in our calculation as if its assignment were certain.

[13] R. Finkelstein and J. H. Van Vleck, J. Chem. Phys. 8, 790 (1940).

[14] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1950), p. 233.

It is seen in Fig. 3 that there is very little crossing of the energy levels at low *Dq*. But at higher *Dq* the energy levels tend to bunch together or cross one another. When the levels come very close to one another, spin-orbit coupling must be taken into account. From Table I it is seen that the majority of the levels have the same representation if spin-orbit coupling is considered. These levels will, therefore, perturb each other. Usually this pertuibation is fairly small as the spin-orbit coupling constant is relatively small for Co^{2+} (-178 cm^{-1}). For large *Dq*, or whenever levels come very close to one another this perturbation may amount to a few hundred cm^{-1}. The calculations should be properly made in the spin-orbit manifold. Because these matrices are on the whole fairly large they could only be solved by electronic computers. We hope to do this calculation as a function of *Dq* and λ, the spin-orbit coupling constant, in the near future.

It is obvious from Fig. 3 that the Stark separations are a large fraction of the separation between the various terms. Moreover, the off-diagonal elements in the matrices used to calculate Fig. 3 are fairly large. It is, therefore, not proper to speak anymore of the atomic states but more appropriate to designate the states with their irreducible representations Γ_i. We shall indicate in parentheses their atomic parentage.

III. EXPERIMENTAL TECHNIQUES AND RESULTS

Preparation of Crystals

Magnesium oxide single crystals containing cobalt were grown from the melt by a brute force method. These crystals melt at about 2800° C and, therefore, usual techniques for growing crystals were not applicable. A furnace was built with Norton fused MgO bricks surrounded by two layers of ordinary fire bricks. Two carbon electrodes of about $1\frac{1}{4}$ in. diameter were inserted through appropriate holes at opposite ends of the furnace. The ends of the 25 in. long carbon rods were connected by means of copper clamps to an arc-welding unit. The clamps were water-cooled during and for several hours after the operation. The arc was operated at about 40 volts and 350 amperes. During the operation one has to add about a quarter pound of MgO powder every few minutes. After three to four hours' operation at peak power, the power is slowly decreased. The furnace is then hot for another 24 hours or longer. Small crystals are usually found among the sintered polycrystalline mass. Care must be taken during the operation that the MgO should not clog up and that there should be sufficient material near the tip of the electrodes. It is preferable to use this crystalline mass for the start of another trial if in the first trial no single crystals were obtained.

In order to get cobalt into the MgO crystals small amounts of $CoCO_3$ were added to the MgO powder. CoO unfortunately melts at lower temperature. The single crystals obtained were nearly always clear with only a very light pink tint. The color of the polycrystalline mass varied from white to dark red. The region close to the electrodes, i.e., the hottest region, usually yielded sintered crystals of white color.

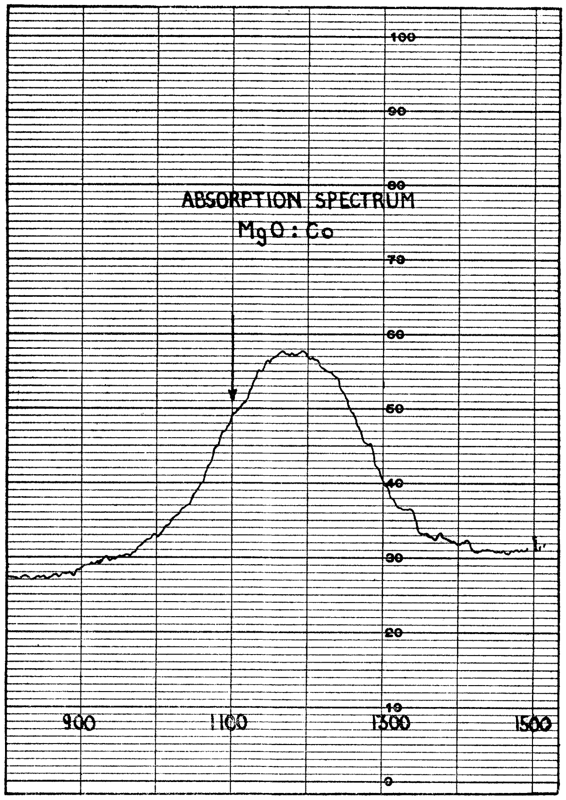

FIG. 4. Infrared spectrum of Co^{2+} in MgO at room temperature. There is a smaller peak at about 11 000 A.

Chemical analysis of the single crystals showed that cobalt was present at approximately 0.01–0.2%. This was sufficient for microwave measurements of the paramagnetic resonance spectra but not sufficient for a clear detection of the optical spectra.

To obtain crystals which had more Co^{2+}, we diffused cobalt into single crystals of MgO at 1300°C for ten days. One obtains a thin layer near the surface of the crystal in which the concentration of cobalt is sufficiently high so that optical measurements can be performed. Unfortunately the diffusion is not very even over the whole surface area. This depends apparently on the contact of the surrounding crystalline powder with the MgO single crystal.

