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# Magnetic Properties and Crystal Chemistry of Nickel Chromite Single Crystals

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Single crystals of nickel chromite were prepared, and magnetization measurements along several crystallographic directions were carried out at liquid helium temperature to obtain information about the origin of the small magnetic moment in this crystal. The temperature dependence of the tetragonality, $c/a$, of the crystal was obtained, and the transition temperature was determined as 275°K. It was found that the direction of easy magnetization is <111> and that even in this direction the magnetic moment at 4.2°K is only 0.2 Bohr magnetons per molecule.

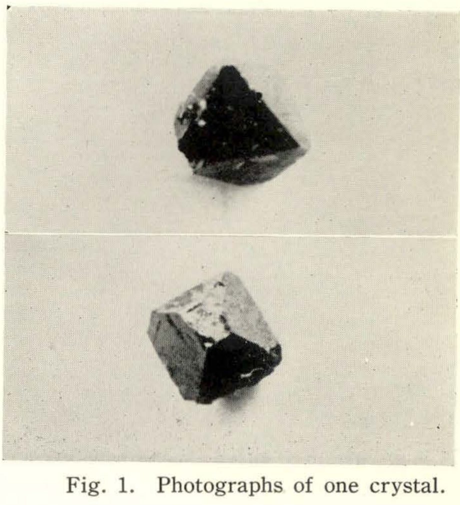
## Introduction

The canted spin problem in spinel-type crystals, especially in chromites, has been one of the main subjects in research on oxide magnetism for several years. There have been some investigations of the magnetic properties of chromites and of various ferrite-chromite series. E. W. Gorter[1] has studied the magnetic properties of the manganese ferrite-chromite series, and Pickart and Nathans[2] have determined the spin structure of this series by neutron diffraction. Hastings and Corliss[3] have reported in this Conference that manganese chromite has a screw-type spin structure. Prince[4] has also performed a neutron diffraction experiment on copper chromite. Lotgering[5] has studied the magnetic properties of some chromites. Miyahara and Ohnishi[6], and Muramori[7] have investigated the ferrite-chromite series of copper and magnesium. Tsushima[8] has also studied the magnetic properties of the series of nickel and cobalt.

In this report we shall examine the evidence for the existence of canted spin arrangements in crystals of nickel chromite. For this purpose it is desirable to investigate a single crystal specimen, since much more information can be obtained from single crystals than from polycrystals. An accurate determination of magnetization can be made despite of the presence of a large crystalline anisotropy, by applying the external field along an easy direction of the single crystal.

## Sample Preparation and Experimental Data

Single crystals of nickel chromite were grown artificially by a flux method. By heating a mixture of nickel chromite and bismuth trioxide to 1250°C in a platinum crucible, and slow cooling to 700°C at the rate of 1.8°C per hour, we were able to prepare single crystals. When we used sodium fluoride, potassium fluoride, sodium carbonate, and lead oxide as the flux, we were unsuccessful in growing crystals. Each of our crystals grew as a small octahedron of about 20 mm$^3$ in volume. A photograph of one crystal is shown in Fig. 1. Chemical analysis showed that the molar ratio of $NiO:Cr_2O_3$ in the crystals was $1:1.00_2$ and that the bismuth contamination was less than 0.02% by weight. Although nickel chromite has a cubic spinel structure at room temperature, it is tetragonally distorted at lower temperatures as a consequence of the Jahn-Teller effect of nickel ions. We determined the cubic-to-tetragonal



(a)

(b)

Fig. 1. Photographs of one crystal.

transition temperature as 275°K by means of $X$-ray diffraction. This temperature is slightly lower than that reported by Lotgering[5]. The variation of the tetragonality, $c/a$, of the face-centered unit cell is illustrated in Fig. 2. The value at liquid nitrogen temperature is 1.04, which agrees well with Prince's[9] data.

We measured the magnetization at liquid helium temperature in various crystallographic directions. We know the Curie temperature of the crystal as 60°K from our previous experiment on a polycrystalline specimen[8]. In Fig. 3 is shown a magnetization curve in the direction 10° from a ⟨100⟩ direction in a (001) plane. Saturation is not attained even at 20

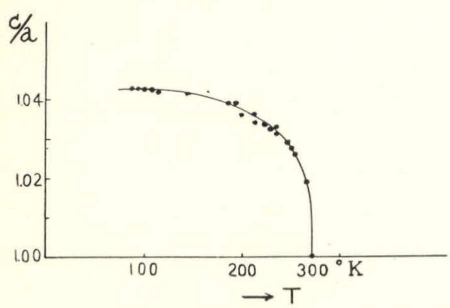



Fig. 2. Temperature dependence of tetragonality of a face-centered unit cell.

