Ultrasonic attenuation measurements in the presence of a magnetic field should provide the answer to this question. Geometric resonances in these experiments give a measure of maximum and minimum diameters of the Fermi surface[9] and tend to see the grosser aspects of the Fermi surface rather than small pockets. Thus resonances associated with the second-zone surface should be seen. If this surface intersects the zone boundary, then the resonances should become profoundly modified when the field orientation is such that the diameter in question leads to the region of intersection. Such modifications have been seen by Morse and Gavenda[10] in the resonances in copper. If the surface does not intersect the zone, the simple resonance should be seen for all orientations. Very possibly the results of such a measurement would not be simple and some interpretation would be necessary, but they should shed light on the question. Attempts are being made at this laboratory to observe the geometric resonances in aluminum.

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zone which contain electrons and which give rise to the high-frequency de Haas–van Alphen oscillations. Remaining portions of surface could be distorted to explain the remaining data. Heine discarded this possibility on the basis that theoretically one would expect these surfaces to be flatter than the de Haas–van Alphen data allow. It was seen in Sec. IV, however, that this is not true, so they cannot be discarded on such grounds. This possibility is not considered here because it requires rather major deviations from what is expected theoretically (deviations comparable with those required by Heine's model). If it were to turn out that the second-zone Fermi surface does intersect the zone face, and that major deviations are, in fact, required this possibility should be reconsidered.

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Paramagnetic Resonance Spectra of Chromium and Manganese in the Spinel Structure*

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The paramagnetic resonance spectrum of Cr^{3+} was measured on the single crystal of ruby spinel $MgAl_2O_4$ at the wavelengths of 3 cm, 1.2 cm, and 8.6 mm. The spectrum confirms that Cr^{3+} is at a B site and can be described with an axial spin Hamiltonian $S=\frac{3}{2}$, $2D=0.990\pm0.005$ cm^{-1}, $g_{\parallel}=1.986\pm0.001$, $g_{\perp}=1.989\pm0.002$.

The paramagnetic resonance spectrum of Mn^{2+} was measured on the single crystal of $ZnAl_2O_4$ at 3 cm. The spectrum consists of six nearly isotropic lines with $A=74.9\pm0.5\times10^{-4}$ cm^{-1}, $g=2.000_2\pm0.001$. The cubic or axial splitting was less than 8×10^{-4} cm^{-1}. The spectrum is indicative that Mn^{2+} is located at an A site.

I. INTRODUCTION

The mineral spinel, $MgAl_2O_4$, and other crystals isomorphous with it, are of the general composition MR_2O_4 in which M and R are divalent and trivalent ions, respectively. The system forms a close-packed structure. The lattice can be considered to consist of two sublattices. One type of cation is surrounded by six oxygen ions arranged approximately at the corners of an octahedron and this is in general referred to as the B site. In the A site the cation is surrounded by four tetrahedrally situated nearest-oxygen neighbors.[1]

Spinel-type compounds containing ions belonging to the first transition group have become recently important. They are nonconducting and antiferromagnetic or ferrimagnetic. The magnetic properties of these materials are determined to a large extent by their relative distribution of the ions M and R at the octahedral or tetrahedral sites.[2–6]

The distribution of the various ions among A and B sites has been investigated by x-ray and neutron diffraction.[7–10] Recently a simple theoretical explanation of the cation distribution has been given by McClure[11] and by Dunitz and Orgel[12] using crystal-field and symmetry considerations.

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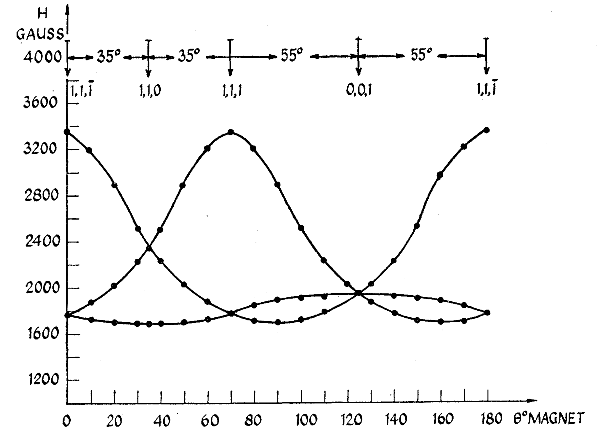

FIG. 1. The paramagnetic resonance spectrum of Cr^{3-} at 9.4 kMc-sec. The magnetic field is rotated in a plane defined by the directions [111] and [001].

We have embarked on a systematic study of the spinel-type crystals using paramagnetic resonance techniques. This technique determines the lowest energy levels in a magnetic field. The order of these energy levels is determined by the symmetry and the strength of the crystal field acting on the paramagnetic ion. It is not difficult to discriminate between octahedral and tetrahedral symmetries, since the sign of the cubic field parameter is either positive or negative, respectively. We hope to obtain in this way new data on the properties of ions in the tetrahedral symmetry for which only few magnetic and optical data are available.