Paramagnetic Resonance Spectrum

The paramagnetic resonance spectrum was measured at 1 cm at liquid helium temperature. Eight hyperfine lines were detected whose position was isotropic. The spectrum can be described by the simple spin Hamiltonian

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+A\mathbf{S}\cdot\mathbf{I}, \tag{7}$$

with $g=4.278_5\pm0.001$, $A=(97.7_9\pm0.2)\times10^{-4}$ cm^{-1}.

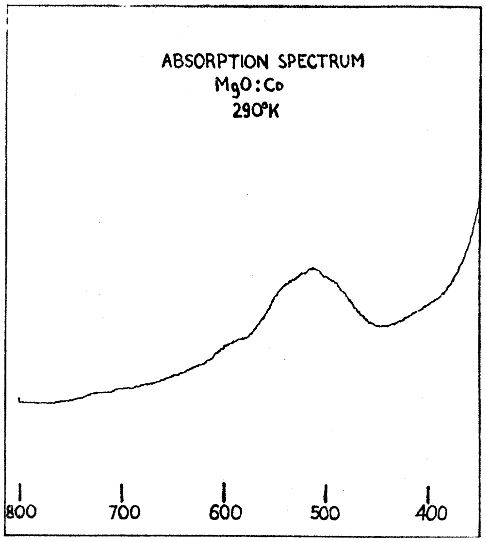

FIG. 5. Absorption spectrum of Co^{2+} in MgO at room temperature. The strong absorption after 3500 A is that of the MgO crystal.

Optical Spectrum

The optical spectrum was scanned on the Cary spectrophotometer in the visible range, and on the Beckman DK spectrophotometer in the infrared and ultraviolet region (from 20 000 A–3000 A). Figure 4 shows the infrared line at 8470 cm^{-1}. A careful investigation of this line reveals a shoulder at 9060 cm^{-1}. This line becomes slightly better resolved at liquid nitrogen temperature. The visible spectrum as recorded on the Cary spectrophotometer is shown in Figs. 5 and 6. It is seen that the main peak around 5100 A becomes better resolved and the line width slightly narrowed at lower temperature. The region after 4000 A shows the anomalous large absorption of MgO. We investigated this region by comparing two crystals, one with and one without cobalt, with approximately the same thickness. The region between 6000–4700 A shows four (or at least four) absorption lines. There are several ways of reconstructing the experimental absorption lines by means of individual Gaussian absorption lines. The most likely possibility is that there is an intense and broad line at about 19 600 cm^{-1} with two less intense and narrower lines at about 18 700 and 20 500 cm^{-1}, and an even less intense but fairly wide line at 17 200 cm^{-1}. Another less likely possibility is shown in Fig. 7. This shows a superposition of a broad line at 19 800 cm^{-1} (2250) and less intense lines at 19 500 (600) and 18 650 (600) and 17 100 (1200) cm^{-1}. The last line is marked "background" in the figure. The numbers in parentheses are the half-widths of these lines.

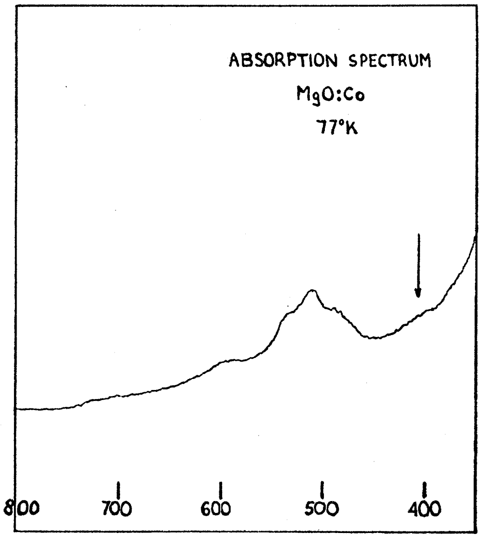

FIG. 6. Absorption spectrum of Co^{2+} in MgO at liquid nitrogen temperature. The lines are better resolved and the new band at about 24 600 cm^{-1} becomes noticeable.

In addition there are weak absorption lines at 13 750 (*vw*), 14 200 (*vw*), 24 600 (*w*), 28 500 (*vw*) cm^{-1}. There is a stronger absorption line at 32 000 cm^{-1}. There is a doubtful line at about 25 000 cm^{-1}.

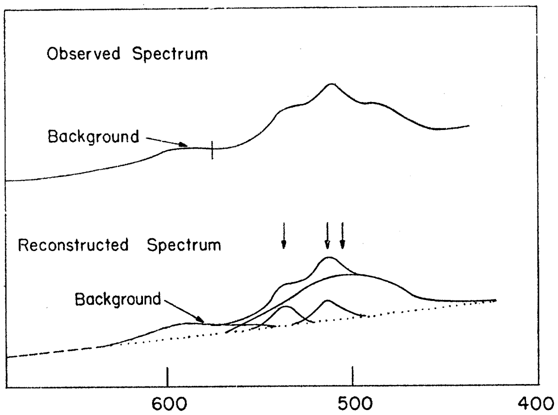

FIG. 7. Possible reconstruction of the central absorption lines in the absorption spectrum of Co^{2+} in MgO. The line marked background is a weak line centered at 17 100 cm^{-1}.

