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Optical Spectrum of Co^{2+} in the Cubic Crystalline Field of CaF_2†

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The optical spectrum of Co^{2+} in CaF_2 is analyzed. Absorption bands are found at 3 μ, 1.5 μ, and 550 mμ. These bands show fine structure. In addition there are weak and narrower bands at 19 220, 19 580, 20 450, 21 750, 22 000, and 25 750 cm^{-1}, and intense lines at 44 250 and 48 200 cm^{-1}. The spectrum is interpreted to arise from transitions from the orbital singlet to various Stark levels split by spin-orbit interaction, and yields values of $Dq=340\pm10$ cm^{-1}, $E(P)=14\,000\pm100$ cm^{-1}, and $E(G)=16\,250\pm100$ cm^{-1}. The spectrum of Co^{2+} in the eight coordinated cubic symmetry is compared with Co^{2+} in octahedral and tetrahedral symmetry as well as with Cr^{3+} in octahedral symmetry.

INTRODUCTION

Recently, one of us (W.L.) has reported in detail on the interpretation of the paramagnetic and optical spectra of Co^{++} in the octahedral cubic field of MgO.[1] It was shown that it is possible to fit the optical absorption spectrum to a simple energy level scheme with the use of a few parameters. These parameters are the crystal field strength, usually denoted by Dq, and the separation between the term values of the d^7 configuration in the crystal when $Dq=0$. Most of the energy levels split up in a number of Stark levels. The number of transitions between the ground state and the various excited Stark levels is usually larger than the number of free and independent parameters necessary in the cubic field scheme. One has, therefore, independent checks in the correctness of the interpretation and the assignment of the various transitions. The most significant result of this and other investigations of the series[2,3] is that the Slater integrals seem to be reduced by about 10% in the octahedral field of six surrounding oxygen atoms.

This paper reports the optical absorption spectrum and the interpretation of the spectrum of Co^{++} in the crystal of calcium fluoride. The crystal field caused by eight surrounding charges is of considerable interest. First, the sign of the cubic field (Dq) of an eight-coordinated complex is the opposite of that of an octahedral coordination. This has the important result that the order of the Stark levels of a given term is reversed. In the particular case of Co^{++} the lowest level will be an orbital singlet (Γ_2), and the spectrum will resemble that of d^3 configuration (V^{++} or Cr^{+++}) in an octahedral field. Secondly, it was of interest to see what the crystal field strength and the magnitude of the Slater integrals are in this symmetry, and to compare these results with those of octahedral complexes. Thirdly, we thought that these results might shed some light on the much studied spectra of Cr^{+++} in Al_2O_3 or the alums with their many and sharp lines. Finally, we wanted to correlate our results with the results of paramagnetic resonance measured by the Oxford group.[4]

THEORY

Calcium fluoride crystallizes in what is called the fluorite structure. Each calcium ion is surrounded by eight F^- ions at the corners of a cube and each F^- ion by four Ca^{++} ions at the corners of a regular tetrahedron. The crystal field caused by the eight nearest neighbors, expressed in spherical harmonics, is

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

and for a sixfold coordination

$$V=V_0+D_4[(7/2)Y_4^0+\tfrac{1}{4}(70)^{\frac{1}{2}}(Y_4^4+Y_4^{-4})]. \quad (2)$$

We have terminated the series at the fourth power of Y since matrix elements involving higher order spherical harmonics do not contribute so long as one is concerned with the energy levels within the d^n configuration. V_0 in Eqs. (1) and (2) are constants. These shift all the levels of a given configuration by the same amount. It signifies to a large extent the lattice energy and the heat of solution of the paramagnetic ion. These constants, however, will differ for different configurations. Assuming point charges, D_4 is given by $(Z_ie^2r^4/a^5)\times(4\pi/9)^{\frac{1}{2}}$, where a is the interionic distance. Such a naive model gives the ratio of the crystal field strength for the two symmetries, assuming D_4 having the same magnitude, as 8:9 and with the opposite sign.

We have calculated the energy level scheme as a function of both positive and negative Dq for all the levels of the d^7 configuration at the Rehovot computer. These have also been calculated by Tanabe and Sugano[5] and our results are in agreement. We have used the representation of Finkelstein and Van Vleck,[6] in which the energies of the various term values are along the diagonal. This has the advantage that these term values can be treated as parameters to

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[1] W. Low, Phys. Rev. **109**, 256 (1958).

