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On the Magnetic Properties of a $CrBr_3$ Single Crystal

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Magnetic properties of single crystals of $CrBr_3$ have been measured with a magnetic balance and also with a torque magnetometer. The ferromagnetic Curie point has been found to be 37°K from the temperature dependences of magnetization and of torque. Based on the data of the magnetic susceptibility above the Curie point, the paramagnetic Curie point θ_p, Curie constant C_M and the effective Bohr magneton number have been determined to be 47°K, 1.84 and 3.85 μ_B respectively. From the saturation magnetization at 4 2°K, the moment of chromium ion is estimated to be 3 μ_B, coinciding with the spin moment obtained from the susceptibility measurement above the Curie temperature. Direction of easy magnetization lies along the c-axis of the hexagonal lattice, and the second order and the fourth order anisotropy constants are estimated to be $K_1=-5.08\times10^5$ and $K_2=0.65\times10^5$ erg/cc respectively. In the present results, there is found a small deviation in the torque curves from simple sinusoidal form, $L=K\sin 2\theta$, which is discussed on the basis of the higher order term of magnetic anisotropy in the high field strength range and also of the domain-theoretical consideration in the low field strength range.

§ 1. Introduction

Several anhydrous di- or trihalides of the elements of the iron group shown an interesting magnetic property which is known to be metamagnetism. For these compounds, the paramagnetic Curie temperatures θ_p have a positive sign, and in the temperature range below these points the magnetic susceptibilities depend on the magnetic field strength. In spite of $\theta_p>0$, it was discovered by neutron diffraction experiments that the magnetic spin ordering in the crystal lattice of these compounds is antiferromagnetic. On the other hand, the chromium trihalides, $CrCl_3$(1) and $CrBr_3$(2)(3), are considered to have different magnetic properties in comparision with those mentioned above, but any detailed study was not yet undertaken. On this point of view, the magnetic properties of a single crystal of $CrBr_3$ were investigated by the present author.

§ 2. Experimental Results

A single crystal of $CrBr_3$ was prepared by heating the powdered chromium (99.3%) in the vapour of bromine (99.9%) up to about 750°C. A schematic diagram of the apparatus for growing $CrBr_3$ crystals is shown in Fig. 1. The crystals were grown up to about $4\times7\times7\ \mathrm{mm}^3$ in dimension and were cooled in the furnace F_1. The $CrBr_3$ crystals appeared in the form of hexagonal plates with a cleavage plane of (0001), dark green in color.

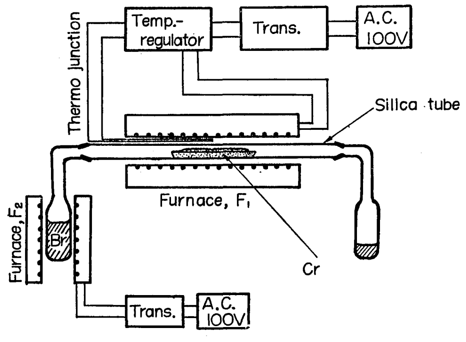

Fig. 1 A schematic diagram of the apparatus for growing the $CrBr_3$ crystals: Powdered chromium was placed in furnace F_1 and heated to 750°C. Bromine vapor was prepared by heating bromine in a glass container to 50°C by furnace F_2.

Chemical analysis showed that the $CrBr_3$ crystals thus obtained contained only trivalent chromium ions. It was also confirmed by a Debye-Scherrer X-ray pattern that the crystal was hexagonal in structure with the lattice constants $a=3.66$ Å and $c=18.30$ Å, which agreed closely with the results of the previous work⁽⁴⁾.

Temperature dependence of specific magnetization σ and of susceptibility χ above the Curie point were also measured and the results are shown in Figs. 2 and 3. The ferromagnetic Curie temperature was estimated to be about 37°K by plotting the σ^2–T curve. In Fig. 3, the inverse susceptibility is also plotted against the temperature, which shows that the paramagnetic susceptibility above the Curie temperature obeys the epuation

$$\chi=\frac{0.0063}{T\text{-}47}\ ,$$

whence the paramagnetic Curie point was determined to be $\theta_p=47$°K and the Curie constant, C_M, and the effective Bohr magneton number, p_{eff}, are 1.84 and 3.84 μ_B respectively.