IV. DISCUSSION

Optical Spectrum

We shall first discuss the optical spectrum, as the understanding of the paramagnetic resonance spectrum is contingent on the proper assignment of the energy levels. It is obvious that the broad and relatively intense line at 8470 cm^{-1} is the transition between the ground state $\Gamma_4(^4F)$ and the $\Gamma_5(^4F)$. The very intense line (slightly more intense than the infrared line) at 19 600 cm^{-1} (or 19 800 cm^{-1} depending on the way in which the lines are superimposed) is the transition to the $\Gamma_4(^4P)$ level. Both these levels are more intense as they involve one electron jump. These two lines permit the evaluation of the two parameters, Dq and E_P, and then the calculation of the $\Gamma_2(^4F)$ level. Fairly good fit is obtained with $Dq=960$ cm^{-1} and E_P at 12 500 cm^{-1}. This gives three levels at 8470, 18 000, and 19 800 cm^{-1}. Small variations in E_P affect in the main the transition to the ${}^4P$ level, and only in second order the transition to the Γ_2 level. It is not easy to decide whether the 18 700 or the 17 200 cm^{-1} band is the transition to the Γ_2 level. This transition is expected to be somewhat weaker as it involves to a first approximation a two-electron jump and the transition probability is, therefore, smaller. Ballhausen and Jorgensen[15] have measured the absorption spectrum of Co^{2+} in a number of solutions. They find peaks, for example, in $Co(H_2O)_6{}^{2+}$ at 8000, 16 000, and 20 500 cm^{-1} and in the more covalent $Co(NH_3)_6{}^{2+}$ at 9000, 18 500 and 21 100 cm^{-1}. $MgO:Co^{2+}$ obviously lies in between these two cases and one cannot easily decide on this evidence either. Moreover, the line at 20 000 cm^{-1} is a fairly broad band which is incompletely resolved in the spectra of Co^{2+} in solutions. We shall present some evidence to show that the $\Gamma_2({}^4F)$ level falls at 18 700 cm^{-1} and that the line at 17 200 cm^{-1} represents a transition to the ${}^2G$ level.

It is somewhat more difficult to account for the weak absorption lines in part because of the possibility of contamination of the crystal with other impurities like Fe^{2+}, Fe^{3+}, and Mn^{2+} and possibly even Co^{3+}. Assuming $Dq=960$ cm^{-1}, we calculate the four Stark levels originating from the parent ${}^2G$ level (see Fig. 3) at 9500, 18 140, 18 300, and 24 900 cm^{-1}. Now the two observed 9060 and 24 600 cm^{-1} are obviously the two transitions to the $\Gamma_3({}^2G)$ and $\Gamma_1({}^2G)$ levels. The E_G is, therefore, reduced by about 300–500 cm^{-1} compared to that of the free ion $E_G{}^0$.[16] (We list for easy comparison the significant energy levels as tabulated by Moore[12] in Table II.) We expect the other two levels $\Gamma_4({}^2G)$ and $\Gamma_5({}^2G)$ to fall at 17 700 and 17 850 cm^{-1}. These levels are, therefore, expected to be very close to the calculated $\Gamma_2({}^4F)$ level at $\sim$18 000 cm^{-1}. This bunching of a number of levels indicates that one should take into account spin-orbit interaction as that might provide considerable perturbation of these levels. Inspection of Table I shows that all the levels in question, Γ_4, Γ_5, and Γ_2 contain the irreducible representation Γ_8. These levels then will interact via the spin-orbit coupling (and to a minor extent also with the ${}^4\Gamma_4({}^4P)$ level. The matrices for the intermediate coupling scheme for $3d^7\,4s^2$ have been calculated by Marvin.[17] Inspection of these matrices shows that the off-diagonal elements are fairly large, i.e., $(5/8)^{\frac{1}{2}}\xi_{3d}$, $(66/25)^{\frac{1}{2}}\xi_{3d}$ where $\xi_{3d}=540$ cm^{-1}. One can, therefore, expect repulsions of the order of 600 cm^{-1} as required to fit the experimental results. Our assumption that the Γ_2 is the higher level is not based only on the slight difference as calculated but rather on the larger intensity of the 18 700 cm^{-1} line compared with the broader but weaker 17 200 cm^{-1} line. While the transition to the Γ_2 level is expected to be of smaller intensity as it involves a two-electron jump to a first approximation, the intercombination lines are expected to be still weaker. This is borne out from the two transitions at 9060 and 24 600 cm^{-1} which are by far weaker than the line at 18 700 cm^{-1} and also weaker than the 17 200 cm^{-1}. The intensity of the latter line is probably somewhat stronger because of the admixture of the ${}^4F$ level by means of the spin-orbit interaction.