[2] W. Low, Phys. Rev. **109**, 247 (1958).

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

[4] M. Baker (to be published). We are indebted to Dr. Baker for communicating to us his results prior to publication.

[5] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753 (1954); **9**, 766 (1954).

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

be adjusted to fit the experimental spectrum. This has been outlined in reference 1 and the reader should consult this paper for details and notation.

In the next section it will be shown that in some cases the fine structure of various orbital Stark levels is resolved. We, therefore, have diagonalized the total matrix including spin-orbit coupling for the first few levels. To first order, the levels are given as follows:

$$\begin{array}{llll} & & & \text{Cubic field} + \text{spin-orbit coupling} \\ {}^4F & \Gamma_2 & \Gamma_8 & -12Dq \\ & \Gamma_5 & \Gamma_8+\Gamma_7 & -2Dq+\frac{3}{4}\lambda \\ & & \Gamma_8 & -2Dq-\frac{1}{2}\lambda \\ & & \Gamma_6 & -2Dq-(5/4)\lambda \\ & \Gamma_4 & \Gamma_6 & +6Dq-\delta+(15/4)\lambda \\ & & \Gamma_8 & +6Dq-\delta+\frac{3}{2}\lambda \\ & & \Gamma_7+\Gamma_8 & +6Dq-\delta-(9/4)\lambda \\ {}^4P & \Gamma_4 & \Gamma_6 & E(P)+\delta+(15/4)\lambda_p \\ & & \Gamma_8 & E(P)+\delta+\frac{3}{2}\lambda_p \\ & & \Gamma_7+\Gamma_8 & E(P)\delta-(9/4)\lambda_p, \end{array} \tag{3}$$

where λ is the spin-orbit coupling in the crystal (-180 cm^{-1} in the free ion), δ is the mutual repulsion between the two Γ_4 levels, and $E(P)$ is the energy separation of the center of gravity of the P term from that of the F term when $Dq=0$.

In the second order the ground state Γ_2 is shifted slightly and the Γ_7 and Γ_8 levels are split by about λ^2/Δ, where Δ is the separation between adjacent orbital Stark levels. This turns out to be not entirely negligible, but in view of the limited accuracy of the experimental results the second order correction is neglected.

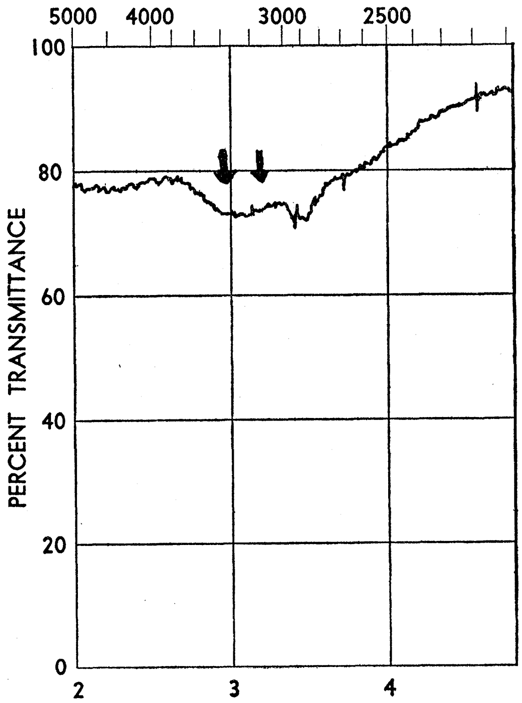

FIG. 1. Optical absorption in the infrared, $T=290$°K. The structure at 2950 cm^{-1} is probably not connected with Co^{++}.

EXPERIMENTAL RESULTS AND INTERPRETATION

Single crystals of CaF$_2$ containing Co^{++} were grown as outlined in reference 1. The exact amount of Co^{++} is not known but is estimated to be about $0.1-0.3$ mole percent. The crystals are of a beautiful wine red color. CaF$_2$ cleaves readily along the [111] directions. The crystal is transparent when cleaved along this direction and needs no additional polishing.

