Paramagnetic Resonance and Optical Absorption Spectra of Cr^{3+} in MgO†

W. Low*

Enrico Fermi Institute for Nuclear Studies, University of Chicago, Chicago, Illinois

(Received September 21, 1956)

The paramagnetic resonance spectrum of the trivalent chromium ion has been detected at a wavelength of 1.2 cm. The spectrum is isotropic with one line at $g = 1.9800 \pm 0.0006$. The hyperfine structure of the Cr^{53} isotope in its natural abundance was detected. The hyperfine structure constant $A = (1.60 \pm 0.03) \times 10^{-4}$ cm^{-1} permits an evaluation of the nuclear magnetic moment as 0.475 nm. The narrow line and the failure to observe any ground state splitting show that the trivalent chromium ion is exposed to a very pure cubic field. There is no indication of associated vacancies with the Cr^{3+} ion. Optical absorption lines were found at 16 000, 22 700, and 29 700 cm^{-1} as well as a beginning of absorption at 46 000 cm^{-1}. The 16 000 cm^{-1} line is caused either by a quartet-doublet transition or by the Cr^{2+} ion. The other absorption lines can be fitted with $Dq = 2270$ cm^{-1} and the ^4P state at 10 000 cm^{-1} above the ^4F state. An analysis of the paramagnetic and optical absorption spectra indicate very strong crystal field and some covalent bonding. Probably the Cr^{3+} and the surrounding six oxygen atoms have to be regarded as a very tightly knit unit.

1. INTRODUCTION

TRIVALENT chromium has three d electrons and a ground state of $^4F_{\frac{3}{2}}$. A cubic crystalline field splits the sevenfold-degenerate level into a low singlet and two higher triplets. The ground state responsible for the paramagnetic resonance absorption acts like a ^4S state, as the next highest triplet is separated by $10Dq$ or about 10^4 cm^{-1}. Spin-orbit coupling does not remove the fourfold spin degeneracy of the ground state.

There has been considerable experimental[1,2] and theoretical[3,4] work on Cr^{3+}. The chromium alums have been studied in detail, probably to a greater extent than any other crystal containing chromium. These alums are subject to a small trigonal field superimposed on the dominant cubic field. This results in a partial removal of the spin degeneracy and the ground state is split into two Kramers doublets. The separation of these doublets is as much as 0.12–0.18 cm^{-1} for the various alums. In a strong magnetic field the remaining degeneracy is removed, and experimentally one observes three electronic transitions. In a cubic field, in the absence of internal magnetic fields, these three transitions should coincide, and only one line should be observed.

Actually the chromium spectrum is complicated by the fact that there is a stable isotope of about 9.55% abundance with nuclear spin of $\frac{3}{2}$. This results in small but detectable paramagnetic hyperfine structure. This structure has so far been detected only in crystals enriched in Cr^{53} and thus the spin of $\frac{3}{2}$ was established.[5,6]

In this paper we report the detection of the hyperfine structure in an unenriched sample. This detection of the hyperfine lines with intensities of less than 1/40 of the main line due to the main isotope proved to be possible only because of the very narrow line width of the various lines.

The measurement of only one electronic transition and the very narrow lines enables one to measure the g factor fairly accurately. The deviation of the g factor from that of the free electron gives a measure of the contribution of the exited triplet state to the ground state. This contribution is proportional to λ/Δ, where λ is the spin-orbit coupling and Δ the separation of the first triplet from the singlet in the crystal. A knowledge of Δ can be obtained from the optical absorption spectrum of Cr^{3+}.

The spectrum of Cr^{3+} has some additional interest for the theory of the solid state. During the investigation of Fe^{3+} in MgO, it was found that the trivalent ferric ion in the divalent lattice behaves as if it is surrounded by a cubic field to a very high approximation.[7,8] Apparently there are no associated vacancies. As both Fe^{3+} and Cr^{3+} have effective S ground states, we were led to believe that the chromium ion as well would be surrounded by a cubic field. The observed single absorption line and the very narrow lines indeed confirm this.