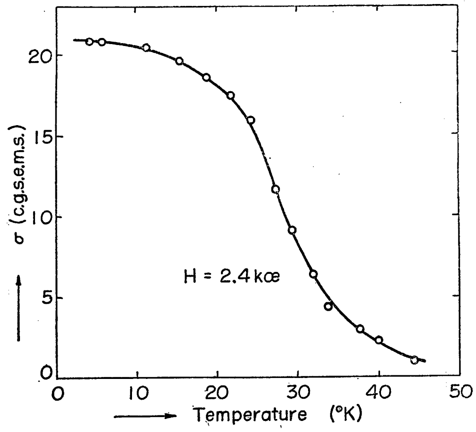

Fig. 2. Temperature dependence of magnetization.

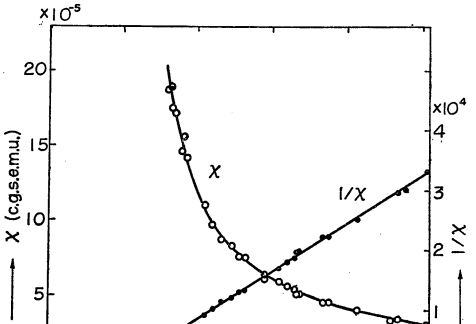

Fig. 3. Temperature dependence of the susceptibility above the Curie point. (Inverse susceptibility is also plotted).

Torque measurement was performed by means of a torque magnetometer. A single crystal specimen used in the present experiment was spherical in shape, 2 mm in diameter. Some typical torque curves at 4.2°K in the a–c placn are shown in Fig. 4. The stable position for the specimen could not be found when the magnetic field was oriented near a-direction of the crystal. When the applied field was 2.4 koe, the torque maximum appeared at $\theta=48°$, θ representing the poler angle of the field direction from c-axis, but it displaced towards the a-axis with increasing field strength. The deflection θ reached its maximum value 62° at about 7 koe and then decreased with the further increase of magnetic field strength. The maximum

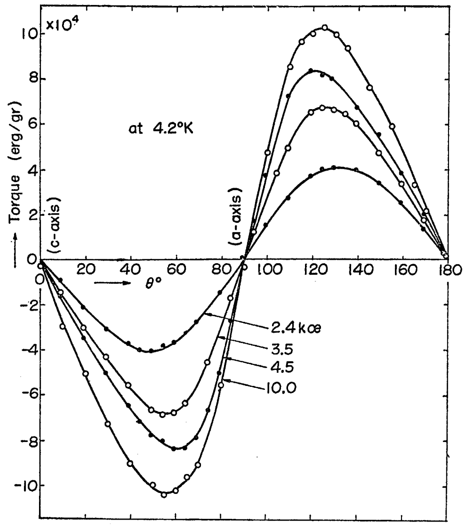

Fig. 4. Torque curves at 4.2°K-

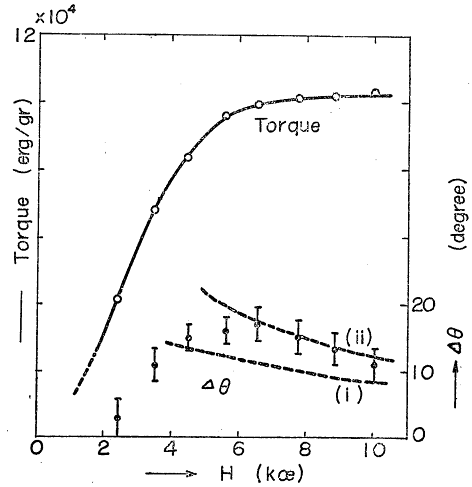

Fig. 5. Field dependences of the value of the torque maximum and of $\Delta\theta$.

torques and deviations $\Delta\theta$ of the torque maximum position from 45° for each curve are plotted against the applied field strength in Fig. 5. *A* temperature dependence of the value of the torque maximum measured in the field strength of 10 koe is shown in Fig. 6. Further torque measurements were performed above the Curie temperature, and $(\chi_c-\chi_a)$ calculated by using the value of torque is shown in Table 1.

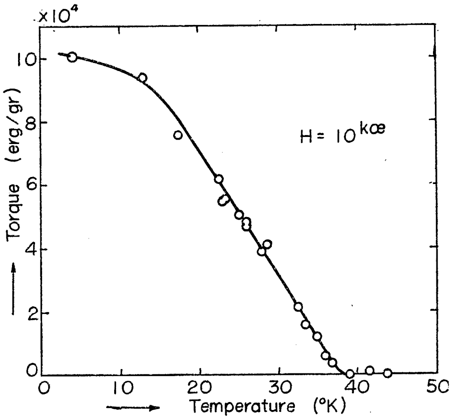

Fig. 6. Temperature dependence of torque.