The infrared spectrum was investigated on a Perkin-Elmer spectrophotometer. The visible and ultraviolet spectrum was obtained on a variety of spectrometers, among them Beckman *DK* and a Cary spectrophotometers.

In Fig. 1 is shown the weak infrared spectrum. It consists of one wide or bell-jar line of width of about 400 cm^{-1}, and centered about 3350±50 cm^{-1}. Actually the line can be resolved into at least two components one at 3200 cm^{-1} the other at 3440 cm^{-1}. In addition there are weak lines at 1550 cm^{-1} and 1425 cm^{-1} with a width of about 50 cm^{-1}. These two far infrared and narrow lines are probably crystal vibration spectra. The next group of lines occur at about 1.5 μ and 550 mμ and are shown in Figs. 2 and 3. Figure 2 shows the spectrum at room temperature and underneath the spectrum of pure CaF$_2$ crystals of approximately the same thickness. If the background is subtracted, one finds that the best fit gives two lines, one a wide line with its center of gravity at about 5900±100 and the other a narrower line at 6600±100 cm^{-1}. The wide line seems to consist of two lines at 5800 and 6100 cm^{-1}. The next group of lines at 550 mμ is similar in structure to that of 1.5 μ. There is a wide line, probably a doublet centered at 17 800±200 cm^{-1}, and a narrower line on top at 18 550±50 cm^{-1}. In addition there are a number of certain but weaker lines at 19 220±100, 19 580±100, and 20 450±100 cm^{-1}; a doublet at 21 750 and 22 000 cm^{-1}, and a line at 25 750 cm^{-1}. There are relatively strong absorption lines at 44 250 and 48 200 cm^{-1}. A number of very weak lines are found between 28 000 and 37 000 cm^{-1}, some of which are doubtful. These are shown in Figs. 4 and 5.

A casual inspection of the relatively strong groups at 3 μ and 550 mμ shows that the crystal field strength is relatively weak and about 340 cm^{-1}. A detailed calculation and the experimental values are given in Table I.

The experimental values listed in column 3 have been evaluated as follows. Assuming that the multiplet structure in each of the three groups arises from spin-orbit interaction as given in Eq. (3), we have constructed the unperturbed value in a slightly arbitrary fashion. We have assumed that the line of the multiplet lying at the highest wave number is the transition to $\Gamma_8+\Gamma_7$ and that the wide line at lower wave numbers includes

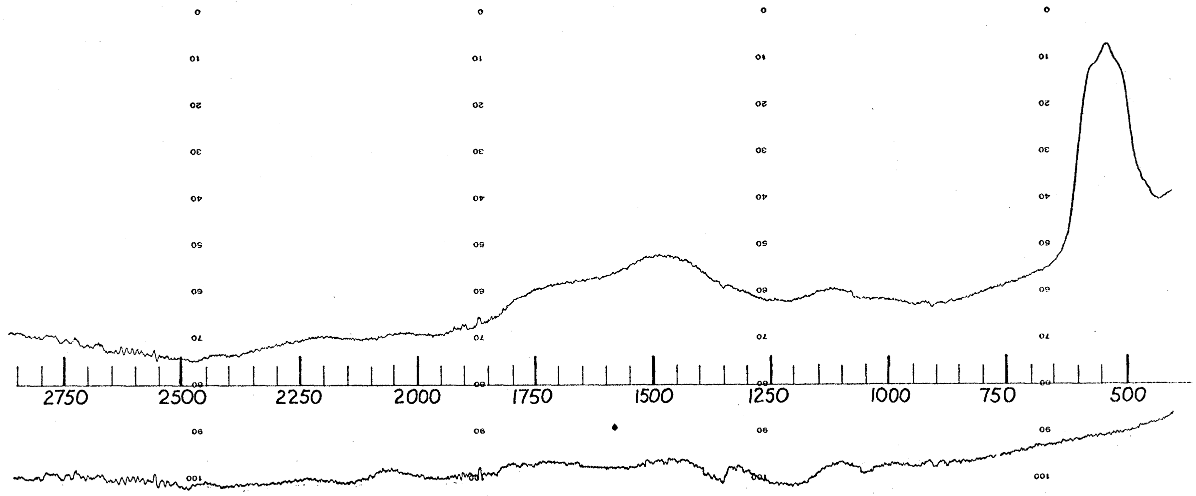

FIG. 2. Optical absorption spectrum in the visible range, $T=290°K$. The line at the bottom shows the absorption of a pure CaF_2 crystal.

