Table I. The frequency of the lowest transverse optic mode at $\tilde{q}=0$ for five different temperatures.

Temperature (°K)	Frequency (10^{12} sec^{-1}) Neutron	Far infrared
90	1.23 ± 0.03	1.2[a]
142	1.72 ± 0.04	
203	2.24 ± 0.05	
296	2.73 ± 0.05	3.0[a] 2.63[b]
430	3.32 ± 0.07	

[a] See reference 3.
[b] See reference 4.

The temperature dependence of the dielectric constant ϵ is given by:

$$\epsilon \propto 1/(T - T_c),$$

where T_c is the Curie temperature. If only the lowest transverse optic mode is strongly temperature dependent then its frequency is given by[1]

$$\nu \propto (T - T_c)^{1/2}.$$

Figure 2 shows the good agreement obtained between this relation and the experimental measurements. A linear regression line through the five points give a Curie temperature of 32 ± 5°K. The other line on the figure shows the temperature dependence of the reciprocal of the dielectric constant,[5] which above 70°K predicts a Curie temperature of 28°K. The Curie temperature has also been deduced from measurements of the microwave losses by Rupprecht and Bell,[6] who obtain a temperature of 37°K.

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MAGNETIC ROTATION OF VISIBLE LIGHT BY FERROMAGNETIC $CrBr_3$

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Radiation passing through a magnetic crystal will interact with the magnetization to some degree. Rotation of plane-polarized light, magnetic birefrigence, and circular dichroism are manifestations of this interaction. This paper includes a description of exceedingly large rotations observed in visible light transmitted by ferromagnetic $CrBr_3$ single crystals as well as an outline of the theory of these rotations.

This material was found to be ferromagnetic only recently.[1] Its Curie point is at about 37°K, and its magnetization at 0°K is $3.0\ \mu_B/Cr^{+++}$ ($4\pi M_0 = 3520$ gauss). The crystals are of hexagonal symmetry, and the anisotropy is such that the magnetization prefers to lie along the sixfold axis.[1,2] The nuclear magnetic resonance of the Cr^{53} nucleus in this compound has been studied[3] as has the electron spin resonance[2] in the ferromagnetic and paramagnetic states.

The technique for growing the crystals was similar to that described by Tsubokawa.[1] Chromium tribromide has a layer structure in which hexagonal nets of chromium ions are covalently bonded[4] between two layers of bromine ions. Its poor mechanical properties make the preparation of good samples difficult. We used thin sheets from 4 to 40 μ thick whose surfaces were parallel to the hexagonal plane.

The upper curve in Fig. 1 shows the course of the absorption[5] at 4.2°K from the near infrared to a band edge in the green. It is necessary to make these observations with the crystals in a saturated condition. If this is not done

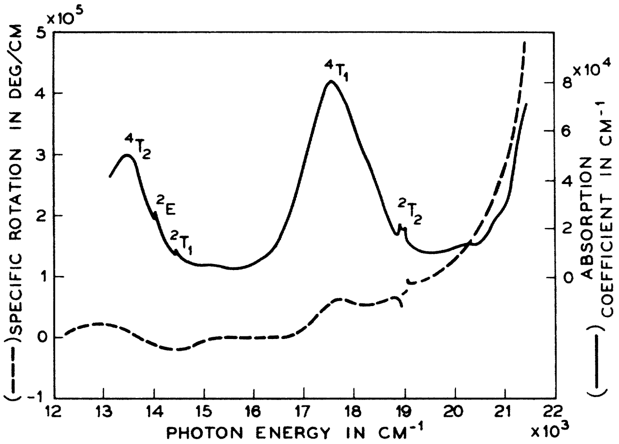

FIG. 1. The upper curve is a plot of the absorption as measured at 4.2°K. The lower curve shows the magnetic rotation as measured at 1.5°K with a saturating field along the line of sight and parallel to the c axis. The absorption curve is taken largely from data by S. Trummer.

the very fine grained domain structure actually diffracts a large fraction of the light. This will be discussed in a separate paper.[6] Note that there are several deep broad absorption bands, and some rather sharp lines as is usual in the absorption spectrum of the Cr^{+++} ion in crystals. If the magnetization and the line of sight lie along the c axis, it is found that the details of the absorption are slightly different for the two senses of circularly polarized light. For instance, the sharp lines at about 19 000 cm^{-1} appear only for one sense of circular polarization. Perhaps more important, the position of the band edge is distinctly different for the two senses.

The difference in absorption for two senses of circular polarization means that there will be a rotation of the plane of polarized light in that region in which the two dispersions differ. Figure 1 also gives the rotation encountered over the visible portion of the spectrum. This is a magnetic rotation; it is nonreciprocal, and varies as the projection of the magnetization on the direction of propagation of the light. Thus the data were taken with the magnetization and the c axis along the line of sight. It will be seen that there are slight anomalies associated with the bands, and with the lines at about 19 000 cm^{-1}.

By far the largest rotation is associated with the band edge near 20 000 cm^{-1} where values of over 500 000°/cm were measured. By way of comparison, the specific magnetic rotation of yttrium iron garnet is in the range of 2000°/cm,[7] and the absorption is such that the maximum usefully attainable rotation is perhaps 25°. For iron metal the specific rotation has been reported to be about 200 000°/cm,[8] but the metal is so opaque that only about 9° has been observed. Here the rotation is in the range of 200 000°/cm in a region where the absorption is relatively low. Rotations of perhaps 2000° can be obtained. Experiments utilizing this rotation for the microwave modulation of light are now in progress. Much of the difficulty lies in the sample preparation.

