YU ISSN 0015-3206
FZKAAA 21 (1) 11 (1989)

ELECTRICAL CONDUCTIVITY AND THERMOELECTRIC POWER OF $CuSbSe_2$ IN THE SOLID AND LIQUID STATE

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Received 21 March 1988

Revised manuscript received 12 September 1988

UDC 538.93

Original scientific paper

Measurements of the electrical conductivity and thermoelectric power of $CuSbSe_2$ semiconductor in the solid and liquid states were carried out in a wide range of temperatures. The experimental data were analyzed in terms of a model developed for the density of states and electrical transport in solid amorphous semiconductors. Positive thermoelectric power suggests a large predominance of holes in electrical transport.

1. Introduction

Ternary chalcopyrite semiconductors have recently attracted a great deal of attention because of their possible applications in electro-optical devices[1] and infrared generation and detection. They can be regarded as valence analogs of the III—V and II—VI semiconductors, respectively[2], and they crystallize in the chalcopyrite structure[3,4] which is closely related to zinc blende. Their physical properties have not been studied in detail, the electrical properties of some of these compounds in the crystalline state have been studied mainly from room temperature to the melting point[4].

The mechanism of electronic conduction in amorphous materials is of considerable interest. Various models were suggested[5-7], and it has been demonstrated that more semiconductors retain their predominantly covalent semiconducting properties in the amorphous and liquid states whereas others aquire metallic properties above the melting point.

The aim of the present contribution is to study the electrical conductivity and the thermoelectric power of $CuSbSe_2$ in the solid and liquid state in a wide range of temperature. $CuSbSe_2$ possesses the chalcopyrite structure[3,4] and its melting point is 452 °C.

2. *Experimental details*

$CuSbSe_2$ samples were prepared by melting the proper amounts of highly pure component elements (99.999%). The material was sealed in evacuated quartz tubes at 10^{-3} Pa and heated at 1200 °C for 12 h with frequent rocking to ensure homogenization of the melt. Then the tubes were quenched in ice to obtain the samples in amorphous state.

The solid material is then heated in inert atmosphere until it melts and then transfered to the measuring cell.

Measurements of the electrical conductivity and thermoelectric power were carried out in the measuring cell which was fitted with graphite electroned, heaters and thermocouples for accurate measurements of temperature up to 0.2 °C. A highly stabilized power supply, sensitive voltmeter and a sensitive galvanometer capable of measuring current as low as 10^{-9} A were used[8].

X-ray examination of the samples $CuSbSe_2$ in the solid phase — using X-ray diffractometer type PW 1730/10 Philips showed that the material is amorphous.

3. *Results and discussion*

Figs. 1 and 2 show the temperature dependence of the electrical conductivity and thermoelectric power. In the solid state the activation energy is 0.11 eV. The low value of the activation energy suggests that $CuSbSe_2$ should remain extrinsic *p*-type semiconductor. Positive values of thermoelectric power indicate a large predominance of holes in electrical transport.

At the melting point, a sudden decrease in the electrical conductivity and thermoelectric power is observed which may be attributed to changes in the short range order on melting and the subsequent decrease in carrier mobility. In the liquid state the electrical conductivity increased and the activation energy is 0.2 eV. The thermoelectric power decreases as temperature rises which may be attributed to changes in the short-range order and the energy band structure due to weakening of the intermolecular forces. The measured transport data in liquid state can be interpreted in terms of the model developed by Mott[9,10]. According to this model the main difference between amorphous and crystalline state is that the electronic states at the band edges are tailed in the forbidden gap and become localized. To explain the positive sign of the thermoelectric power usually observed, it is supposed that the range of localized states in the conduction band is wider than in the valence band. Moreover, two conduction processes may occur:

a) conduction due to holes excited in extended states at E_v,

b) conduction due to holes excited in localized states near the band edges with an activated mobility.