TABLE II. Optical energy levels of Co III (from Moore[a]).

Designation	J	Energy level in cm^{-1}
${}^4F$	9/2	0
	7/2	841.2
	5/2	1451.3
	3/2	1866.8
${}^4P$	5/2	15 201.9
	3/2	15 428.2
	1/2	15 811.4
${}^2G$	9/2	16 977.7
	7/2	17 766.2
${}^2H$	11/2	22 720.3
	9/2	23 434.3
${}^2D$?	?	23 058.8

[a] See reference 12.

The ${}^2P$ and ${}^2H$ levels have the same electrostatic energy. If these were true experimentally we calculate the $\Gamma_4({}^2P)$ level to be at 23 350 cm^{-1}, far above the observed line at 20 500 (or 19 500) cm^{-1}. It is, however, well known that experimentally the ${}^2P$ level is several thousand cm^{-1} below the ${}^2H$ level.[18] Trees[19] has remarked that the deviation of the theoretically computed energy levels from the experimental values could be reduced by adding a term proportional to $L(L+1)$. This equals 2 for ${}^2P$ and 30 for ${}^2H$ and even a small coefficient of proportionality will yield a large energy difference. Racah[20] has explained this empirical correction term $\alpha L(L+1)$ to arise from the dipolar interaction between d orbits, which takes the form $2\alpha\sum \mathbf{l}_i\cdot\mathbf{l}_k$ and which distorts the orbits.

One can evaluate the parameter α from the observed ${}^4P$, ${}^4F$, ${}^2G$, and ${}^2H$ levels as listed in Table II and from the theoretical energy levels expressed in terms of

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[15] C. J. Ballhausen and C. K. Jorgensen, Acta Chem. Scand. **9**, 397 (1955).

[16] In all calculations we have always considered intervals between the centers of gravity of the various multiplets (i.e., the difference ${}^4P-{}^4F=E_P{}^0=14\,561$ cm^{-1}). We have assumed that the optical transition when measured at room temperature is also the difference between the center of gravity of the multiplets. The center of gravity in a cubic field, however, will differ somewhat from that of the free ion. As these calculations are only a first approximation and spin-orbit coupling has not been taken into account, we have assumed that these two centers of gravity are the same. The error in most cases is not more than $\lambda\sim|200|$ cm^{-1} and often much less.

[17] H. H. Marvin, Phys. Rev. **47**, 521 (1935).

[18] See reference 14, pp. 234–235.

[19] R. E. Trees, Phys. Rev. **83**, 756 (1951); **84**, 1089 (1951).

[20] G. Racah, Phys. Rev. **85**, 381 (1952); G. Racah, Proc. Rydberg Cent. Conf. on Atomic Spectr., Fysiograf. Sallskap. Lund, Handl. **65**, 31 (1954). We are indebted to Professor Racah for pointing out this correction term.

Slater integrals, i.e.,

$$\begin{aligned} {}^4P &= 3F_0-147\ F_4+2\alpha, \\ {}^4F &= 3F_0-15\ F_2-72\ F_4+12\alpha, \\ {}^2G &= 3F_0-11\ F_2+13\ F_4+20\alpha, \\ {}^2H &= 3F_0-6\ F_2-12\ F_4+30\alpha. \end{aligned} \tag{8}$$

Using the center of gravity of each term in Table II, we find $\alpha=82$ cm^{-1}. The difference in energy between the ^2P and ^2H level is approximately 2300 cm^{-1} and the calculated ^2P level of the free ion $[E_0(^2P)]$ is 19 800 cm^{-1}. The Stark level $\Gamma_4(^2P)$ is then found to be at 21 000 cm^{-1} above the ground state. This is not far from the observed 20 500 (or 19 500) cm^{-1} level. Again one should use the intermediate coupling scheme as the $\Gamma_4(^4P)$ and $\Gamma_4(^2P)$ levels interact.[17] If not for this interaction, the $\Gamma_4(^2P)$ level would fall still lower and the $\Gamma_4(^4P)$ level a little higher. In view of the assumptions already made, it hardly pays to refine these calculations. It suffices to say that the ^2P level is depressed from that of the free ion by about 1000–500 cm^{-1}.

We have to account still for a number of very weak lines and one relatively intense line at 32 000 cm^{-1}. The line at 28 500 is very likely the transition to the $\Gamma_4(^2H)$ level which is calculated to be at 29 200 cm^{-1}. The lines stretching from 13 000–14 500 cm^{-1} are very likely caused by impurities which are present in the crystal. The most likely impurity is Fe^{3+} which is known to be present from its paramagnetic resonance spectrum and which could give rise to a weak band at 14 000 cm^{-1}. We have no explanation of the band at 32 000 cm^{-1}.[21]

Figure 8 shows a Grotian term scheme with the most probable assignment of the terms and the observed transitions. On the left are indicated the free-ion values (dotted line) and the extrapolated energy values of the ion in the crystal. We see that all the energy levels are lower in comparison with the free-ion value. A reduction of the Slater integral F_2 by about 8–10% explains this systematic difference of the energy level scheme compared with that of the free ion. The theoretical ratio of the P-F:G-F separation is 15 F_2:4 F_2 and the experimental ratio 2000:400 cm^{-1}, in good agreement.

