JOURNAL OF MATERIALS SCIENCE 6 (1971) 136-139

Some Electrical Properties of Synthetic Klockmannite, CuSe*

Z. OGORELEC, D. SELINGER
Institute of Physics, University of Zagreb, Yugoslavia

This paper describes the synthesis of CuSe and the examination of prepared samples by means of density measurements, Debye-Scherrer analysis and measurement of its electrical properties. Considering the temperature-dependence of electrical conductivity and the values of thermoelectric power and the Hall constant, one may conclude that synthetic klockmannite behaves as a metal.

1. Introduction

Klockmannite, or cupric selenide, is a compound in which an interesting rectifying effect was observed during the early stages of semiconductor research. When CuSe was brought in contact with a proper metal an asymmetrical resistance or rectification appeared [1, 2]. In examining this effect and trying to find an explanation for it, we were confronted with the fact that many basic properties of the compound are still unknown. Moreover, one can find contradictory conclusions about the nature of this compound. Early measurements by Schroeter [3], although non-reproducible and dependent on the conditions of sample preparation, showed metallic conduction. The same results were obtained by Meissner [4]. Nevertheless many textbooks on solid state treat CuSe automatically as a semiconductor, probably owing to the rectifying effect mentioned before. In order to solve the problem definitely whether the rectification has to be ascribed to a possible semiconductivity of CuSe, or to some barrier formed on its surface, the basic electrical properties of this compound must be known with greater certainty.

2. Preparation and Control of the Samples

Cupric selenide was prepared by a direct synthesis of pure (5N, Fluka, Switzerland) and precisely weighed components in an evacuated and sealed quartz tube at 600° C [5]. After the synthesis was completed (8 h), the tube was cooled to room temperature over a period of 24h. Gray-black ingots of about $8 \times 2 \times 0.5$ mm^3 were obtained. Single crystals of CuSe are not obtainable because of the phase transition at 53° C [6].

Three samples with nominal compositions $Cu_{0.9}Se$, CuSe and $Cu_{1.1}Se$ were prepared in order to find out the influence of stoichiometric deviations. Inspection by means of a metallographic microscope showed that the CuSe and $Cu_{1.1}Se$ samples were compact and homogeneous and that the $Cu_{0.9}Se$ sample was full of microcracks and bubbles. Thus, an excess of selenium appears undesirable in the synthesis. This conclusion was borne out by density measurements. These were performed on rectangular samples, measuring the volume with a micrometer, and the mass with a Mettler balance. The following results were obtained:

$Cu_{0.9}Se$: (5.68 ± 0.02) g cm^{-3}
CuSe : (5.88 ± 0.01) g cm^{-3}
$Cu_{1.1}Se$: (5.93 ± 0.03) g cm^{-3}

Comparing these values with 6.12 g cm^{-3} calculated from X-ray data [7], one will see that the measured density of $Cu_{0.9}Se$ considerably differs both from this value and from the densities of the other two samples. Therefore, the selenide with composition $Cu_{0.9}Se$ was left out from further examinations.

The remaining two samples were subjected to Debye-Scherrer powder analysis. The angles of the obtained patterns were compared with the angles which were calculated considering the hexagonal $P6_3/mmc$ lattice of the low-tempera-

---

*Part of this work was reported at the 5th Congress of Yugoslav Physicists, Mathematicians and Astronomers, Ohrid 1970.

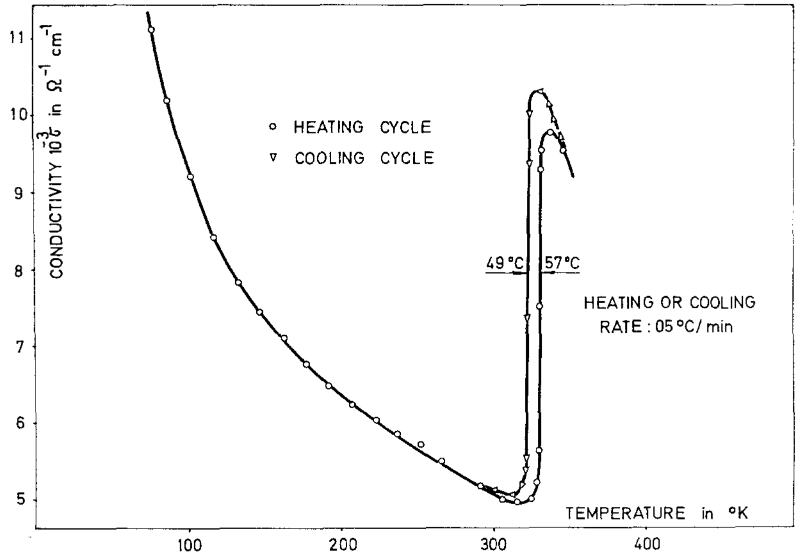

Figure 1 Electrical conductivity of CuSe versus temperature.

ture phase of CuSe [6]. Satisfactory agreement was found.