the transitions to the two levels of Γ_8 and Γ_6. Correcting now these levels for the spin-orbit interaction, using $\lambda_0=-180$ cm^{-1}, the free-ion spin-orbit interaction, we have constructed the unperturbed degenerate orbital levels at 6200 and 18 200 cm^{-1}. These values are probably not much in error, as can be seen as follows. The total width of the three transitions should correspond approximately to the multiplet separation given by Eq. (3). The group at 3 μ is about 400 cm^{-1} wide, in agreement with the theoretical value of 2λ or 360 cm^{-1}. The group at 1.5 μ has a width of 800 cm^{-1}, and that at 550 mμ of about 750 cm^{-1}, compared with the theoretical value of 6λ or approximately 1100 cm^{-1} and 900 cm^{-1} (the spin-orbit coupling λ_P of the P state is about -150 cm^{-1}).

As seen in column 4, the difference between the calculated value and the experimental value is within the error of the measurements, except for the transition Γ_3 and $\Gamma_4(^2G)$ levels in which the calculated level is lower than the experimental value. There is an additional anomaly in that this transition is of much larger intensity than the transition to Γ_1 or Γ_5 levels. This is explained by the proximity of the $\Gamma_4(^4P)$ level. The $\Gamma_4(^2G)$ level borrows intensity from the $\Gamma_4(^4P)$ state, and this also causes the shift of about 400 cm^{-1}.[7] The order of this shift is reasonable. The agreement between the experimental results and the theoretical calculation is really too good, if one takes into account all the assumptions.

These remain the doublets at 22 000 cm^{-1}. The

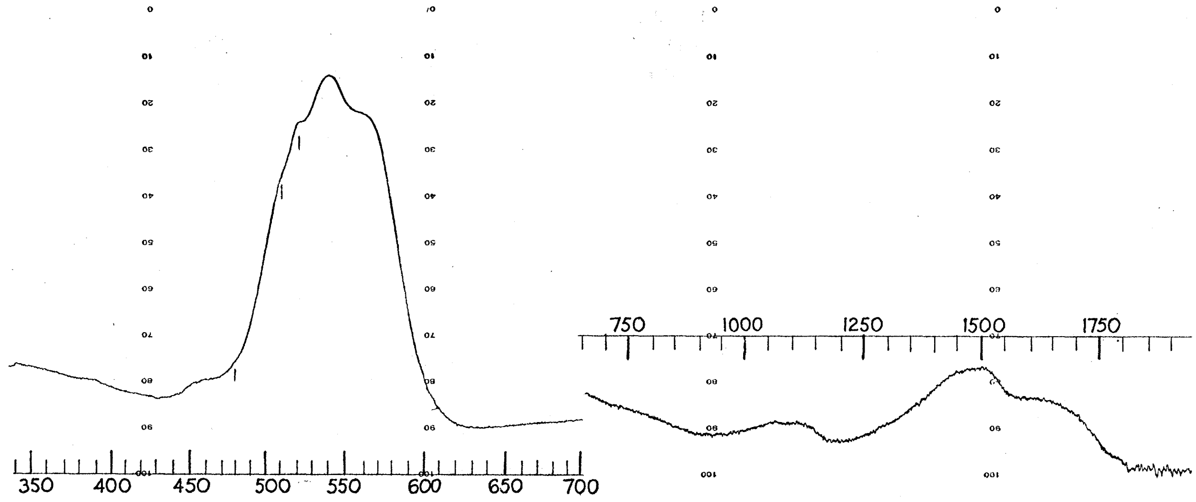

FIG. 3. Optical absorption spectrum in the visible range, $T=90°K$.

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[7] See reference 2 for a similar interaction between Γ_3 states in the Ni^{++} spectrum.