It is worthwhile to compare these results with those of Ni^{2+}. In Ni^{2+} we have been able to observe nearly all possible transitions between the Stark levels of the $3d^8$ configuration. In the case of Co^{2+} we have also been able to observe a number of intercombination lines, in the main transition to Γ_4 levels. In Ni^{2+} the intercombination lines were of much larger intensity than in Co^{2+}. This is probably connected with the much larger spin-orbit coupling constant (in Ni^{2+}:$\lambda=-324$ cm^{-1}; in Co$^{2+}\lambda=-180$ cm^{-1}) which breaks down the usual selection rules $\Delta S=0$. In Ni^{2+}, as in Co^{2+}, the Slater integrals are reduced from their free-ion values. The reduction is slightly larger in Ni^{2+}. We have investigated the systematic variation of this reduction as a function of the crystal field strength Dq in Ni^{2+} and in other ions.[22] The reduction of these integrals is a nearly linear function of Dq. If we take Ni^{2+} salts with comparable $Dq=960$ cm^{-1}, the reduction of F_2 there is definitely larger than the reduction found in Co^{2+}.

The change in the central-field approximation may be realized in a crystal in a number of ways. One possibility pointed out in the discussion on Ni^{2+} by the author[3] is the shielding effect of the surrounding ligands which have in part overlapping wave functions on the magnetic electrons. The term values, therefore, are similar to that of Fe^{1+} rather than Co^{2+}. Another possibility, and evidence to this effect will be given in the discussion of the paramagnetic resonance spectrum, is that charge transfer occurs. Such a charge transfer would demand a renormalization of the wave functions and a corresponding decrease of the central field, i.e., of the F_2 integral.

It is also interesting to compare the crystal field strength Dq for the three ions Fe^{2+}, Co^{2+}, and Ni^{2+} all in the same surroundings. The values found from the

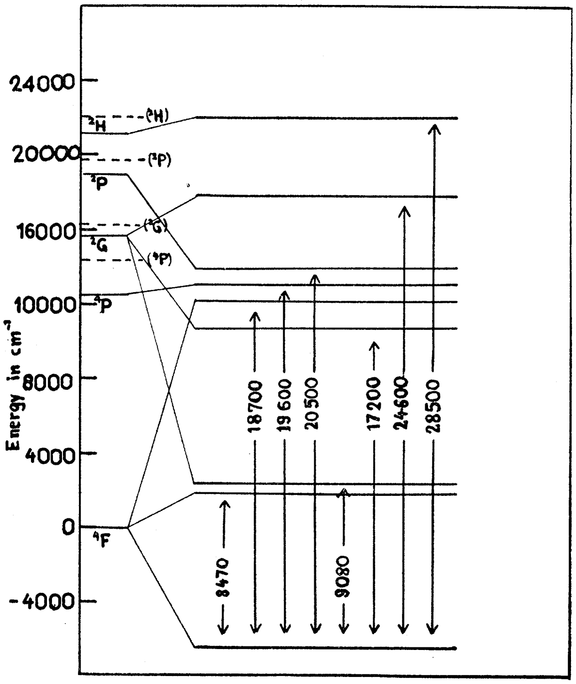

FIG. 8. Energy level diagram as constructed from the observed absorption lines of Co^{2+} in MgO. The dotted lines at the left indicate the energy levels of the free ion.

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[21] The solution of the matrices with $Dq=960$ cm^{-1} yields the following values. Γ_4: $^2H=29\,150$ cm^{-1}, $^2H=35\,000$, $^2F=44\,400$ cm^{-1}; Γ_5: $^2D=25\,860$, $^2H=35\,970$, $^2F=44\,100$ cm^{-1}; Γ_3: $^2D=30\,850$, $^2H=34\,270$ cm^{-1}. None of these transitions could conceivably give a line which would be stronger by a factor 2–3 than any of the observed intercombination lines. Possibly the line at 32 000 cm^{-1} might be some Co^{3+} complex or a charge-transfer band. The doubtful line at about 25 000 cm^{-1} might be a transition to the $\Gamma_5(^2D)$ level.