In Sec. 2 an outline of the theory is given, and in Sec. 3 the paramagnetic resonance spectrum is described. Section 4 describes the experimental results of the optical absorption experiments. In Sec. 5 the significance of these results are discussed. It is shown that the chromium ion and the six oxygen atoms are tightly knit and form considerable π bonding.

2. THEORY

The matrix elements of Cr^{3+} expressed in multiples of Dq are given by Finkelstein and Van Vleck.[4] The

[1] D. M. S. Bagguley and J. H. E. Griffith, Proc. Roy. Soc. (London) A204, 188 (1950).

[2] B. Bleaney, Proc. Roy. Soc. (London) A204, 203 (1950).

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

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

[5] B. Bleaney and K. D. Bowers, Proc. Phys. Soc. (London) A64, 1135 (1951).

[6] K. D. Bowers, Proc. Phys. Soc. (London) A65, 860 (1952).

[7] W. Low, Proc. Phys. Soc. (London) (to be published).

[8] W. Low, Bull. Am. Phys. Soc. Ser. II, 1, 283 (1956).

significant ones for the discussion of the experimental results are

	$^4A_{2g}(^4F)$ Γ_2	$^4T_{2g}(^4F)$ Γ_5	$^4T_{1g}(^4F)$ Γ_4	$^4T_{1g}(^4P)$ Γ_4	
$^4A_{2g}(^4F)$ Γ_2	-12				
$^4T_{2g}(^4F)$ Γ_5		-2			
$^4T_{1g}(^4F)$ Γ_4			6	4	(1)
$^4T_{1g}(^4P)$ Γ_4				4	$E(^4P)$,

where $E(^4P)$ is the energy of the ^4P state of the ion measured from the ground state (i.e., from $^4F=0$). The energy $E(^4P)$ is treated as a parameter, as this energy in a crystal is not necessarily that of the free ion and usually is smaller. $\Gamma_2, \Gamma_4, \Gamma_5$ are the cubic representations of the various states and A_{2g}, T_{2g}, T_{1g} are the same states in Mulliken's notation. Dq is a measure of the crystal field strength and depends on the geometry of the complex. Solution of the above matrix yields a singlet (Γ_2) at $-12Dq$, a triplet (Γ_5) at $-2Dq$, the next triplet (Γ_4) at

$$\frac{6Dq+E(P)}{2}-\left[\left(\frac{E(P)-6Dq}{2}\right)^2+(4Dq)^2\right]^{\frac{1}{2}},$$

and the P state (Γ_4) at (2)

$$\frac{6Dq+E(P)}{2}+\left[\left(\frac{E(P)-6Dq}{2}\right)^2+(4Dq)^2\right]^{\frac{1}{2}}.$$

The $^4F(\Gamma_4)$ and $^4P(\Gamma_4)$ states perturb each other appreciably, the ^4P state being raised by the off-diagonal elements.

The singlet and next higher triplet levels are separated by $\Delta=10Dq$. The contribution of the triplet to the orbital moment of the ground state is expressed in the deviation of the g factor from the "spin only" value, i.e.,

$$g-g_e=-8\lambda/\Delta. \quad (3)$$

Spin-orbit coupling does not remove the spin degeneracy of the ground state since $D_{\frac{3}{2}}\times\Gamma_2=\Gamma_8$, but the two triplets Γ_4, Γ_5 are split into four components each, Γ_6, Γ_7, and $2\Gamma_8$, with splittings small compared with $10Dq$.