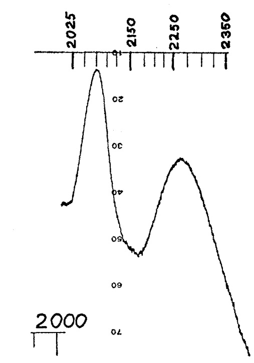

FIG. 4. Ultraviolet spectrum, $T=90°\text{K}$.

calculated values of ^2H Stark levels, assuming that $E(H)$ is about 22 000 cm^{-1}, range from 25 000 cm^{-1} (Γ_5) to 29 000 cm^{-1} (Γ_4). The ^2P level, after taking care of the Trees correction, falls at 23 400 cm^{-1}. Therefore, it is very likely that the doublet at 22 000 cm^{-1} is two close-lying Γ_6 and Γ_8 levels of the ^2P state. The discrepancy of about 1500 cm^{-1} is not very alarming since the actual position $E(^2P)$ is unknown in the gaseous ion. The calculated value of the ^2P level, even if the Trees correction is taken into account, is often too high by about 1000 cm^{-1} compared with the experimental value in the iron group spectra.

The two strong lines at 44 300 and 48 000 cm^{-1} are likely to be transitions to another configuration. The next configuration having the same multiplicity is $3d^64s\ ^4D$ and centered about 56 000 cm^{-1} above the ^4P level in the free ion. In view, however, of the fact that V_0 in the cubic potential equation (1) may differ by a considerable amount, this configuration as well as others may fall considerably lower than in the free ion. If this interpretation is correct, then the separation of 4000 cm^{-1} indicates a Dq' value of about 400 cm^{-1} for this configuration.

We have considered the possibility that the fine structure of the three bands at 3 μ, 1.5 μ, and 550 mμ may be caused by axial crystal fields rather than by spin-orbit coupling. In order to check this, the spectrum was taken at two different and arbitrary orientations. No significant difference in the spectra was found. Because of the relatively large line width, even at liquid air temperatures, this check may not be conclusive. Further work at very low temperature may narrow the lines sufficiently so that the fine structure can be resolved completely. Even if axial fields were present, it would not cause a significant change in Dq or in $E(P)$ and $E(G)$.

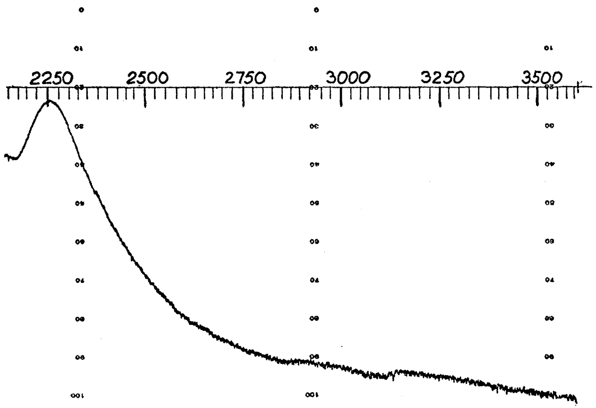

FIG. 5. Ultraviolet spectrum, $T=90°\text{K}$.

COMPARISON WITH SPECTRA OF d^7 OR d^3 CONFIGURATIONS IN CUBIC FIELDS

A. Comparison with Ni^{++} in an Octahedral Field

Table I indicates that the crystal field theory accounts reasonably well for the observed spectrum. Additional support for our interpretation of the first three bands is given by the comparison with the strong absorption bands of Ni^{++} in the octahedral field of MgO.[2] Ni^{++} has d^8 electrons. If we neglect the spin-orbit coupling, than the first three bands of Ni^{2+} have the same group representations, and the same behavior as a function of the crystal field strength as Co^{++} in the fluorite symmetry. A comparison of the two spectra shows indeed many similarities. For example, the third band $\Gamma_2(F)\rightarrow\Gamma_4(P)$ is 2−3 times more intense than the first two ions. This is somewhat strange and difficult to explain. In the strong-crystal-field limit this transition represents a two-electron jump, i.e., $(d\epsilon^6d\gamma^2)\ ^3\Gamma_2(F)\rightarrow(d\epsilon^4d\gamma^4)\ ^3\Gamma_4(P)$ and $(d\epsilon^5d\gamma^2)\ ^4\Gamma_2(F)\rightarrow(d\epsilon^3d\gamma^4)\ ^4\Gamma_4(P)$, respectively. Presumably in the relatively small crystal field the Γ_4 level is a mixture of the two configurations $d\epsilon^4d\gamma^3$ and $d\epsilon^3d\gamma^4$. Even so it is not quite clear why the third band in both these ions is so much more intense than the first two bands.

