Growth by Chemical Transport and Some Properties of Ferromagnetic CuCr_2Se_4 Single Crystals*

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CuCr_2Se_4 single crystals were grown by a chemical transport method. The single crystals obtained were crystallographically characterized by means of optical microscopy, the Laue method, and X-ray topographic techniques. The magnetic properties for these crystals have been studied. These results are summarized as follows.

(1) CuCr_2Se_4 single crystals, octahedral up to about 3 mm on edge, were grown by a chemical transport method from the CuCr_2Se_4 polycrystalline powder at a feed end temperature of 950°C and a growth end temperature of 800°C using an iodine carrier.

(2) The optimum temperature conditions of the chemical transport using the iodine carrier for crystal perfection were determined to be 850–900°C for the feed end and 800°C for the growth end.

(3) The saturation magnetization was determined to be 270 emu/cc, and the magnetic anisotropy constant K_1 was found to be -0.9×10^5 erg/cc at room temperature. The high-temperature susceptibility obeys the Curie-Weiss law. The paramagnetic Curie temperature and the Curie constant were determined to be 441 K and 2.55 emu·deg/mol, respectively. The ferromagnetic Curie temperature was determined to be 430 K.

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I. Introduction

The compound CuCr_2Se_4 , with normal spinel structure, was synthesized by Hahn et al.⁽¹⁾ for the first time. Lotgering⁽²⁾ has studied the magnetic and electrical properties and concluded that it has ferromagnetic properties below 460 K and metallic conduction. These properties are anomalous in comparison with the properties of corresponding oxide spinels which exhibit ferrimagnetic properties, or the properties of other chromium chalcogenide spinels such as CdCr_2Se_4 , HgCr_2Se_4 etc which show ferromagnetic and insulating or semiconducting behavior. For this particular interest many studies have been made using polycrystalline powder specimens^{(3)~(5)}.

For single crystal CuCr_2Se_4 , it has been reported only by Lotgering⁽²⁾ that platelike single crystals, 5 mm × 3 mm × 0.3 mm maximum in size, were grown by a chemical transport reaction using an iodine carrier. The temperature conditions and other details, however, were not reported. With single crystal

magnetic properties such as magnetic anisotropy have never been investigated so far.

In the present study chemical transport methods were carried out under various conditions with iodine carrier. As a result, large octahedral single crystals, up to 3 mm on an edge, or platelike single crystals, up to 10 mm × 10 mm × 0.03 mm, were obtained, and the growth conditions were established. These single crystals were crystallographically characterized by means of optical microscopy, X-ray Laue photography, and X-ray Lang topographic techniques. The magnetic properties such as susceptibility, magnetization, and magnetic anisotropy were measured with single crystal CuCr_2Se_4 .

II. Single Crystal Growth of CuCr_2Se_4 by Chemical Transport

Polycrystalline powder of CuCr_2Se_4 to be used as starting material was synthesized as follows. A mixture of high purity powders of copper (99.9%, particle size of a few μm), chromium (99.9%, 100 mesh), and selenium (99.999%) weighed in a mole ratio of 1:2:4 were sealed in an evacuated quartz ampoule of about 100 mm long by 10 mm I.D. The ampoule was heated in a horizontal resistance furnace at 630°C for 50 hr before furnace-

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cooling. The X-ray powder pattern showed that the powder synthesized has a homogeneous CuCr_2Se_4 spinel phase with no traces of other phases. It is essential for the synthesis of the homogeneous CuCr_2Se_4 spinel to use the fine powdered copper in this process. When the copper powder of 100 mesh, larger than that used above, was taken as starting material, it was necessary to regrind the product and then reheat under the same conditions to obtain a complete reaction. For syntheses at above 650°C , the pure CuCr_2Se_4 spinel phase is not obtained but a phase of CuCrSe_2 is observed.