[22] W. Low, Phys. Rev. **109**, 247 (1958), preceding paper.

optical spectrum are 1060 cm^{-1},[23] 960 cm^{-1}, and 850 cm^{-1}. Superficially there seems to be a relation between the number of $d\epsilon$ electrons and the decrease in crystal field strength. The comparison, however, is somewhat in doubt as the ionic radius of Fe^{2+} is probably larger than that of Co^{2+} or Ni^{2+}, and is a poor fit in the MgO lattice. Moreover, paramagnetic resonance spectra give ample evidence[2] of a considerable amount of covalent bonding in Fe^{2+}. Unfortunately the intercombination lines in Fe^{2+} have not been detected so far and, therefore, we do not know how much the F_2 have been reduced. Attempts in this direction will be made. A fuller discussion of the comparison of the optical spectra of $3d$ ions in MgO and in Al$_2$O$_3$ will be published elsewhere.

Paramagnetic Resonance Spectrum

We can now discuss the measured g factor and hyperfine structure of the paramagnetic resonance spectrum. From the optical spectrum we find that the ground state can be represented in terms of Eq. (3) by

$$\psi = 0.980\phi - 0.204\pi.$$

Therefore, from Eq. (2),

$$\alpha = \tfrac{3}{2}[(0.980)^2 - (0.204)^2] = \tfrac{3}{2}(0.919).$$

From Eq. (6) we can estimate the orbital reduction factor. This factor is defined as[11]

$$\langle \Phi_n | L | \Phi_m \rangle = k_{nm} \langle d_n | L | d_m, \qquad (9)$$

where Φ are the modified molecular orbitals appropriate for octahedral symmetry[24,25]:

$$\begin{aligned}
\Phi_{xy} &= N_\pi\{d_{xy} + \tfrac{1}{2}\eta_\pi(p_y{}^1 - p_y{}^4 + p_x{}^2 - p_x{}^5)\},\\
\Phi_{yz} &= N_\pi\{d_{yz} + \tfrac{1}{2}\eta_\pi(p_z{}^2 - p_z{}^5 + p_y{}^3 - p_y{}^5)\},\\
\Phi_{xz} &= N_\pi\{d_{xz} + \tfrac{1}{2}\eta_\pi(p_x{}^3 - p_x{}^6 + p_z{}^1 - p_z{}^4)\}, \qquad (10)\\
\Phi_{3z^2-r^2} &= N_o\{d_{3z^2-r^2} + (\eta_\sigma/12)^{\frac{1}{2}}\\
&\quad \times (\sigma_x{}^1 - \sigma_x{}^4 + \sigma_y{}^2 - \sigma_y{}^5 - 2\sigma_z{}^3 + 2\sigma_z{}^6)\},\\
\Phi_{x^2-y^2} &= N_\sigma\{d_{x^2-y^2} + \tfrac{1}{2}\eta_\sigma(-\sigma_x{}^1 + \sigma_x{}^4 + \sigma_y{}^2 - \sigma_y{}^5)\}.
\end{aligned}$$

The numbers 1, 2, 3 and 4, 5, 6 refer to the neighbors on the positive and negative x, y, z axes. N is the renormalization constant. Tinkham[25] has discussed in detail these normalization constants. The normalization constant in the evaluation of the spin-orbit matrix is different and defined by

$$\langle \Phi_n | \lambda L | \Phi_m \rangle = N_n N_m \langle d_n | \lambda L | d_m \rangle. \qquad (11)$$

The reason for this difference is that in Eqs. (9) and (10) we operate within the Kramers doublet whereas in Eq. (11) we have to take into account the higher lying Γ_5 level. As discussed by Tinkham, the normalization constant in Eq. (11) is usually smaller than the factors k_{nm} in Eq. (9). Unfortunately this factor is unknown in Eq. (6). It enters into the second-order correction to the g factor and can be expressed in an apparent reduction of the spin-orbit coupling constant. We shall estimate that the reduction of the spin-orbit coupling is approximately that of Ni^{2+} or about 0.75 λ_0. As already discussed in the paper on Ni^{2+}, the whole calculation is dependent on the assumption that the wave function near the nuclei is not changed drastically from that of the free ion.[3] At any rate, since this reduction of the spin-orbit constant enters only as a correction, the error in k will not be appreciable. We find that $k = 0.89$. If we assumed that the spin-orbit constant in Eq. (6) were the same as in the free ion, k would be lowered to about 0.85.

This value of k justifies the interpretation of the cobalt spectrum in ZnF$_2$ by Tinkham,[25] who assumed a value of $k = 0.9$. However, the value of this reduction constant differs very much from that measured in Fe^{2+} where we find $k = 0.80$.[2] Such a low value seems to indicate considerable π bonding in Fe^{2+}, at least much more than in Co^{2+}. Possibly this can be explained by the smaller ionic radius of Co^{2+} compared with Fe^{2+} and the better fit, therefore, in the MgO lattice.