B. Comparison with Co^{++} in Octahedral and Tetrahedral Symmetry

The spectrum of Co^{++} in MgO can be interpreted with $Dq=960$ cm^{-1}, $E(P)=12\,500$ cm^{-1}, $E(G)=16\,100$ cm^{-1}; or a depression of 2050 cm^{-1} and 450 cm^{-1}, respectively, from the free-ion values.[1] This should be compared with the results given in Table I. These relations indicate the strong correlation between the crystal field strength and the decrease in the term values (see Sec. C for more details).

The crystal field strength in the octahedral symmetry is about 2.8 times stronger than in the fluorite symmetry. A calculation of the crystal field potential using a point charge model indicates that this is to be expected. The interionic distance of Ca−F is about 2.36 A and that of Mg−O is about 2.10 A. Since the charge on the oxygen is twice as much as that on fluorine, one finds that Dq of MgO is $(2.36/2.10)^5\times9/8\times2=4$ times that of the CaF$_2$. It is seen, as indeed expected, that the model of point charges cannot predict the crystal field strength. The calculation of Dq from first principles is a rather difficult problem and depends on a detailed

TABLE I. Comparison of experimental absorption lines with calculated transition frequencies. The theoretical frequencies have been calculated using $Dq=340$ cm^{-1}. The experimental absorption lines have been corrected for shifts caused by spin-orbit interaction, assuming $\lambda=-180$ cm^{-1} (see text).

Transition from ground state $\Gamma_2(^4F)$	Theoretical frequency (cm^{-1})	Experimental frequency (cm^{-1})	Deviation (cm^{-1})	Energy level in crystal $Dq=0$ (cm^{-1})	Energy level of free ion[a] (cm^{-1})	Difference (cm^{-1})
$\Gamma_5(^4F)$	3400	3350±50				
$\Gamma_4(^4F)$	6040	6200±100	+160±100	$E(P)=14\,000\pm100$	14 565	565±100
$\Gamma_4(^4P)$	18 280	18 200±100	−80±100			
Γ_3, $\Gamma_4(^2G)$	18 800	19 220±50	+420±50	$E(G)=16\,240\pm100$	16 540	300±100
$\Gamma_1(^2G)$	19 650	19 580±100	−70±100			
$\Gamma_5(^2G)$	20 380	20 450±100	+70±100			

[a] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1952), Vol. 2.

knowledge of the microscopic polarizability and on the detailed nature of the wave function as well as on the bonding mechanism.

The small crystal field strength results in narrower lines so that the fine structure is partially resolved. It is, therefore, planned to investigate systematically the spectra of d^7 configurations at liquid helium temperature.

Spectra of Co^{++} in crystals of tetrahedral symmetry have so far not been reported. However, McClure[8] has investigated Co^{++} in ZnO powder and Orgel[9] has summarized solution data for Co^{++} in presumably tetrahedral symmetry. From the spectrum of Co^{++} in ZnO as shown in Fig. 4, reference 8, we infer that $Dq=380-390$ cm^{-1} and that $E(P)$ is less than 11 300 cm^{-1} or depressed by 3300 cm^{-1} from the free-ion value. The solution data of the chloride, bromide, and iodide indicate Dq values from 360–290 cm^{-1} and $E(P)$ from 10 700–9000 cm^{-1}.