An external or internal magnetic field caused by the nuclear magnetic moment removes this degeneracy. Figure 1 shows the energy levels of the ground state in zero magnetic field and in the Paschen-Back region. The dotted lines indicate the energy levels of the even isotopes of chromium. At high magnetic fields the four energy levels diverge linearly, and the three transitions coincide at $h\nu=g\beta H$. The nuclear spin of $\frac{3}{2}$ splits the

energy levels in zero magnetic field. In high magnetic fields, transitions $\Delta M=\pm1$, $\Delta m=0$ are allowed, and one can expect four hyperfine lines each separated from the other by an energy A. The spin Hamiltonian in a cubic field is given by

$$H=g\beta\mathbf{H}\cdot\mathbf{S}+A\mathbf{I}\cdot\mathbf{S}, \quad (4)$$

and the transitions are

$$H=H_0-Am+(A^2/2H)[I(I+1)-m^2+m(2M-1)], \quad (5)$$
$$H_0=g\beta H.$$

3. PARAMAGNETIC RESONANCE SPECTRUM

The paramagnetic resonance spectrum was measured at room and liquid nitrogen temperatures on single crystals containing Cr^{3+} as an added impurity of $<0.01\%$ or $>0.1\%$ by weight. The results here will refer only to the dilute crystal. In the more concentrated crystal there were many lines in addition to those reported here. Some of these lines are caused by Mn^{2+}, Fe^{3+}, and other impurities, others by the high concentration of Cr^{3+} ions. This spectrum is still being investigated.[‡]
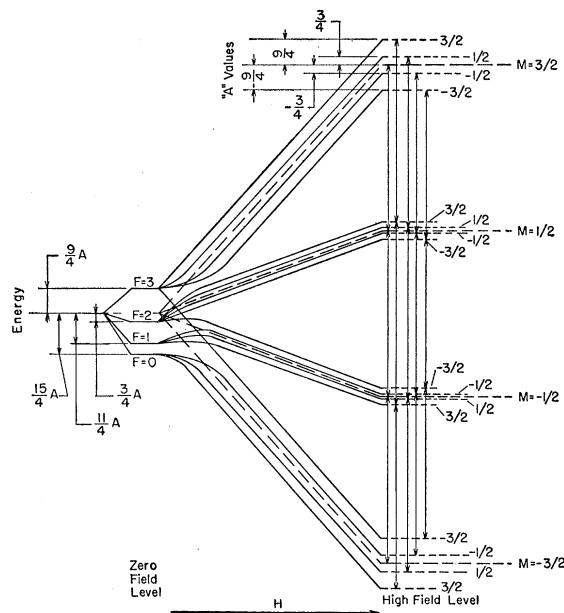

FIG. 1. A schematic energy level diagram of the electronic energy levels in zero and strong magnetic fields, together with the splitting caused by the nuclear spin. The dashed line — — indicates the energy levels of the even isotopes of chromium, the solid line —— those of the odd isotopes of Cr^{53}. The observed transitions are indicated by arrows.

‡ Note added in proof.—The spectrum can be understood if a small percentage of the chromic ions in the crystal containing a high concentration of Cr^{3+} ions are exposed to an axial field the axes of which are along the crystal cubic axes. The spectrum shows three magnetic ions and can be described in terms of the spin Hamiltonian:

$$H=g_{||}\beta HS_z+g_{\perp}\beta(H_xS_x+H_yS_y)+D(S_z-S(S+1))$$
$$+AS_zI_z+B(S_xI_x+S_yI_y)$$

$g_{||}=1.980\pm0.001, \quad g_{\perp}=1.986\pm0.001, \quad D=819\times10^{-4}$ cm^{-1},
$A=B=16.2\pm0.4\times10^{-4}$ cm^{-1}.