Starting from the CuCr_2Se_4 polycrystalline powder synthesized as above and iodine as the carrier, single crystal growth of CuCr_2Se_4 was performed. The mixture of CuCr_2Se_4 powder (2.00 g) and iodine (0.15–0.45 g) were placed at one end of an evacuated quartz ampoule of about 150 mm long by 20 mm I.D. and sealed in it. Prior to feeding in the starting materials, the ampoule is cleaned with a mixed solution of HF and HNO_3 (1:1), dried, and then fired with oxyhydrogentorch. The ampoule was placed in a horizontal two zone Kanthal furnace, heated for 300 hr with an independent temperature control of the feed end, T_1 , and the growth end, T_2 , so that $T_1 > T_2$, and then furnace cooled. Figure 1 shows the details of the

Table 1 CuCr_2Se_4 single crystal growth at a feed end temperature (T_1) of 950°C and growth end temperature (T_2) of 800°C using various amounts of iodine.

I_2	Weight (mg)	Yield (mg)	Shape and maximum size (mm^3)
150		730	Octahedron $1 \times 1 \times 1$
300		1650	Octahedron, Plate $3 \times 2 \times 1.5$ $7 \times 7 \times 0.05$
450		1670	Plate $12 \times 8 \times 0.2$

configuration of the ampoule. CuCr_2Se_4 polycrystalline powder at high temperature is transported to the low temperature end through the chemical transport reaction by iodine, resulting in the formation of CuCr_2Se_4 single crystals at the growth end. Prior to this transport, however, it is necessary to purify the inner-wall of the growth zone of the ampoule from absorbed starting materials by reverse transport using an inverse temperature gradient, $T_1 < T_2$, for 24 hr.

For estimating the amount of iodine needed for this reaction, preliminary chemical transport reactions were carried out at $T_1 = 950^\circ\text{C}$, and $T_2 = 800^\circ\text{C}$, with various amounts of iodine, 0.15 g, 0.30 g, and 0.45 g, respectively. These results are summarized in Table 1. CuCr_2Se_4 single crystals produced increase in quantity and become platelike from octahedral shape with increasing amounts of iodine. The best conditions for crystal growth seems to be that of Exp. No. 2 in Table 1. Therefore the amount of iodine was fixed at 300 mg.

A series of transport experiments were carried out with 300 mg of iodine at various conditions of temperature, i.e. the feed end temperatures T_1 , from 650 to 1150°C and the growth end temperatures, T_2 , from 600 to 1050°C and the temperature differences between the two ends, $T_1 - T_2$, from 50 to 200°C . The shape and size of the single crystals obtained greatly depend on the temperatures of both ends as shown in Fig. 2. Single crystals grew into triangular or hexagonal plates of the (111) plane under the lower temperature conditions, and into octahedra, which consist of a set of {111} planes, under the higher temperature

Fig. 1 Schematic diagram of ampoule arrangement and temperature distribution for CuCr_2Se_4 single crystal growth by chemical transport with iodine carrier. (1) CuCr_2Se_4 polycrystalline powder (0.20 g), (2) CuCr_2Se_4 single crystals grown by chemical transport, (3) solid iodine for carrier, (4) horizontal two-zone furnace, (5) thermal insulator, (6) quartz ampoule of 150 mm long by 20 mm I.D., and (7) alumel-chromel thermocouples.

Fig. 2 Schematic diagram of the CuCr_2Se_4 single crystal morphology relating to the temperature conditions with which the chemical transport reactions were carried out with iodine carrier.

Photo. 1 CuCr_2Se_4 single crystals grown by chemical transport using iodine carrier with T_1 , 950°C , and T_2 , 800°C . These single crystals are octahedral.

conditions. Single crystals were not obtained above these temperatures. Under the optimum condition, $T_1 = 950^\circ\text{C}$ and $T_2 = 800^\circ\text{C}$, large octahedral single crystals up to 3 mm on the edge were obtained (Photo. 1).

III. Experiments

For the identification of the single crystals

obtained, an X-ray powder pattern of the ground material was taken by a highly stable X-ray diffractometer with a scintillation counter using $\text{CuK}\alpha$ radiation. The integrated diffraction intensities were measured and compared with the calculated intensities. Laue photographs were taken by tungsten radiation to determine the orientations of the single crystals.

The lattice constant was determined from X-ray powder diffraction and refined by an extrapolation method from 25 diffraction lines at higher scattering angles using an extrapolation function of $\cos^2 \theta_B(\theta_B, \text{Bragg angle})$.