This interpretation of the above data of ions in tetrahedral symmetries is, however, probably incorrect. The potential for tetrahedral symmetry can be expressed as

$$V=V_0+D_3[(20/3)(Y_3^2+Y_3^{-2})] \\ +D_4[-(14/9)Y_4^0+(1/9)(70)^{\frac{1}{2}}(Y_4^4+Y_4^{-4})]. \quad (4)$$

As long as one operates within the d^7 configuration the second term in the potential (term in Y_3) will not contribute anything to the matrix elements involving the crystal field opotential. Comparison of Eqs. (1) and (4) shows than that the fluorite and tetrahedral potentials have the same sign, and for the same value of D_4 the coefficient for the tetrahedral potential is exactly one half of that for fluorite symmetry. One would expect the spectra in these two symmetries to be similar. Superficially the two spectra are similar, both having apparently an orbital singlet as the ground state. However, as will be shown in detail in a forthcoming calculation on the spectrum of Fe^{++} in tetrahedral symmetry, the second term in Eq. (4) causes considerable admixtures from higher configurations of odd parity.[10] These matrix elements are of such magnitude as to cause relatively large shifts of the various Stark levels. One can, therefore, draw no inferences regarding the crystal field strength Dq or even the energy levels scheme from the experimental spectrum without additional and elaborate calculations.

C. Comparison with d^3 Spectra in Octahedral Symmetry

The optical spectra of d^3, Cr^{3+} complexes, have been studied in detail. The spectra of V^{++} are only known in solution. The spectra of Cr^{3+} are peculiar in that they often show very narrow lines in addition to the broad bands. These have been studied in detail by many authors.[11] We shall not be concerned here with these sharp lines but with the broad bands. The spectrum in $Al_2O_3:Cr^{3+}$ (0.25% by weight) has three absorption bands as shown in Figs. 6 and 7 at 18 150 cm^{-1}, 24 900 cm^{-1}, and 39 050 cm^{-1}. The last band $\Gamma_2\rightarrow\Gamma_4(^4P)$ is reported here for the first time. Assuming a predominantly cubic field, (and not correcting for the trigonal distortion known to exist in Al_2O_3), we calculate the levels at 18 150 cm^{-1}. 24 740 cm^{-1} and 39 325 cm^{-1} using $Dq=1815$ cm^{-1} and $E(P)=9600$ cm^{-1}. The $E(P)$ level is depressed from 13 770 cm^{-1} by about 4000 cm^{-1}.

If we plot a graph in the fractional change of $E(P)$, i.e., $\Delta E(P)/E_0(P)$ against Dq (see Table II), we find that the percentage decrease is a (nearly linear) function of Dq. This again is indicative of the intimate relationship between the crystal field strength and the depression of the Coulomb energy.

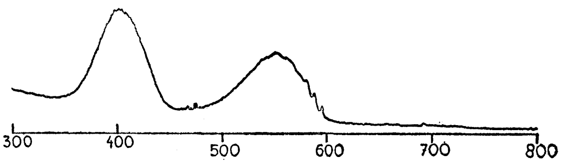

FIG. 6. Optical absorption spectrum of Cr^{3+} in Al_2O_3 in the visible region, $T=77$°K. Note the satellite structure on both transitions starting on the high-wavelength side.

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[8] D. S. McClure, J. Phys. Chem. Solids **3**, 311 (1957).

[9] L. E. Orgel, J. Chem. Phys. **23**, 1011 (1955).

[10] W. Low and M. Weger (to be published).

[11] See, for example, F. H. Spedding and G. C. Nutting, J. Chem. Phys. **2**, 921 (1934); **3**, 369 (1935). J. H. Van Vleck, J. Chem. Phys. **8**, 790 (1940); S. F. Jacobs, thesis, Johns Hopkins, 1956 (unpublished); and private information; has studied these lines very thoroughly.

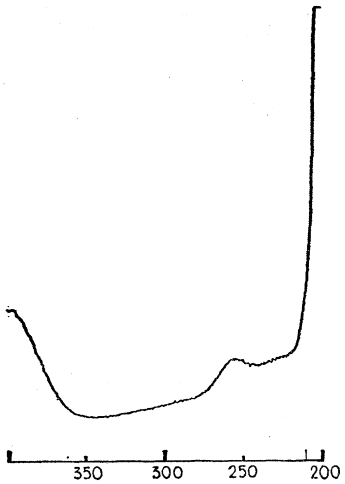

FIG. 7. Optical absorption spectrum of Cr^{3+} in Al_2O_3 in the ultraviolet region, $T=77°K$.