It is the authors' belief that a systematic study of the spinel-type crystals in their paramagnetic phase (i.e., diamagnetic crystals with added paramagnetic impurities) may shed light on their properties in the ferromagnetic phase. The explanation of many of their properties was based on conjectures such as ad hoc assumptions on the role of the Jahn-Teller distortions and covalent bonding.

In this paper we discuss the paramagnetic properties of chromium and manganese substituted spinels. In subsequent articles we shall present optical and magnetic spectra on cobalt and iron spectra in the spinel symmetry.

II. THE SPECTRUM OF Cr^{3+} IN $MgAl_2O_4$

A. Experimental Results

The paramagnetic resonance spectrum of Cr^{3+} was studied in a number of natural crystals. These grow in pink octahedrons. The measurements were made at 3 cm, 1.25 cm, and about 8.6 mm of wavelength.

The spectrum can easily be detected at room temperature. A cursory inspection of the spectrum at 3 cm indicates that there are 4 ions in the unit cell. Each ion shows the same spectrum and corresponds to an ion located in the center of an octahedron of oxygen ions which is distorted along the body diagonal of the cube of the unit cell, i.e., along the [111], $[1\bar{1}1]$, $[11\bar{1}]$, and $[\bar{1}11]$ directions. The spectrum of each ion at 3 cm can be explained with a single spin Hamiltonian of the form

$$H_s=g_{\parallel}'\beta H_zS_z+g_{\perp}'(\beta H_xS_x+\beta H_yS_y), \tag{1}$$

with $S'=\frac{1}{2}$, $g_{\parallel}'=1.986\pm0.002$, $g_{\perp}'=3.924\pm0.002$, in which $g_{\parallel}$ is measured along the body diagonal direction [111] and $g_{\perp}$ along the $[1\bar{1}0]$ direction.

The spectrum has been investigated as a function of the direction of the magnetic field with some of the symmetry planes. In Fig. 1 the spectrum is shown when the magnetic field is rotated in the plane defined by the direction [111] and [001]. In the plane the [111] and $[11\bar{1}]$ directions are located symmetrically with respect to the [110] direction, forming an angle of 35°16′ with it, and are also symmetrical with the [001] direction at an angle of 54°44′. The other directions $[\bar{1}11]$ and $[1\bar{1}1]$ are again symmetrically located with the [001] direction and form an angle of 54°44′ with the plane. Their projections on the plane coincide and we therefore observe only one transition for both these ions at low fields.

In the [111] direction we observe one transition of one ion at $g_{\parallel}$ and one transition at a low field, corresponding to the superposition of the other three ions. (These transitions correspond to $M=-\frac{1}{2}\rightarrow-\frac{3}{2}$, where M is the strong field quantum number. If one uses the quantum notation in which the quantization is along the [111] axis this would correspond to the $\frac{1}{2}\rightarrow-\frac{1}{2}$ transition.) In the [001] direction the four ions occupy equivalent positions and their spectra, therefore, coincide. In the [110] direction the projection of the [111] and $[\bar{1}11]$ coincide and give rise to a transition at $g_{\perp}$ for these ions.

In Fig. 2 the spectrum is shown when the magnetic field is rotated in a plane defined by the directions [111] and $[1\bar{1}0]$. In this plane the projections of the

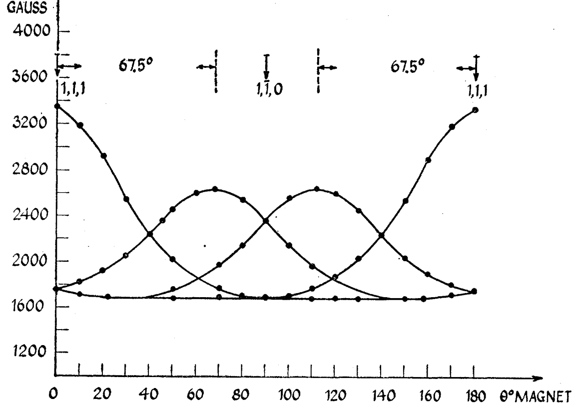

FIG. 2. The paramagnetic resonance spectrum of Cr^{3-} at 9.4 kMc-sec. The magnetic field is rotated in a plane defined by the directions [111] and $[1\bar{1}0]$.

directions $[\bar{1}11]$ and $[1\bar{1}1]$ coincide. Both form an angle of 67°37′ with the $[111]$ direction (i.e., with $\theta=0$) and 28°7.5′ with this plane. The absorption spectrum of these ions appears at a maximum at $\theta=67°37'$. The spectrum is symmetrical with respect to the $[1\bar{1}0]$ plane. The projection of the $[11\bar{1}]$ direction gives a low field absorption. At $\theta=0$ this corresponds to an angle of 70°32′ for these ions. At $\theta=90°$ the transition of the ion at the $[11\bar{1}]$ direction coincides with that of the $[111]$ direction.