As-grown surfaces of the single crystals were observed by a dark field microscope and an interference contrast microscope. The inner-structures of the single crystals grown under various conditions were examined by X-ray topographic technique. The topographs were taken using a Lang camera with a bent crystal monochrometer⁽⁶⁾ by which the divergent beams with $\text{K}\alpha_1$ only were produced. The beam divergency was about $19'$. This method can obtain the topograph image even in a slightly warped single crystal with high resolution. A microfocus X-ray source of $100\ \mu\text{m} \times 100\ \mu\text{m}$ in the focus size was employed. Topographs were made with characteristic $\text{AgK}\alpha_1$ ray on a ILFORD G5 nuclear plate (grain size, $0.28\ \mu\text{m}$; emulsion thickness, $50\ \mu\text{m}$). Specimens examined were as-grown platelike crystals of (111) plane with μt values (linear absorption coefficient $\times$ specimen thickness) equal to 0.3–1.2.

Magnetization measurements were made at room temperature on a lapped spherical specimen of 0.4 mm in dia. ground from an octahedral single crystal by Bond's method with diamond powder of 1000 mesh. It is highly desirable to use a spherical single crystal for the correction of demagnetizing field. These measurements were made using a Princeton Applied Research vibrating sample magnetometer. Magnetization curves were obtained as a function of applied field up to 14 kOe on the three principal symmetry axes of the cubic system ([100], [110], and [111]). Magnetic anisotropy constants were conveniently determined from the areas enclosed by these magnetization curves. For the standard sample a polycrystalline

sphere of nickel (Johnson Matthey Co., Ltd., 99.99%) was used. The ferromagnetic Curie temperature, T_c , was measured from the temperature dependences of the magnetization in low magnetic fields. Measurements of susceptibilities were performed with an as-grown single crystal using a magnetic torsion balance in the temperature range from 400 to 700 K. Mohr's salt ($\text{FeSO}_4(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 6\text{H}_2\text{O}$) was used as the susceptibility reference.

1. Crystallographic properties of CuCr_2Se_4 single crystals grown by chemical transport with iodine

The results of the X-ray powder diffraction of pulverized single crystals are given in Table 2. Every diffraction lines can be indexed with the spinel structure. The calculated intensity, I_{calc} , for normal spinel structure with u -parameter of 0.384, is in agreement with the observed intensity, I_{obs} . The lattice constant of the single crystal is $10.334 \pm 0.002 \text{ \AA}$. This value is almost the same as that of the starting polycrystalline powder ($10.333 \pm 0.002 \text{ \AA}$), but is slightly smaller than that of previous report⁽²⁾. Photograph 2 shows a transmission Laue photograph perpendicular to (111) plane of octahedral single crystal grown with $T_1 = 900^\circ\text{C}$ and $T_2 = 800^\circ\text{C}$. The single crystal seems to be of fairly good quality, because the diffraction

Table 2 Results of X-ray powder diffraction of CuCr_2Se_4 single crystals obtained by chemical transport with iodine carrier, comparing the observed intensity I_{obs} and the calculated intensity I_{calc} .

(hkl)	I_{obs}	I_{calc}
111	11	8
220	17	15
311	46	37
222	90	63
400	97	89
331	3	2
422	4	5
511-333	33	27
440	100	100
531	2	2
620	2	2
533	5	4
622	23	19
444	26	16

Photo. 2 A transmission Laue photograph of a CuCr_2Se_4 single crystal. The X-ray beam is perpendicular to the (111) plane which is the crystal face. Tungsten radiation has been used.

Photo. 3 A transmission Laue photograph of a CuCr_2Se_4 twin crystal.

spots on the Laue photograph are sharp, and do not show streaks and arcs due to strain or misorientations in the single crystal. As in Photo. 3, on the other hand, the Laue photograph of the platelike single crystal seems to have 6-fold rotational symmetry. This arises from the twinning according to the spinel twin law, a rotation of 180° about a 3-fold axis. And also diffuse scatterings (indicated with arrows in Photo. 3) due to the stacking faults in (111) plane are observed. These growth twins and stacking faults were often observed in the platelike crystals.

Photo. 4 As-grown (111) surface of a platelike CuCr_2Se_4 single crystal observed by a dark field microscope.