Figure 2 shows a recording of the spectrum. There is one intense line at $g = 1.9800 \pm 0.0006$ and four components of intensity $1/42 \pm 5\%$ equally spaced with separations of $A = (1.60 \pm 0.03) \times 10^{-4}$ cm^{-1}. The line widths of the central line and the components are roughly equal and approximately 1.5 gauss. The spectrum is isotropic.§

In addition, several closely spaced doublets and singlets at intervals of about 80 gauss were observed. The intensity of these lines is about $\frac{1}{2}$ to $\frac{2}{3}$ of the hyperfine lines, and the lines do not vary in positions for various crystal orientations. Bleaney and Ingram[9] also have reported that in several of their crystals, for example in fluosilicate, weak lines have been observed. The origin of these lines is not understood at present and is being investigated further. It is possible that
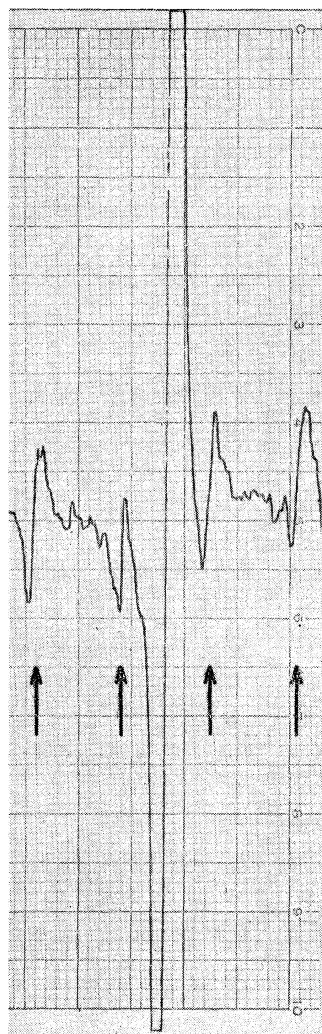

FIG. 2. Paramagnetic resonance spectrum of Cr³⁺ in MgO. The four satellites are the hyperfine lines of Cr⁵³, confirming the spin $\frac{3}{2}$.
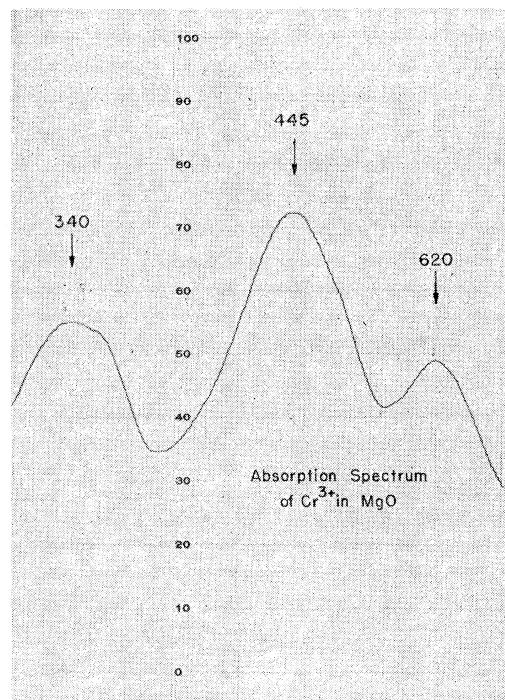

FIG. 3. Optical absorption spectrum of Cr³⁺ in MgO.

they are caused by an additional impurity with a concentration of less than 0.001%. It is also possible that some of these lines are caused by Cr²⁺.

4. OPTICAL ABSORPTION SPECTRUM

The optical absorption spectrum was scanned from 2800 A to 215 A on a Beckmann DK spectrophotometer and from 750 A to 350 A on a Beckmann DU spectrophotometer on single crystals of MgO:Cr³⁺ containing $>0.1\%$ of chromium. Figure 3 shows the absorption peaks at 16 200, 22 700, and 29 700 cm^{-1} as recorded on the Beckmann DU spectrophotometer. There is an indication of a beginning of an absorption line at 46 000 cm^{-1}.