No other transitions are observed at 3 cm up to a field of about 6000 gauss. Similar spectra were observed at 22.84 kMc/sec. It is well known that the ground state of the chromium ion Γ_2 is split into two Kramers' doublets by a trigonal field. The fact that only one transition is observed indicates that the initial splitting $2D$ is larger than 0.8 cm^{-1}.

The initial splitting can be evaluated by a number of methods even if the other transitions corresponding to $M=\frac{1}{2}\rightarrow-\frac{1}{2}$, $\frac{3}{2}\rightarrow\frac{1}{2}$, or $\Delta m=\pm2$, ±3 are not observed. One method is to solve the full spin Hamiltonian,

$$H_s=D[S_z^2-\tfrac{1}{3}S(S+1)]+g_{\parallel}\beta H\cos\theta S_z \\ +\tfrac{1}{2}g_{\perp}\beta H\sin\theta(S_+e^{-i\varphi}+S_-e^{i\varphi}), \quad (2)$$

for a number of angles and find the best possible fit. For this purpose we have solved the matrix of the form

$$W^4-\tfrac{1}{2}(1+20x^2)W^2+4(1-3\cos^2\theta)x^2W+\tfrac{1}{16} \\ +\tfrac{1}{2}x^2(1-6\cos^2\theta)+9x^4=0, \quad (3)$$

where $W=E/2D$ and $x=g\beta H/4D$ for various parameters of x and for angles from $0°\rightarrow90°$ for every 5°. In addition we have obtained the matrix elements $|\langle M'|J_z|M\rangle|^2$ and $|\langle M'|J_x|M\rangle|^2$. Knowing these elements, the intensity of the absorption lines can be calculated for any orientation of the rf field, the axis of quantization, with respect to the static external field.[13]

There are three unknowns, $g_{\parallel}$, $g_{\perp}$, and D, but there are a number of equations corresponding to each angle measured. In particular, the angles $\theta=0$, 54°44′, and 90° are useful since the 4×4 matrix factors into 2×2 matrices. However, the angular variation is not exceedingly sensitive to small variations in D or g if the initial splitting is very large compared with the microwave energy.

We have evaluated D using the computed energy levels and assumed for simplicity that $g_{\parallel}=g_{\perp}$. The value of $g_{\parallel}$ can be obtained accurately by measuring the transitions at $\theta=0°$ since at this angle the transition is independent of D. The value of $g_{\perp}$ can be obtained by fitting it more closely to the computed value. It can also be obtained from perturbation calculation, since $g_{\perp}'$ in the $S=\frac{1}{2}$ formalism is given in terms of $g_{\perp}$ in the $S=\frac{3}{2}$ formalism at 90° by

$$g_{\perp}'=2g_{\perp}[1-\tfrac{3}{4}(g_{\perp}\beta H/2D)]^2. \quad (4)$$

For any other angle g' is a function of $g_{\parallel}$, $g_{\perp}D$ and a complicated function of θ.[14]

A good fit is obtained by taking $2D=0.990\pm0.005$ cm^{-1}, $g_{\parallel}=1.986\pm0.001$, and $g_{\perp}=1.989\pm0.002$.

The values quoted here fit the spectrum at 1.2 cm and 8.6 mm within 0.3%.

We have interpreted the spectrum to correspond to $-\frac{1}{2}\rightarrow-\frac{3}{2}$ and assumed that D is negative. This is consistent with the fact that $g_{\perp}>g_{\parallel}$ since D is given to a first approximation by $D=4\lambda^2[(\Delta_z-\Delta_x)/\Delta_z\Delta_x]$, where λ is the spin coupling and Δ_z, Δ_x are the separations of the next higher orbital level along the z or x axes, respectively. Similarly $g_{\perp}-g_{\parallel}=-8\lambda[(\Delta_z-\Delta_x)/\Delta_z\Delta_x]=-2D/\lambda$.[†] Therefore D is negative, the same as in Al_2O_3.[15]

B. Discussion

The paramagnetic resonance spectrum indicates clearly that the chromium is surrounded by a distorted octahedral configuration (i.e., B site). This is in, agreement with susceptibility and x-ray measurements, and is also predicted from theoretical considerations.[11,12] Another confirmation comes from the optical spectrum of chromium in ruby spinel which does not differ essentially from that in aluminum oxide.