The modified hyperfine structure constant can now be written as

$$A = N^2 P[g_L{}^0 - \tfrac{1}{2}k g_S], \qquad (12)$$

in which we assume that the contributions are reduced by the normalization factors (i.e., the wave function near the nucleus is not very much deformed by means of the charge transfer). If we were to assume the values of P and k of Abragram and Pryce,[9] 0.0225 cm^{-1} and 0.325, we find that $N^2 = 0.945$ which is even larger than k. As the normalization factors are consistently smaller than k, this is a very unreasonable result. We therefore have to assume that either P is larger or k smaller than the values assumed by Abragram and Pryce and by Tinkham. We feel, therefore, that the results of these authors are in need of re-examination.

The fact that the reduction of the F_2 Slater integrals are nearly the same for Ni^{2+} and Co^{2+} and nearly constant for all excited levels, seems to us a strong indication that the dominant mechanism responsible for the reduction is a change in the effective nuclear charge Z_0 which the magnetic electrons see. The shielding effect is of course a function of the overlap with the surrounding oxygen ions. The reduction of the spin-orbit constant λ and hyperfine structure are, therefore, not to be calculated only as a renormalization of the wave functions caused by charge transfer, but also as a reduction caused by a smaller effective charge. It is, therefore, very reasonable to expect that this reduction would be the same, as both the spin-orbit constant and

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[23] W. Low (to be published).

[24] J. H. Van Vleck, J. Chem. Phys. **3**, 807 (1935).

[25] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 549 (1956).

the hyperfine structure are reduced by the same change of the effective charge. This is indeed borne out in the spectrum of Cu^{2+} which has been examined by Bleaney *et al.*[26] On the other hand, it seems to us that it does not necessarily follow, as Owen reasons,[27] that the spin-orbit coupling parameter in the bound ion is approximately the same as in the free ion. It is very likely that the fine structure and the hyperfine structure will always be similarly effected by distortions of the wave functions.

A shielding effect can also explain the results of Tinkham.[25] Tinkham finds that the spin-orbit constants are reduced by a much larger amount than the charge-transfer spectrum, which he observes in the fluorine hyperfine structure in ZnF_2, can account for. He explains this by assuming that the molecular orbitals of the form given in Eq. (10) include atomic wave functions of higher n, but the same symmetry, on the neighboring fluorine ions. These higher n ($n=3$) have much larger overlaps and, therefore, give larger normalization reductions. On the other hand, the hyperfine structure of the fluorine ions are mainly a function of the $n=2$ wave functions. One could, according to our conjecture, explain this anomaly as follows: The hyperfine structure of the surrounding ligands is a measure of the overlap of the wave functions. It measures the probability of the magnetic electrons being on the fluorine ions. This is not dependent, to first order, on the shielding of the nuclear charge. On the other hand, the spin-orbit coupling constant and the hyperfine structure are dependent on this shielding effect as well as on the normalization of the wave function. It is, therefore, expected that the measured spin-orbit constant will be appreciably reduced.

We should like to make a few comments here on the Jahn-Teller effect. The results reported here show that the paramagnetic resonance spectrum is isotropic, and that no distortions within 10^{-3} cm^{-1} exist. The Jahn-Teller effect is expected to be small here, since after spin-orbit coupling is taken into account only a Kramers doublet remains as the lowest state. Indeed it seems nearly a property of the Jahn-Teller effect that whenever one tries to find it, it eludes the possibility of being measured. In Fe^{2+}, which also has a triply degenerate orbital ground state and which even after spin-orbit interaction is taken into account has a triply degenerate state consisting of a mixture of orbital and spin wave functions, no effect is found as well.[2] Öpik and Pryce[28] have remarked that under certain conditions sufficiently strong spin-orbit coupling can stabilize the complex and no distortions would be expected. In Fe^{2+} the spin-orbit coupling is certainly not very strong ($\lambda=-100$ cm^{-1}). Pryce[29] has pointed out that the system will resonate between deformed configurations in such a way as to give an isotropic g value. In such a case, then, this resonance frequency would be very rapid, and it would be interesting if it could be detected.

V. CONCLUSION

In this paper we have presented the optical and paramagnetic resonance spectra of divalent cobalt. It is found that the spectral lines can be arranged into a simple level diagram. The stronger lines correspond to transitions between Stark levels of the same multiplicity and the weaker to transitions in which ΔS changes by one. If the electrostatic energy difference between the ground state and the excited levels is taken as a free parameter to be determined from experiment, the agreement between the calculated and experimental spectra is surprisingly good. Similarly to the spectrum of Ni^{2+}, we find that the Slater integrals have to be reduced by about 10% from those of the free ion. This can be interpreted as arising from two effects. (1) Charge transfer results in a normalization of the wave functions and therefore a reduction of the Coulomb energy. (2) Covalent bonding has the effect of shielding the nuclear charge and thus reducing the Coulomb energy.

The paramagnetic resonance results indicate that the orbital contribution to the magnetic moment is reduced. The orbital reduction factor is 0.89–0.85. This should be compared with 0.80 for Fe^{2+} in MgO,[2] and with $k=0.87$ in $Fe(CN)_6{}^{3-}$ complexes.[30] These results show again and independently that considerable charge transfer occurs. In view of this it is indeed very surprising that the optical spectrum can be accounted for so well.