Table I. The values of $\chi_c-\chi_a$.

Temp.	χ_c-χ_a	Temp.	χ_c-χ_a	Temp.	χ_c-χ_a
43.0°K	116×10^{-6}	64.3°K	4.6×10^{-6}	101°K	0.80×10^{-6}
43.5	106	66.0	3.7	106	0.75
43.8	96	70.0	2.5	109	0.71
43.9	84	73.0	2.1	124	0.57
44.0	67	74.7	1.85	141	0.45
45.0	52	76.3	1.68	154	0.38
45.5	47	77.5	1.59	159	0.37
50.0	26	78.0	1.36	166	0.35
51.2	20	80.0	1.31	178	0.32
53.2	17.0	81.0	1.25	190	0.30
54.0	14.6	86.0	1.14	203	0.27
56.5	11.9	91.0	1.00	223	0.26
56.7	11.6	94.0	0.91	239	0.24
58.0	10.6	97.0	0.86	269	0.23
60.5	8.3	99.0	0.84	293	0.21

The magnetization curves at 4.2°K for the direction of *c*-axis and that perpendicular to it were taken by means of a magnetic balance, and the results are shown in Fig. 7. As it shows, *c*-axis is the direction of easy magnetization and the technical saturation is reached by the field strength of 4 koe. The saturation value at 4.2°K is estimated to be 58 gauss/gr, which corresponds to 270 gauss/cc. The dotted curve in Fig. 7 shows the average value of magnetizations for the directions of easy and difficult magnetization, which agrees very well with that of the powder specimen reported by Hansen⁽³⁾.

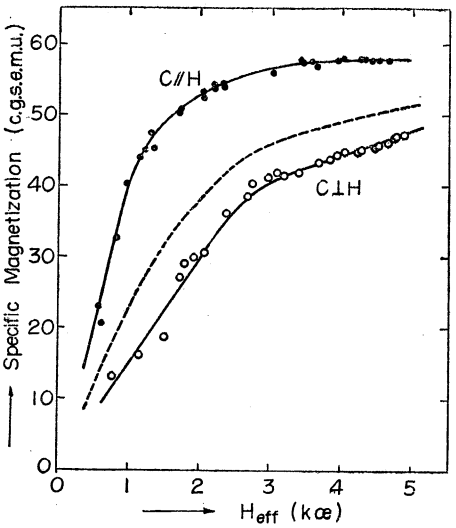

Fig. 7. Magnetization curves parallel to *a*-axis and *c*-axis.

§ 3. Discussions of the Results

A lot of hexagonal halides of the elements of the iron group show metamagnetic properties, whereas, the present compound is considered to be ferromagnetic since this compound does not show any antiferromagnetic behaviors for low magnetic field strength. Also the Curie-Weiss law holds above the critical point and the paramagnetic Curie temperature is higher than the ferromagnetic Curie point.

From the results of the magnetization curves of single crystals and of the torque measurement, it is concluded that the direction of easy magnetization lies along *c*-axis of the crystal. The saturation moment in *c*-direction at 4.2°K would be supposed to be about 3 μ_B from the results obtained. On the other hand, from the susceptibility measurement above the Curie temperature, we determined that the spin quantum number is 3/2. These values agree well with the spin magnetic moment of Cr^{3+} ion.

Paths of superexchange interaction in the present compound may be classified into those in the c-plane as well as along the c-direction. The crystal structure of $CrBr_3$ is shown in Fig. 8, and the path of the interaction in the c-plane is A—O—B which passes through one intermediate anion, while the other along the c-direction is C—O′—O″—D which passes through two intermediate anions. All other kinds of paths are considered to have a negligible contribution to the net interaction since overlapping of the charge clouds of ions in these paths is not expectable to be large from the view point of the ionic radii of Cr^{3+} and Br^-. The angle of A—O—B linkage is calculated to be about 89°. Kanamori⁽⁵⁾ suggested that if the cations are Cr^{3+} and the angle of the linkage, 90°, the sign of super-exchange interaction is ferromagnetic. Hence, the interaction along the c-directions is considered to be also ferromagnetic.