The initial splitting of the order of 1 cm^{-1} in spinel is about three times as large as that in aluminum oxide. It is not quite clear why the trigonal field is so much larger in the spinel structure.

The larger initial splitting may in part be the cause of the low-magnetic moments in spinels containing chromium. The susceptibility χ parallel to z axis is given by $\chi_z=(15g_{\parallel}^2/32T)[1-\frac{4}{5}(D/T)]$. Hence a larger trigonal distortion will give rise to a smaller susceptibility at low temperatures. Baltzer and Wojtowicz[16] have argued that the low-magnetic moments in concentrated chromic spinels are brought about by Jahn-Teller distortions of the lattice. These distortions may arise because of the magnetic interaction of the A and B sites. While this cannot be excluded, our measurements indicate that there is a large distortion even in the paramagnetic spinel.

III. THE SPECTRUM OF Mn^{2+} IN $ZnAl_2O_4$

A. Experimental Results

The spectrum consists of 6 nearly isotropic lines with the following parameters: $A=74.9\pm0.5\times10^{-4}$ cm^{-1}, $g=2.0002\pm0.001$. The full width at half intensity of the hyperfine lines $m=\pm\frac{1}{2}$ was approximately 16

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gauss along the [111] direction, and varied slightly with orientation. Assuming a pure cubic field, we can infer the maximum cubic splitting from the line width. In a cubic field the maximum separation of the $\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$ and $\pm\frac{5}{2}\rightarrow\pm\frac{3}{2}$ transitions would occur at $\pm\frac{5}{2}a$ and $\mp 2a$, where $3a$ is the initial splitting. From the line width variation we infer that $3a<8\times10^{-4}$ cm^{-1}. However, it is quite possible that an axial splitting is present. D, the axial splitting parameter, and a, the cubic splitting parameter, may be of opposite sign and thus in part may cancel each other. The square line shape at the $m=\pm\frac{5}{2}$ lines and the sharper lines of $m\pm\frac{1}{2}$ seem to indicate that the splitting is primarily caused by a cubic field. It would be instructive to confirm this by double-resonance techniques.

B. Discussion

The results reported here are very similar to those obtained by Dorain on ZnO.[17] The spin Hamiltonian in ZnO is axial and the spectrum can be accounted for with $g=2.0016\pm0.0006$, $3a=-6.0\pm1.5\times10^{-4}$ cm^{-1}, $A=76.0\pm0.4\times10^{-4}$ cm^{-1}, and $D=-216.9\pm2.2\times10^{-4}$ cm^{-1}. It is, therefore, reasonable to assume that the Mn^{2+} is substituted for the zinc ion at an A site.

The small initial splitting indicates that the symmetry of the A site must be a nearly perfect tetrahedron. Apparently the tetrahedron is not distorted in the Spinel lattice although the octahedron of Al_2O_3 shows a fairly large distortion.

In a tetrahedron one would expect, from theoretical reasonings, the cubic field splitting to be small. Watatabe[18] has shown that the cubic splitting in cubic crystals is proportional to a first approximation to the square of the crystal field strength. In a tetrahedral symmetry the crystal field strength is about 4/9 that of an octahedral symmetry. The splitting $3a$ of MgO is about 56×10^{-4} cm^{-1}. One would therefore expect that of ZnO to be less than 11×10^{-4} cm^{-1}.

The hyperfine structure constant A is somewhat larger than in tetrahedral ZnS ($\sim65\times10^{-4}$ cm^{-1}). This is indicative that in spinel the covalent bonding is certainly not larger than in ZnS.[19]

Neutron diffractions of manganese ferrite have shown that the manganese spinels have a normal structure, i.e., that the Mn^{2+} occupies an A site.[9,10] Our results confirm this assignment for the diluted spinels.

Susceptibility measurements indicate that the magnetic moment equals 5.65 μ_B for the compound $MnAl_2O_4$ compared with a "spin only" value of 5.92 μ_B.[20] Goodenough and Loeb,[3] as well as Wickham,[21] have suggested that the reduction of the magnetic moment is caused by covalent bonding which induces a large cubic field splitting of the d levels in tetrahedral symmetries. Our results seem to indicate that the manganese ion behaves normally in the diluted crystal and that the susceptibility if measured would yield the "spin-only" value. The reduction of the magnetic moment in the concentrated crystal has very likely its origin in strong exchange interactions. Possibly a fraction of the manganese ion occupies a B site in the $MnAl_2O_4$ spinel. In the B site the Mn^{2+} ions may have an antiparallel alignment compared with the A site. Susceptibility measurements would in this case measure the average magnetic moment and would not be able to discriminate between the two sites. Another possibility is that a small fraction of the manganese ions exist as Mn^{4+} or Mn^{3+} in the $MnAl_2O_4$ spinel. The resultant moment would, therefore, be correspondingly reduced.

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