In view of these results we feel that the calculations of Abragram and Pryce should be readjusted. We also present an alternative explanation of Tinkham's results on the hyperfine structure of the fluorine ions in ZnF_2.

Both in Co^{2+} and in Fe^{2+} we have been unable to detect any distortions of the cubic symmetry as might be expected from the Jahn-Teller effect. If a static effect exists, it must be considerably smaller than it has been considered likely. At any rate, the usual explanation of static deformations of the crystal resulting from the Jahn-Teller effect does not seem to be correct. More experimental work, for example in tetrahedral symmetries, and theoretical investigations are clearly indicated.

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[27] J. Owen, Proc. Roy. Soc. (London) **A227**, 198 (1955).

[28] U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957). We wish to thank Professor Pryce for drawing our attention to this important remark.

[29] M. H. L. Pryce (private communication).

[30] Baker, Bleaney, and Bowers, Proc. Phys. Soc. (London) **B69**, 1205 (1956).

APPENDIX. MATRICES OF SPIN-ORBIT INTERACTION

$$J=7/2:\qquad \begin{array}{cccc} & {}^2G & {}^4F & {}^2F \\ {}^2G & -3/4 & (5/8)^{\frac{1}{2}} & (15/16)^{\frac{1}{2}} \\ {}^4F & (5/8)^{\frac{1}{2}} & 0 & -(3/8)^{\frac{1}{2}} \\ {}^2F & (15/16)^{\frac{1}{2}} & -(3/8)^{\frac{1}{2}} & 1/4 \end{array} \times \xi_{3d}, \tag{A1}$$

$$J=9/2:\qquad \begin{array}{cccc} & {}^2H & {}^2G & {}^4F \\ {}^2H & -3/5 & (66/25)^{\frac{1}{2}} & 0 \\ {}^2G & (66/25)^{\frac{1}{2}} & 3/5 & (5/2)^{\frac{1}{2}} \\ {}^2F & 0 & (5/2)^{\frac{1}{2}} & 3/2 \end{array} \times \xi_{3d}, \tag{A2}$$

$$J=1/2:\qquad \begin{array}{ccc} & {}^4P & {}^2P \\ {}^4P & -5/6 & -(14/9)^{\frac{1}{2}} \\ {}^2P & -(14/9)^{\frac{1}{2}} & -2/3 \end{array} \times \xi_{3d}, \tag{A3}$$

$$J=3/2:\qquad \begin{array}{cccccc} & {}^4F & {}^2D_a & {}^2D_b & {}^4P & {}^2P \\ {}^4F & -2 & -(21/10)^{\frac{1}{2}} & (5/2)^{\frac{1}{2}} & 0 & 0 \\ {}^2D_a & -(21/10)^{\frac{1}{2}} & -3/4 & (21/16)^{\frac{1}{2}} & (2/5)^{\frac{1}{2}} & -(7/8)^{\frac{1}{2}} \\ {}^2D_b & (5/2)^{\frac{1}{2}} & (21/16)^{\frac{1}{2}} & 1/4 & 0 & -(7/8)^{\frac{1}{2}} \\ {}^4P & 0 & (2/5)^{\frac{1}{2}} & 0 & -1/3 & -(35/9)^{\frac{1}{2}} \\ {}^2P & 0 & -(7/8)^{\frac{1}{2}} & -(7/8)^{\frac{1}{2}} & -(35/9)^{\frac{1}{2}} & 1/3 \end{array} \times \xi_{3d}. \tag{A4}$$

VI. ACKNOWLEDGMENTS

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Paramagnetic Resonance Spectrum of Trivalent Gadolinium in the Cubic Field of Calcium Fluoride*

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The paramagnetic resonance spectrum of Gd^{3+} in CaF_2 has been analyzed at 3 cm wavelength at room and liquid helium temperatures. The spectrum shows that the cubic symmetry is essentially preserved around the gadolinium ion. The fourth-order and sixth-order cubic field splitting parameter have been evaluated as $c=+0.0185\pm0.0005$ and $d=-0.0004\pm0.0002$ cm^{-1}, where the total ground-state splitting is $8c-2d$. The g factor is $g=1.991\pm0.002$. Various mechanisms causing the ground-state splitting of an S state in a cubic field are discussed. The preservation of cubic symmetry and the absence of association with vacancies or interstitial ions can be explained by a stabilization of the complex by the spherical charge distribution of the S ion and an effective strong crystalline field.

I. INTRODUCTION

TRIVALENT gadolinium has seven f electrons and a ground state of ${}^8S_{7/2}$. Its paramagnetic resonance spectrum has been extensively studied. The reason for this is in part the ease with which the spectrum can be obtained even at room temperature since the spin-lattice relaxation time is fairly long.[1] Among the single crystals studied are the ethylsulfate,[2,3] the double nitrate,[4] the anhydrous trichloride,[5] and the hydrated trichloride.[6] The paramagnetic resonance

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