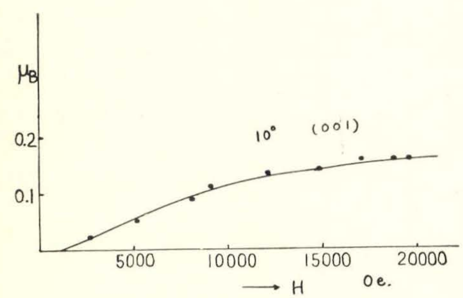



Fig. 3. Magnetization curve in a direction 10° from <100> in (001).

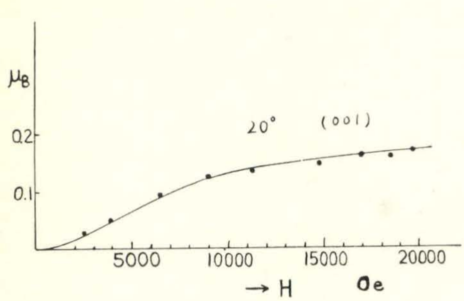



Fig. 4. Magnetization curve in a direction 20° from <100> in (001).

kOe. Fig. 4 shows a magnetization curve in the direction 20° from a ⟨100⟩ direction in a (001) plane. Fig. 5 shows the magnetization curves for the principal axes of the crystal. The ⟨111⟩ direction is found to be the easy axis, and in this direction saturation is reached at $H$=20 kOe. Even parallel to the easy axis, the saturation magnetic moment is only about

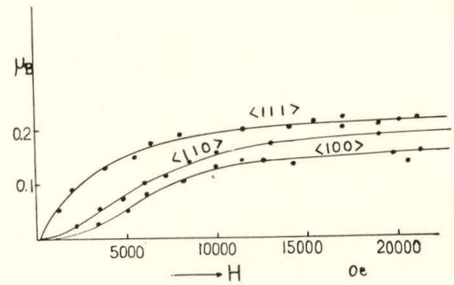



Fig. 5. Magnetization curves for principal axes of a crystal.

0.2 Bohr magnetons per molecule, which is very small compared with the value of 4 Bohr magnetons predicted by the simple Néel model of ferrimagnetism. In both the ⟨110⟩ and ⟨100⟩ directions, the magnetization is not saturated at the maximum measuring field. The crystalline anisotropy is very large.

## Discussion

Although the true origin of the small magnetic moment in nickel chromite is not clear now, we have found from single crystal measurements that it is an intrinsic property of the material and not simply a reflection of incomplete magnetic saturation. Even in the ⟨111⟩ easy direction the saturation moment is very small. The origin of the small magnetic moment in chromites may be attributed first to a triangular configuration of spins in sublattices as proposed by Yafet and Kittel[10], who extended the Néel theory to further subdivisions of the two sublattices, in order to treat the problem for more complicated coupling between the subsites. They showed that the ground state of the system is not necessarily one with the sublattice magnetizations aligned antiparallel as in Néel's model, but can be one with subsite-moments directed at angles to one another. Prince[4] reported that he has discovered the Yafet-Kittel ordering in copper chromite by low temperature powder neutron diffraction measurements, while Pickart and Nathans[2] did not find any evidence for ordered triangular configurations in the manganese ferrite-chromite series. Recently Jacobs[11] observed a high field susceptibility in the nickel ferrite-chromite series which could be caused by a triangular configuration of spins. We have found no magnetic symmetry in our magnetization measurements which would correspond to such a spin configuration as the Yafet-Kittel model. We must then think of another model. Baltzer and Wojtowicz[12] consider that if the octahedral site of a spinel is affected by a sufficiently large tetragonal or trigonal distortion, the doublet state of $Cr^{3+}$ ions with spin 1/2 becomes the ground state. The excitation from this ground state to a high spin state by application of a high magnetic field would provide another possible explanation for Jacobs' experiment. There is also the possibility of screw-type spin configurations[13] to explain the low magnetic moment in nickel chromite. Prince[9] made a neutron diffraction experiment on nickel chromite powder. He observed several extra peaks of magnetic origin, but structure analysis as low as classes m'm'2 and mm'2' of magnetic space groups failed to turn up any structure which is consistent with the diffraction data. More precise neutron diffraction measurements on a single crystal specimen will be necessary to obtain the true spin configuration.

### Acknowledgements

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## DISCUSSION

S. IIDA: Since the crystal structure is not cubic, it may not be assumed to have easy axis exactly along [111].

T. TSUSHIMA: My experiment shows that the easy axis is along ⟨111⟩ within the experimental error. We don't think that the tetragonal deformation has such a large effect on the magnetic symmetry as to change the easy direction appreciably.