The third band of Cr^{3+} spectrum is of considerable smaller intensity than the first two bands. Since we have a strong crystal field this represents a double electron jump. Presumably the small but not negligible intensity of this band is caused by the trigonal component of the crystal field potential.[12]

Nevertheless the Cr^{3+} spectrum is distinctive in its difference rather than in its resemblance to the Co^{++} spectrum. We do not intend to discuss the details of the Cr^{3+} spectrum which is very complicated, and despite the pioneering work of Van Vleck[11,6] is not yet understood entirely. Here we only want to point out the main differences:

(a) The Cr^{3+} spectrum shows many sharp lines whereas the Co^{++} spectrum does not.

(b) Superimposed on the first two bands of the Cr^{3+} spectrum is an additional spectrum, resembling a vibration spectrum with some peculiarities. The most intense peak of this spectrum falls where the crystal field transition $\Gamma_2 \rightarrow \Gamma_5$ is of negligible intensity.

The reasons for these differences may be connected with the strong crystal field which exists in chromium complexes. The Stark splittings are larger than the term separations of the free ion. In the trivalent ions one may have to consider an energy level scheme of the complete XY_6 complex. Possibly the differences may be also connected with the trigonal field of Al_2O_3. Similar peculiarities are found in Al_2O_3 containing other trivalent ions, for example: vanadium.

CONCLUSION

The small crystal field strength lets us predict that the paramagnetic resonance spectrum would be found at $g=2.0023-(8\lambda/3400)$, if the spin-orbit constant λ is the same as that of the free ion $g=2.42$. The spin-lattice relaxation time will be considerably reduced from that of the Cr^{3+} ion since the separation between the ground state is only 3400 cm^{-1} instead of 18 000 cm^{-1}. Indeed we have been unable to observe any paramagnetic resonance spectrum at liquid air temperature or at liquid hydrogen temperature.

TABLE II. Comparison of crystal field strength (Dq) and $E(P)$ for d^3 and d^7 configurations.

Ion	Crystal	Dq in cm^{-1}	$\Delta E(P)$	$[\Delta E(P)/E_0(P)]$ ×100%
Co^{2+}	CaF_2	340	565±100	3.8±0.7
Co^{2+}	MgO	960	2050±200	14 ±1.4
Cr^{3+}	Al_2O_3	1815	4000±400	29 ±3

The failure to observe any resonance, however, is disconcerting. Baker reports that he observed a spectrum at 20°K with $S=\frac{1}{2}$, $g_\perp=3.4$, $B=0.017$ cm^{-1}, and $g_\parallel \sim 6.6$, which he attributes to Co^{++} since the hyperfine structure showed a spin of 7/2.[4] Moreover, he also obtained a well-resolved anisotropic fluorine hfs, and an indication that the interaction is with four fluorine atoms only. The anisotropic hfs interaction with the fluorines can be explained, according to him, if strong covalent bonding exists so that the Russell-Saunders coupling is broken down. However, the large g factor is indicative that the ground state cannot be an orbital singlet which would result from a strong bonding model.

Our results cannot be reconciled with these paramagnetic data. The optical spectra indicates very conclusively that the ground state is an orbital singlet and that Russell-Saunders coupling is a good approximation. It is difficult, therefore, to obtain such a large and anisotropic g factor. Secondly, the small crystal field and the small reduction of the $E(P)$ level suggest that the complex is essentially ionic. The extensive hfs interaction with the fluorines can, therefore, also not be explained. We strongly suxpect, that the spectrum may be that of V^{++} in the symmetry of CaF_2. The predicted g factors in this case would be similar to that of Co^{++} in octahedral symmetry, and would obey the approximate relation $g_\parallel+2g_\perp=13$, which is seen to hold true $(6.6+2\times3.4=13.4)$.*

ACKNOWLEDGMENTS

We are grateful to Dr. A. Halperin for permitting the use of the various optical spectrophotometers in his laboratory and to Dr. J. M. Baker for advance information regarding his paramagnetic resonance results.

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[12] C. J. Ballhausen (private communication).

* *Note added in proof.*—This assumes that the lowest level is the doublet at $15/4\lambda$. Since, however, λ is positive for V^{++} it is unlikely that this doublet would be lowest. We have not yet calculated what g factor would be obtained for the doublet level and quartet level at $-9/4\lambda$.