3. Electrical Conductivity

The electrical conductivity of cupric selenide was measured on prismatic samples using two contacts as current leads and two other contacts as potential probes. All contacts were made with a Ga-Al alloy. A source of constant current was used and the voltage drop was measured by a millivoltmeter with very high internal resistance. The measurements, carried out in a temperature range of 78 to 400° K, were found to be completely reproducible. The results are shown in fig. 1.

As can be seen, conductivity decreases with increasing temperature up to about 300° K, where it suddenly starts to increase. This jump is caused by the phase transition. At the temperature of the phase transition a hysteresis can be observed which cannot be reduced by using a smaller heating or cooling rate. The hysteresis was smallest at 0.5° C/min and then had about 8° C width. The temperature of 53° C, referred to as the transition point, lies in the middle of this interval. The electrical conductivity of the high-temperature phase of CuSe also decreases with increasing temperature.

Samples with the nominal compositions CuSe and $Cu_{1.1}Se$ showed exactly the same temperature dependence of conductivity, which was only slightly different in magnitude. Between 78 and 300° K, experimental points can be fitted to the equation $\sigma = \sigma_0 T^{-a}$, where $\sigma_0 = 10^5 \Omega^{-1}\,\mathrm{cm}^{-1}$ and $a = 0.5$. This means that the conductivity of CuSe only changes with variation in temperature of carrier mobility, i.e. that from the point of view of conductivity, it exhibits a metallic character.

4. Current-voltage Characteristic

The same character of CuSe is shown by its I-V characteristic. This was measured on a needle-like sample placed in a stagnant atmosphere. As the voltage increased, the heating of the sample became noticeable and its temperature increased. Heating increased the sample resistance, which caused a deviation from Ohm's law (fig. 2). At about 50 mV and 4 A the sample was at 53° C and transformed into the high-temperature phase. The curvature of the I-V characteristic in this region shows that the high-temperature phase too has a metallic nature, which is not so evident in fig. 1.

5. Thermoelectric Power

Expecting a very small thermoelectric power α of CuSe and a constancy of α over a relatively wide temperature range, we chose measurement by the simple integral method: one end of a prismatic sample was held at 0° C, while the temperature of the other was changed. Thermoelectric voltage was measured between the ends. The results are shown in fig. 3. As can be seen, thermoelectric voltage increases linearly with rising temperature. No indication of the phase

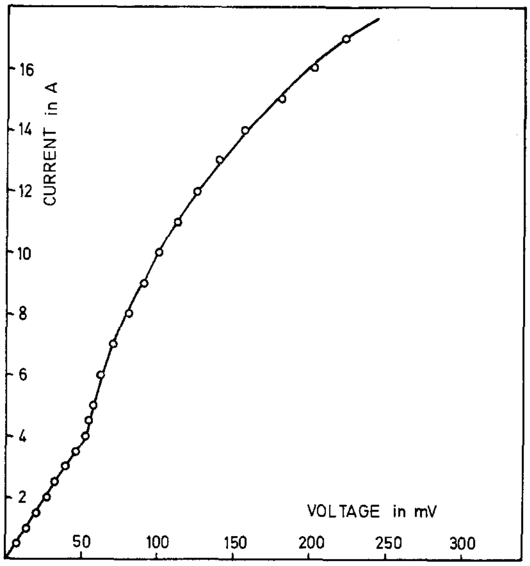

Figure 2 Current-voltage characteristic of CuSe.

transition and no difference between the heating and cooling cycles were observed. The linearity of the thermoelectric voltage between 20 and 100° C gives a constant thermoelectric power $\alpha_{\mathrm{sum}} = + 3.7 \mu\mathrm{V}/°\mathrm{C}$. However, in our experiment this was a power against copper. Absolute thermoelectric power (against Pb) was obtained by adding $\alpha_{\mathrm{Cu}} = + 3.2\ \mu\mathrm{V}/°\mathrm{C}$. Thus we have $\alpha_{\mathrm{CuSe}} = + 6.9\ \mu\mathrm{V}/°\mathrm{C}$, a typical value for a metal.