The effect of the exchange coupling between Cr^{+++} ions in this ferromagnetic crystal is to split the $^4A_2$ ground multiplet by about 10 cm^{-1}, so that at 1.5°K only $S_z = \frac{3}{2}$ is significantly populated. A comparison of our data with the correlation diagrams given by Tanabe and Sugano[9] leads to the assignments given in Fig. 1. The observed circular polarization of the $^4A_2 \rightarrow {}^2T_2$ transition corresponds to the strongest of the transitions from the lowest component of the ground state to the components of $^2T_2$. Analysis of the details of the absorption and rotation for the transition $^4A_2 \rightarrow {}^2T_2$ yields information on parameters needed in treating the absorption edge.

There are several plausible assignments for the intense absorption band, assuming O_h site symmetry and appreciable overlap between $4p$ holes on neighboring Br ions: (1) $t_{2g}^* \rightarrow t_{1u}^*$, (2) $t_{1u}(\sigma) \rightarrow t_{2g}^*$ or e_g^*, or (3) $t_{1u}^n(\pi)$ or $t_{2u}^n(\pi) \rightarrow t_{2g}^*$ or e_g^*. An energy level diagram[10] for CrBr_3 is given in Fig. 2 with these assignments indicated. The cases (2) and (3) correspond to the so-called charge-transfer transitions for which Clogston[11] has given a qualitative explanation in the case of yttrium iron garnet.

Note that only states of $^4T_2$ symmetry are accessible from the $^4A_2$ ground state by electric dipole transitions. Following Tanabe and Kamimura[12] the effective Hamiltonian for a $^4T_2$ state can be written for the magnetization along the c axis (z axis)

$$H_{\mathrm{eff}} = F(1 - T_z^2) + \lambda(S_x T_x + S_y T_y) + \lambda_0 S_z T_z + g_{\parallel} \mu_B S_z H_z^{\mathrm{ex}}.$$

In this, we have adopted the molecular field approximation. The symbol F stands for the trigonal splitting of the T_2 state, λ and λ_0 are

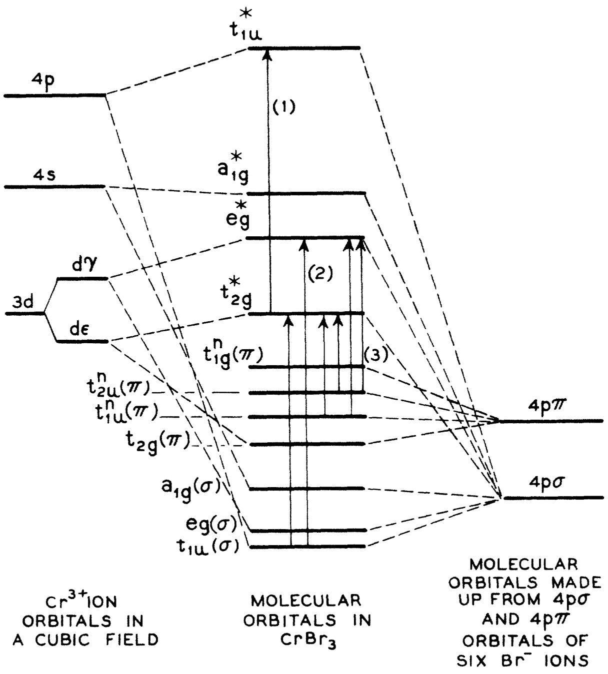

FIG. 2. Schematic energy diagram of $CrBr_3$. All orbitals up to $t_{1g}^n(\pi)$ which have mainly the character of Br^- orbitals are completely occupied. The orbitals having the character of the Br^- σ and π orbitals are indicated by (σ) and (π). The orbitals with an asterisk are all antibonding ones, and they have mainly metallic character. The t_{2g}^* orbitals are occupied by three electrons, and the remaining antibonding orbitals are vacant. The order of the nonbonding orbitals described by the superscript *n* was determined by considering the nodal pattern of these orbitals.[10]

anisotropic spin-orbit constants, H^{ex} is the magnetic field acting on the magnetic moment of the Cr^{+++} ions, and T_z corresponds to the z component of the orbital angular momentum of the P state. For this equation we have used a representation for which T_z and S_z are diagonal. Assuming $|F|$, $|\lambda_0|$ and $|\lambda| \gg |H^{\text{ex}}|$, we find that a $^4T_2$ state is split into six Kramers doublets corresponding to $m_z = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$, where m_z is the eigenvalue of the operator $T_z + S_z$. The transition from the $S_z = \frac{3}{2}$ component of the ground state to the $m_z = \frac{1}{2}$ and $\frac{5}{2}$ components of the $^4T_2$ state are possible for the right-hand and left-hand circular polarizations, respectively. A large rotation of the plane of polarization would be expected for a large energy difference between the states corresponding to $m_z = \frac{1}{2}$ and $\frac{5}{2}$. This energy difference is determined by F, λ, and λ_0 in which λ and λ_0 take different values in the three possible transitions.

In summary, we have observed in $CrBr_3$ exceedingly large magnetic rotations of linearly polarized light associated with a band edge in the green. These rotations are many times larger than those seen in ferrimagnetic oxides containing Fe^{+++}. The edge must arise from transitions between the $S_z = \frac{3}{2}$ component of the $^4A_2$ ground state and the $m_z = \frac{1}{2}$ and $\frac{5}{2}$ components of states of symmetry $^4T_2$. Several assignments for these transitions have been given. In later papers we will report the absorption and rotation in detail and consider at length the rotations associated with the band edge and with the transitions to the doublet levels. The rotation constitutes valuable extra evidence in the assignment of a transition to the absorption edge. We are studying the utilization of the rotation for the microwave modulation of light and are examining other compounds for similarly favorable rotation and absorption properties.

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