Photo. 5 Growth spiral patterns observed on a (111) surface of a CuCr_2Se_4 single crystal. This photograph was taken by an interference contrast microscope.

Some microscopic features on as-grown (111) surface of the single crystals are shown in Photos. 4 and 5. Typical growth steps parallel to $[110]$, are seen in Photo. 4. Photograph 5 shows growth spirals observed by an interference contrast microscope. The spiral patterns observed have 3-fold rotational symmetry corresponding to the symmetry of CuCr_2Se_4 .

Small pits are also observed at each center of the triangular spirals. They are screw dislocations running across the plane of this photograph. The surface is likely to be etched during the vapor growth process, resulting in the formation of the dislocation etch pits.

Some features of the crystal imperfections observed in as-grown single crystals by X-ray Lang topography are shown in Photos. 6~8. Photograph 6 shows the growth twins, as mentioned above, in a crystal grown with $T_1=950^\circ\text{C}$ and $T_2=800^\circ\text{C}$, i.e. in Photo. 6(a), only one part of the twin satisfies the Bragg condition, diffracting from the (004) plane, which is inclined to the crystal face (111) by $+54.7^\circ$. Photograph 6(b) is the image from the other part of the twin, diffracting from (004) plane inclined to the crystal face (111) by -54.7° . Such complicated twins as the one described above were often observed. Another type of crystal imperfection observed is shown in Photo. 7, which shows a topograph of (004) diffraction of a single crystal grown with $T_1=950^\circ\text{C}$ and $T_2=800^\circ\text{C}$. The white dots or rods, indicated with arrows in the photograph, are out of the Bragg condition and are accompanied with strain fields around them. They may be precipitations of some impurities or misorientations in the crystal⁽⁷⁾. Photograph 8(a) is the (004) topograph of a single crystal of fairly good quality grown under the conditions of $T_1=900^\circ\text{C}$ and $T_2=800^\circ\text{C}$. The diffraction intensity is roughly uniform over the crystal image, except the area that is out of the Bragg condition due to the slight bending of the specimen. Photograph 8(b) is the enlargement of the area indicated by a rectangle in (a). The equispacing fringe pattern observed seems to be a rotational Moiré pattern of lattice. It is desirable to confirm this problem in future. The ferromagnetic domain structures in the crystals are likely to be involved in these rather complicated contrasts on the X-ray topographs described above. For this interest, further investigation may be needed through measurements such as magnetic anisotropy and magnetic striction etc. for CuCr_2Se_4 single crystal.

2. Magnetic properties of CuCr_2Se_4 single crystals

Magnetization curves, which were obtained

Photo. 6 X-ray Lang topographs indicating the twinning of a CuCr_2Se_4 crystal grown by chemical transport with iodine carrier with $T_1, 950^\circ\text{C}$, and $T_2, 800^\circ\text{C}$. (a) is a topograph from (004) diffraction of one part of twin, and (b) is from (004) diffraction of the other part of twin. $\text{AgK}\alpha_1$ radiation was used.

Photo. 7 An X-ray Lang topograph of a CuCr_2Se_4 single crystal grown by chemical transport with iodine carrier ($T_1: 950^\circ\text{C}$, $T_2: 800^\circ\text{C}$). $\text{AgK}\alpha_1$ radiation was used, diffracting from the (004) plane. Impurity precipitations are indicated with arrows.

at room temperature on the three principal symmetry axes of the cubic system ([100], [110], and [111]) for a single crystal sphere, are shown in Fig. 3 as a function of the effective magnetic field, H_{eff} . In spherical specimens the effective magnetic field is uniform in any

direction of magnetization and is described as

$$H_{\text{eff}} = H_{\text{app}} - \frac{4}{3}\pi M \quad (1)$$

where H_{app} is the applied field and M is the magnetization. From Fig. 3, we see that the [111] direction is the easy direction of magnetization and the saturation magnetization is 270 emu/cc at room temperature. The magnetic anisotropy constants K_1 and K_2 can be described as

$$\begin{aligned} K_1 &= 4(S_{110} - S_{100}) \\ K_2 &= 27(S_{111} - S_{100}) - 36(S_{110} - S_{100}) \end{aligned} \quad (2)$$

where S_{hkl} corresponds to the area enclosed by the magnetization curve for the given direction $[hkl]$ and is equal to

$$S_{hkl} = \int_0^{M_s} H_{hkl} dM \quad (3)$$

K_1 value thus obtained is given in Table 3, but K_2 value cannot be determined with sufficient accuracy. K_1 and K_2 should be measured over a wide temperature range.