6. Hall Effect

The measurements of this effect on CuSe were not completely successful. This was due to the extremely low Hall voltage we had to measure. For example, at room temperature and on the sample with thickness 0.5 mm, in a magnetic field of 10 kOe and for the current through the sample of 2A, we estimated the Hall voltage V_{H} to be as low as $\sim 1\ \mu\mathrm{V}$. The measurements were made with significant errors, so that this value has to be considered only as an order of magnitude. If we take $V_{\mathrm{H}} = 1\ \mu\mathrm{V}$, the Hall constant is $R_{\mathrm{H}} = 2.5 \times 10^{-4}\ \mathrm{cm}^3\ \mathrm{C}^{-1}$. The experiment showed that it has a positive sign. The small Hall constant indicates a very high concentration of charge carriers.

7. Conclusions

Apart from qualitative evidence of the metallic character of CuSe which can be drawn from the experiments just described, the following approximative calculations can be given:

(i) Using the well-known equation for the thermoelectric power of metals

$$\alpha = \frac{\pi^2 k^2 T}{e E_{\mathrm{F}}}$$

where k is Boltzman constant, T absolute temperature, and e electronic charge, the Fermi energy E_{F} can be calculated. With measured value of α, this equation gives $E_{\mathrm{F}} = 3.2$ eV at 300° K.

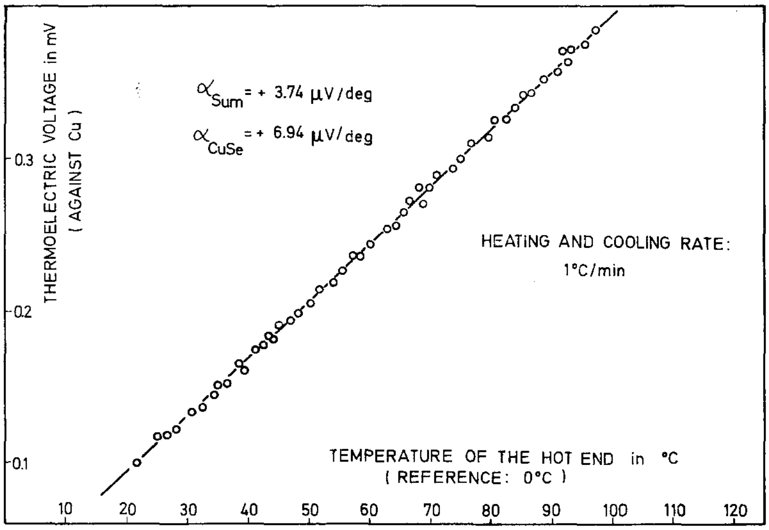

Figure 3 Thermoelectric voltage generated in CuSe sample.

(ii) Knowing the Fermi energy, the concentration of charge carriers can be evaluated. This calculation is made possible by the equation

$$E_F = \frac{h^2}{2m^*}\left(\frac{3n}{8\pi}\right)^{2/3}$$

in which h is Planck's constant and m^* the effective mass of carriers. Provided that $m^* = m$, one obtains $n = 3 \times 10^{22}$ cm^{-3}.

(iii) This high value for the concentration of charge carriers, which was evaluated from the thermoelectric power, is supported by the value which can be calculated from the Hall constant. Using the equation $R_H = 1/ne$ and inserting the experimental R_H into it, one obtains $n = 2 \times 10^{22}$ cm^{-3}. The similarity of the numbers is probably accidental, but the order of magnitude is the same.

(iv) The concentration of carriers together with the experimental temperature-dependence of conductivity enables us to determine the equation for the mobility of carriers: $\mu = \mu_0 T^{-a}$, in which $\mu_0 = 25$ cm^2/Vsec and $a = 0.5$. This equation gives $\mu = 1.4$ cm^2/Vsec at 300° K.

Although roughly estimated, all basic parameters determined in our experiment are plausible and show that cupric selenide behaves as a typical metal. Therefore, the rectifying effect discovered in CuSe cannot be ascribed to the bulk semiconducting properties of this compound. However, further examination of the nature of the charge carriers is still necessary. The signs of thermoelectric power and the Hall constant indicate that they may be holes.

References

1. H. K. HENISCH, "Rectifying Semiconductor Contacts" (Clarendon Press, Oxford, 1957).
2. N. G. KLUCHNIKOV, *J. Techn. Phys.* **24** (1954) 833.
3. F. SCHROETER, Thesis, Berlin, 1909.
4. W. MEISSNER *et al*, *Ann. Phys.* **17** (1933) 393.
5. B. ČELUSTKA and Z. OGORELEC, *Croat. Chem. Acta* **41** (1969) 73.
6. R. D. HEYDING, *Canad. J. Chem.* **44** (1966) 1233.
7. J. W. EARLEY, *Amer. Mineralogist* **34** (1949) 435.

Received 10 November and accepted 17 November 1970.