There are a number of reasons against assigning the 16 200-cm^{-1} line to the $^4A_{2g}(\Gamma_2) \rightarrow {}^4T_{2g}(\Gamma_5)$ transition: (1) If this were so, then the $^4A_{2g}(\Gamma_2) \rightarrow {}^4T_{1g}(\Gamma_4)$ transition presumably is at 22 700 cm^{-1} which can be fitted by taking $E(P) \sim 9800$ cm^{-1}. The next $^4A_{2g}(^4F) \rightarrow {}^4T_{1g}(^4P)$ absorption line is predicted from equation 2 at 35 700 cm^{-1}, which is about 6000 cm^{-1} above the observed 29 700-cm^{-1} line. This is far outside the experimental error. (2) The intensity of the $^4F - {}^4P$ transition is expected to be larger than that of a transition within the ^4F multiplet ($\Delta L = 0$) analogously to the Ni absorption spectrum. Experimentally it is found that the 29 700-cm^{-1} absorption line is weaker than that at 22 700 cm^{-1}. (3) In all hydrated ions the Dq value is larger than 1620 cm^{-1}; for example, in $[Cr(H_2O)_6]^{3+}$ absorption lines are found at 17 480 and

[9] B. Bleaney and D. J. E. Ingram. Proc. Phys. Soc. (London) A63, 408 (1950).
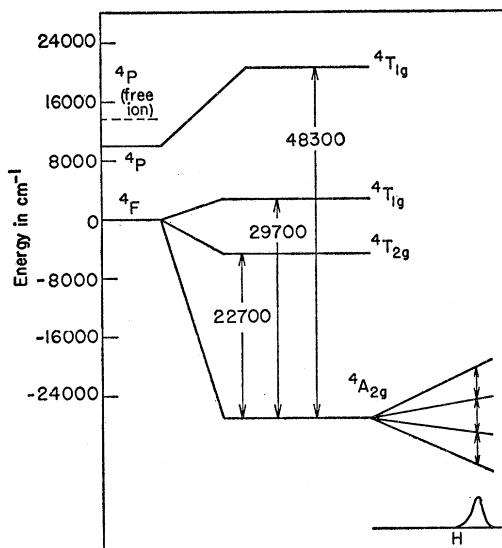
FIG. 4. Energy level diagram of Cr^{3+} in MgO. The spectrum is fitted to the observed lines at 22 700 and 29 700 cm^{-1}, predicting a line at 48, 300 cm^{-1}. The energy level of $E(P)$ of the ^4P state is lowered by about 3000 cm^{-1} compared to that of the free ion (dashed line — —).

24 500 cm^{-1},[10] and in $[Cr(NH_3)_6]^{3+}$ at 21 500 and 28 500 cm^{-1}.[11] We would expect the crystal field strength to be larger in MgO than in the hydrated ions. There has been considerable evidence for this from optical absorption and paramagnetic resonance spectra on Ni^{2+}, Fe^{2+}, Fe^{3+}, and Mn^{2+} in MgO.[12] A Dq value as large as in $[Cr(NH_3)_6]^{3+}$ or even larger can be expected.

We are inclined to assign the 22 700-cm^{-1} absorption line to the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition ($Dq = 2270$ cm^{-1}). The $^4A_{2g} \rightarrow {}^4T_{1g}$ transition at 29 700 cm^{-1} and the $^4A_{2g}(^4F) \rightarrow {}^4T_{1g}(^4P)$ transition at 48 300 cm^{-1} are calculated by assuming $E(P) = 10\,000$ cm^{-1}. The beginning of the new absorption peak at about 46 000 cm^{-1} is probably this $^4F \rightarrow {}^4P$ transition. The energy level diagram is shown in Fig. 4.