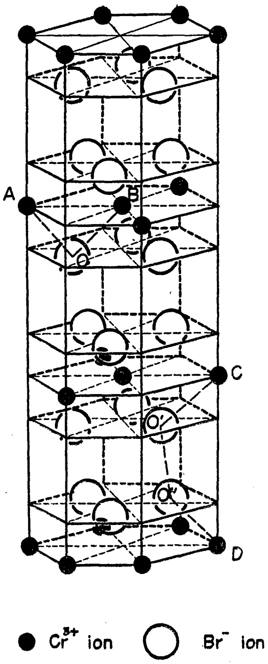

Fig. 8. Crystal sturcture of $CrBr_3$.

Next the behavior of the torque curve is discussed. In the strong field range, the maximum of the torque curve shown in Fig. 4 reaches a saturation value; Based on the uniaxial anisotropy energy,

$$U = K\cos^2\theta,$$

(K represents the anisotropy constant) and from the saturation value of torque maximum, K is estimated to be -4.8×10^5 erg/cc. In this case the dependence of the position of torque maximum, $\theta_m = \pi/4 + \Delta$, on the magnetic field strength is given by

$$\sin(2\Delta) = \left[\sqrt{1+32\,(K/HI_s)^2} - 1\right] \Big/ (8K/HI_s)$$

neglecting the higher order terms in K/HI_s*, where H is the magnetic field strength and I_s, the value of the saturation magnetization. Putting the obtained values of K and I_s mentioned above into the equation, the value of Δ is obtained as shown by the dotted curve (i) in Fig. 5. As it shows, discrepancy of the order of a few degrees exists between theoretical and experimental results. Such a difference may be due to the higher order term of the anisotropy energy. Introducing a higher order term of the anisotropy energy

$$U = K_1\cos^2\theta + K_2\cos^4\theta,$$

the saturation value of maximum torque is expressed by

$$L_{max} = -(K_1 + K_2),$$

at sufficiently strong field strengths. On the other hand, the position θ_m of maximum torque is given by

$$\theta_m = \pi/4 + \Delta + \Delta',$$

$$\Delta = K_2/(K_1 + K_2),$$

$$\Delta' = \frac{(A\cos 2\Delta - 4B\sin 4\Delta)(A\cos 2\Delta - \mathrm{B}\sin 4\Delta)}{A\cos 2\Delta - \dfrac{(A\sin 2\Delta + 2B\cos 4\Delta)^2}{4B\sin 4\Delta}} \cdot \frac{1}{HI_s}$$

with $A = -(K_1 + K_2)$ and $B = -\frac{K_2}{2}$. The fittest curve (ii) shown in Fig. 5 has been obtained by choosing the values

$$K_1 = -5.08\times10^5 \text{ and } K_2 = 0.65\times10^5 \text{ erg/cc.}$$

On the other hand, as the field strength decreases, the torque curve takes again a sinusoidal form as expressed by

$$L = A\sin 2\theta,$$

where A is a canstant. Such a fact is qualitatively explained by the fact that the magnetic moment of the specimen I lies along easy direction of magnetization by the application of very weak fields and is also proportional to the effective field strength in the direction: The magnetization in c-direction is expressed to be

$$I(H) \backsim H\cos\theta.$$

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* The value of K/HI_s takes a value 0.18 at $H =$ 10 koe.

The torque value is expressed by

$$L = IH \sin\theta .$$

Eliminating I, from the above equations the following expression for L is obtained

$$L \backsim H^2 \sin 2\theta .$$

Hence in this case the torque curve approaches to a sinudoidal form, as is observed by the field strength of 2.4 koe.

The anisotropy constant is also calculable from the area between the magnetization curves along the direction of easy and difficult magnetization. Extrapolating the magnetization curves of the a-direction, we can evaluate the anisotropy constant to be about -5×10^5 erg/cc which agrees closely with the value K_1 estimated from the torque curve.

The anisotropy constant calculated basing on the dipole-dipole interaction is 3.66×10^5 erg/cc, which has the opposite sign as compared with the experimental value. Such discrepancy will be solved by considering the interaction energy between the spin and the orbital moment of chromium ion under the influence of bromine ions, especially that of the polarized bromine ions in the crystal lattice of this compound. A detailed calculation by Dr. Yamada of this Institute is now in progress.

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