The ferromagnetic Curie temperature, T_c ,

Photo. 8 (a) is an X-ray Lang topograph of a CuCr_2Se_4 single crystal of fairly good quality grown by chemical transport with iodine carrier ($T_1: 950^\circ\text{C}$, $T_2: 800^\circ\text{C}$). $\text{AgK}\alpha_1$ radiation was used, diffracting from (004) plane. (b) is an enlargement of the area indicated by a rectangle in (a).

Fig. 3 Magnetization of CuCr_2Se_4 single crystal as a function of the effective magnetic field at 293 K.

was measured by the method proposed by Miyatani⁽⁸⁾. That is, the temperature dependences of the magnetization were measured in various applied fields, which were lowered from 13 kOe to 5 Oe by degrees, and the results are shown in Fig. 4. T_c in Table 3 was determined from the extrapolation of the kink points which were seen sharply on the curves in Fig. 4. This differs significantly from the

Table 3 Magnetic data for CuCr_2Se_4 single crystal. The values in parentheses were obtained by Lotgering⁽²⁾.

Lattice constant ($\text{\AA}$)	10.334 (10.337 ⁽²⁾)
Magnetic moment (emu/cc) (at room temperature)	270
Magnetic anisotropy constant, K_1 (erg/cc) (at room temperature)	-0.9×10^5
Curie temperature, T_c (K)	430 (460 ⁽²⁾)
Paramagnetic Curie temperature, θ (K)	441 (465 ⁽²⁾)
Curie constant, C (emu · deg/mol)	2.55 (2.50 ⁽²⁾)

value reported by Lotgering⁽²⁾ who measured T_c in an applied field of 10 kOe. This difference between these results is probably due to difference in the field strengths used.

The temperature dependence of the susceptibility χ above T_c was studied in the temperature range from 440 to 700 K, as shown in Fig. 5. The inverse of the observed susceptibility is linear against temperature and can be well expressed by Curie-Weiss law. From this curve the paramagnetic Curie temperature θ and the Curie constant C were determined and are

Fig. 4 Magnetization of CuCr_2Se_4 single crystal as a function of temperature in the external fields indicated.

Fig. 5 Temperature dependence of the inverse susceptibility of CuCr_2Se_4 single crystal.

listed in Table 3. The value of C obtained is in agreement with that of another report⁽²⁾, and also is roughly equal to the Curie constant $2.88 \text{ emu} \cdot \text{deg/mol}$ which is the spin-only value given by the model $\text{Cu}^{1+}(\text{Cr}^{4+} \cdot \text{Cr}^{3+})\text{Se}_4^{2-}$ ⁽²⁾⁽⁹⁾. On the other hand, the value of θ is rather smaller than that reported by Lotgering⁽²⁾.

IV. Conclusion

CuCr_2Se_4 single crystals were grown by a chemical transport method. The single crystals obtained were crystallographically characterized by means of optical microscopy, Laue photography and X-ray topographic techniques. The magnetic properties for these single crystals have been studied. These results are summarized as follows.

(1) CuCr_2Se_4 single crystals, octahedral up to about 3 mm on edge, were grown by chemical transport from CuCr_2Se_4 polycrystalline powder using iodine carrier with the temperature of the feed end, 950°C , and of the growth end, 800°C .

(2) The optimum temperature conditions for the chemical transport using iodine carrier for crystal perfection were determined to be $850\text{--}900^\circ\text{C}$ for the feed end, and 800°C for the growth end.

(3) The saturation magnetization was determined to be 270 emu/cc , and the magnetic anisotropy constant K_1 was found to be $-0.9 \times 10^5 \text{ erg/cc}$ at room temperature. The high-temperature susceptibility is well expressed by the Curie-Weiss law. The paramagnetic Curie temperature and the Curie constant were determined to be 441 K and $2.55 \text{ emu} \cdot \text{deg/mol}$, respectively. The ferromagnetic Curie temperature was determined to be 430 K .

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