There remains the problem of assigning the 16 200-cm^{-1} transition. This may be the transition $^4F(\Gamma_2) \rightarrow {}^2G(^2\Gamma_3)$. It is impossible to calculate this transition without a knowledge of the energy level of $E(G)$ and the perturbing levels of $E(H)$ and $E(D)$ of the G, H, and D states in the ion. Assuming that they are not radically different from those of the free ion and the large value of $Dq = 2270$ cm^{-1}, one finds that the $^2\Gamma_3$ state can be depressed sufficiently to bring it close to 16 000 cm^{-1}. This transition is forbidden because of the change in multiplicity, and only a weak line would be expected.|| Another and more likely possibility is that

[10] H. Hartmann and H. L. Schafer, Z. Naturforsch. **6a**, 760 (1951).
[11] M. Lindard and M. Weigel, Z. anorg. Chem. **266**, 49 (1951).
[12] W. Low (to be published).
|| Note added in proof.—Assuming that the energy level of the ^2G state in the crystal is the same as that of the free ion (center of gravity at 14 750 cm^{-1} above that of the ^4F level) we calculate the $^2\Gamma_3$ level to be at 16 900 cm^{-1} in fair agreement with the line at

this transition is caused by the Cr^{2+} ion. The value 16 200 cm^{-1} is somewhat high compared with 14 000 cm^{-1} for Cr^{2+} in solution,[13] but higher Dq values are always found for the iron group in MgO crystals.

5. DISCUSSION

The detection of only one electronic transition, and the isotropic narrow central and hyperfine lines, indicate that the trivalent chromium ion in the divalent MgO lattice is exposed to a cubic field of high purity. One may infer that despite the excess charge on the chromium there are no associated vacancies in the neighborhood of the chromium ion. Even small distortions of the crystalline electric field would split the ground state (in alums this splitting is several thousand gauss), or at least broaden the absorption line considerably. We have reported in a previous communication[8] the spectrum of Fe^{3+} in MgO and from its pattern and angular variation with the magnetic field deduced that the ion is surrounded by a cubic field. Cr^{3+} with its $3d$ electrons (a filled subshell) and Fe^{3+} with its $5d$ electrons ($^6S_{5/2}$ state) have a symmetrical charge distribution in their ground states. These trivalent ions are a poor fit in the lattice because of the extra positive charge. This symmetrical charge attracts the oxygen ions, drawing them closer to the trivalent Cr^{3+} ion, and set up a stronger crystalline electric field. One probably has to regard these trivalent ions and the surrounding six tightly bound oxygen ions as a unit. Charge compensation in the crystal is effected either by excess oxygen ions[14] or by vacancies distributed at random throughout the crystal.

Confirmation of strong crystalline fields and covalent bonding is obtained from an analysis of the observed paramagnetic and optical absorption data. The crystalline field strength parameter Dq is approximately equal to those of fairly strong covalent complexes (Table I). Taking $\Delta = 22\,700$ cm^{-1}, $g = 1.9800$ we find $\lambda = 63$ and the ratio of $\lambda/\lambda_0 = 0.69$, $E/E_0 = 0.72$, where λ_0 and E_0 are the spin-orbit coupling and energy level of the ^4P

TABLE I. Cubic field strength parameter Dq, spin-orbit coupling λ, and energy level of the ^4P state for chromium complexes.

Substance	Dq in cm^{-1}	$E(P)$ in cm^{-1}	λ/λ_0	E/E_0	Reference
$Cr(H_2O)_6^{3+}$	1760	10 200	0.63±0.06	0.74	a
$Cr(NH_3)_6^{3+}$	2150	10 000	⋯	0.72	b
MgO:Cr^{3+}	2270	10 000	0.69±0.02	0.72	This paper

a See reference 13.
b M. Linhard, Z. Electrochem. **50**, 224 (1944).

16 200 cm^{-1}. We also compute the $^2\Gamma_5$ level to be at 26 500 cm^{-1}. There is an indication of a shoulder at 27 000 cm^{-1} superimposed on the 29 700 cm^{-1} line. The relative large intensity of the quartet-doublet transitions is explained if one includes spin-orbit interaction.[4] This causes quartet admixtures to the doublet states and one cannot speak any more of pure ^2G or ^4F levels. Experiments at low temperatures are planned to verify this assignment.
[13] D. S. McClure, Technical Report No. 3, 1955 (unpublished).
[14] J. E. Wertz and J. L. Vivo, Phys. Rev. **100**, 1792 (A) (1955).

state of the free ion respectively. ($\lambda_0=91$ cm^{-1}, E_0 = 13 770 cm^{-1}.[15]) This is in approximate agreement with the values calculated for $[Cr(NH_3)_6]^{3+}$ (see Table I). Note that the relative error is estimated from the error in measurement of the g factor and does not include the error in Δ.

Owen[16,17] has discussed in detail the influence of covalent bonding on the magnetic and optical measurements. The main effects are a large splitting Δ and a partial transfer of unpaired electrons to the attached atoms of the complex. This transfer reduces the Coulomb interaction between the d electrons and causes, therefore, a reduction in $E(P)$. The modified orbits reduce the contribution of the orbital magnetic moment to the g factor and account for the apparent reduction of the spin-orbit coupling.

As Cr^{3+} has three $d\epsilon$ electrons, it can form only π bonds with the surrounding oxygen atoms. The reduction of the spin-orbit coupling is caused mainly by the covalent π bonds. Apparently the wave function of the magnetic electrons extends far out on the oxygen atoms. The unit is not unlike a molecule.

Additional indication of π bonding is found from the reduced hyperfine structure. The observed A and g are compared with previous measurements in Table II. The hyperfine structure in Cr^{3+}, as in Mn^{2+}, arises only from configurational admixtures[18] of the type $3s3d^n4s$. Table II shows a correlation of the amount of bonding and the reduction of the hyperfine structure constant. An inverse correlation exists between the observed g factor and the hyperfine structure constant: the larger the hyperfine structure (the more ionic the crystal), the smaller the g factor. A similar relation exists in the isoelectronic V^{2+}. Van Wieringen[19] has made extensive measurements on Mn salts and found a relation between the amount of covalency and reduction of the hyperfine structure. Since the whole problem of configurational interaction in paramagnetic resonance spectra is still an open question,[20] it is not yet worthwhile to undertake calculations how bonding might affect the amount of promotion of electrons into states of $3s3d^n4s$.

[15] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1948), Vol. 2, 1952.

[16] J. Owen, Proc. Roy. Soc. (London) A227, 183 (1955).

[17] J. Owen, Discussions Faraday Soc. 19, 127 (1955).

[18] A. Abragram and H. M. L. Pryce, Proc. Roy. Soc. (London) A205, 136 (1951).

[19] J. S. Van Wieringen, Discussions Faraday Soc. 19, 118 (1955).

[20] Abragram, Horowitz, and Pryce, Proc. Roy. Soc. (London) A230, 169 (1955).

TABLE II. Values of g factor and hyperfine structure constant A for Cr^{3+} and V^{2+} in various crystals.

Crystal	g factor	A in 10^{-4} cm^{-1}	Reference
KAl(SeO$_4$)$_2$·12D$_2$O:Cr^{3+}	1.976 ±0.002	18.5 ±1	a
MgO:Cr^{3+}	1.9800±0.0006	16.0 ±0.3	This paper
K$_3$[CO(CN)$_6$]:Cr^{3+}	1.992 ±0.002	14.7 ±1	a
(NH$_4$)$_2$Zn(SO$_4$)$_2$·6H$_2$O:V^{2+}	1.951	88 ±2	a
MgO:V^{2+}	1.9803±0.0005	74.24±0.2	a
K$_4$Fe(CN)$_6$·3H$_2$O:V^{2+}	1.992	56	b

a These data are taken from K. D. Bowers and J. Owen, Repts. Progr. Phys. 18, 304 (1955).

b W. Low, Phys. Rev. 101, 1827 (1956).

Assuming that the magnetic field set up by the unpaired electrons (due to configurational interaction) is the same for Cr^{3+} and V^{2+}, then one can evaluate the nuclear magnetic moment of Cr^{53}. Taking A(V^{51}) = 74.24×10^{-4} cm^{-1} and the nuclear moment of V^{51} as 5.145 nm, we find the value of 0.475 nm for Cr^{53}. This is in surprising good agreement with the value -0.4735 found by nuclear induction.[21,22] This agreement may be, however, fortuitous as the amount of covalent bonding differs probably in V^{2+}.

6. CONCLUSION

We have shown that the combined paramagnetic and optical absorption spectra can yield important information concerning both the ground state and excited states of single crystals. In MgO:Cr^{3+} it is found that there exist a very strong crystalline field and considerable covalent bonding. The effect of this is to reduce the orbital contribution to the g factor, to reduce the hyperfine structure splitting, and to shift the optical transitions to shorter wavelengths.

The very narrow line width and the isotropic paramagnetic absorption line have indicated that the Cr^{3+} ions are exposed to very pure cubic fields. This is a result of some importance to the solid state physics of impurity centers and vacancies. It indicates that no vacancies are in the near neighborhood of the Cr^{3+} ions.
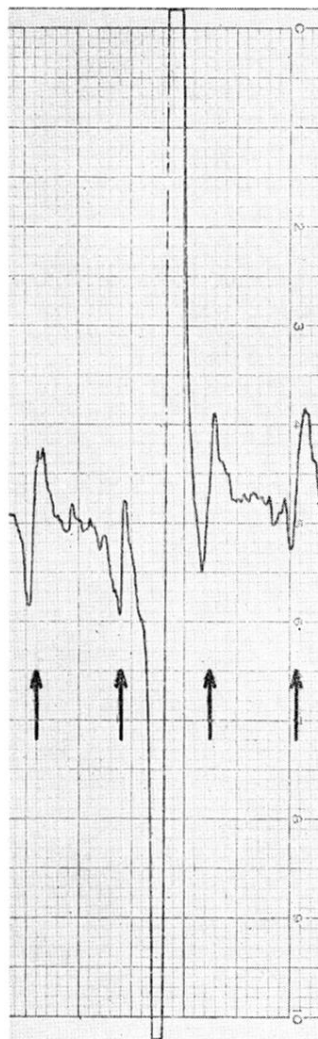
A by-product of these measurements is the evaluation of the nuclear magnetic moment of Cr^{53} as 0.475 nm in agreement with previous values.

[21] F. Alder and K. Halbach, Helv. Phys. Acta 26, 426 (1953).

[22] C. D. Jeffries and P. B. Sogo, Phys. Rev. 91, 1286 (1953).

FIG. 2. Paramagnetic resonance spectrum of Cr^{3+} in MgO. The four satellites are the hyperfine lines of Cr^{53}, confirming the spin $\frac{3}{2}$.
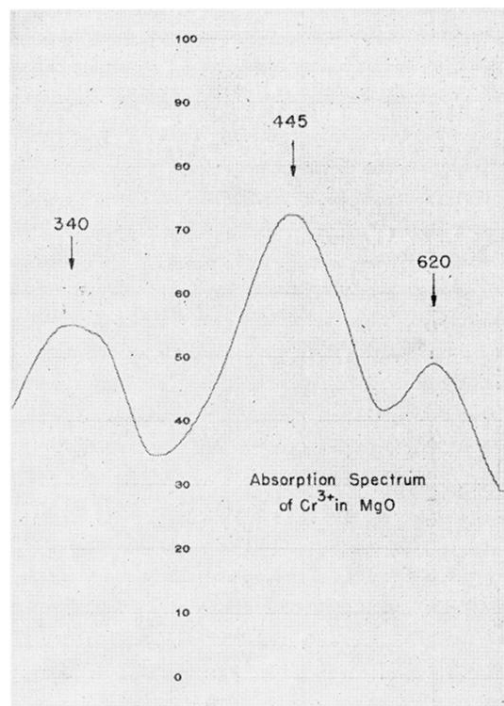
FIG. 3. Optical absorption spectrum of Cr³⁺ in MgO.