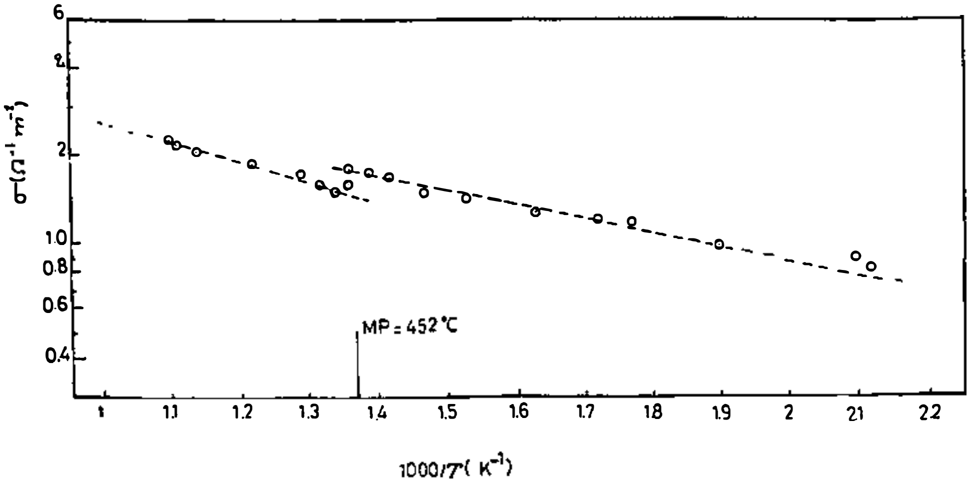

Fig. 1. Temperature dependence of the electrical conductivity of $CuSbSe_2$ in the solid and liquid state.

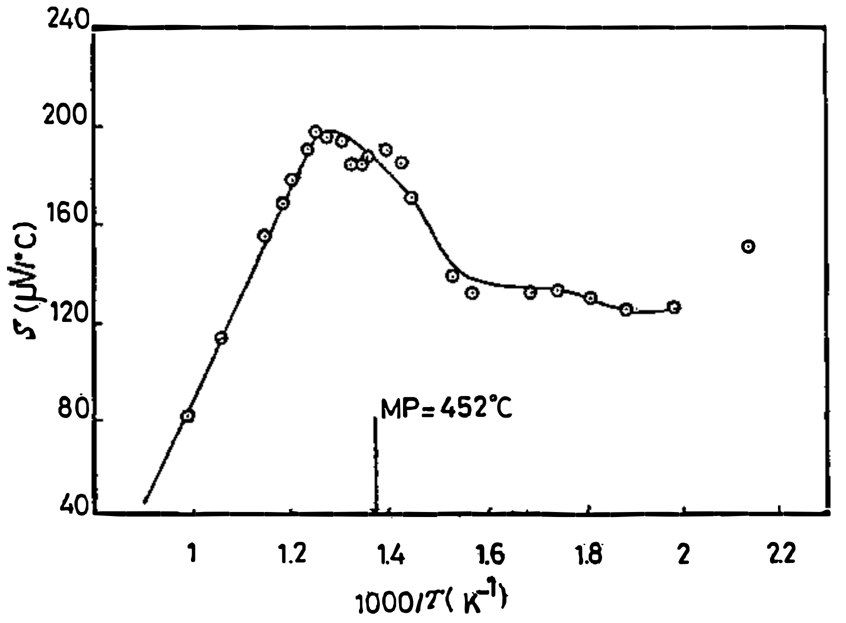

Fig. 2. Temperature dependence of the thermoelectric power of $CuSbSe_2$ in the solid and liquid state.

The present results show that conduction due to defect states occurs with an activation energy 0.2 eV. Mott[11] and Cutler[10] have shown that when the activation energy for the hole mobility is small compared with the energy gap, the electrical conductivity is given by:

$$\sigma = \sigma_0 \exp \frac{E_f - E_v}{kT}. \tag{1}$$

The value of σ_0 varies with the conduction process and can be calculated from the intercept of $\log \sigma$ curve at $\frac{1}{T} = 0$ which is equal to $4\,\Omega^{-1}\mathrm{m}^{-1}$. Moreover, $(E_f - E_v)$ depends on the temperature and is given by[11]:

$$E_f - E_v = E(0) - \gamma T. \tag{2}$$

When $E_\sigma = E_s$ the temperature coefficient γ may be calculated directly from the thermoelectric power which is given by:

$$S = \frac{k}{e}\left(\frac{E_f - E_v}{kT} + A\right) \tag{3}$$

$$S = \frac{k}{e}\left(\frac{E(0)}{kT} - \frac{\gamma}{k} + A\right)$$

where kTA is the average energy of the transported holes measured with respect to E_v; A depends on the nature of the scattering process, e is the electron charge and k is Boltzmann's constant.

The kinetic term A is of order unity for conduction in extended states[10,12] when the density of states and the mobility are temperature independent. The value of the coefficient γ is found to be 4.12×10^{-4} eV/K which gives the temperature dependence of the energy gap for liquid $CuSbSe_2$. γ can be determined from the intercept of thermoelectric power curve on the $\frac{1}{T} = 0$ axis of a plot of S versus $\frac{1}{T}$.

Mott[10] had attributed the linear decrease of the gap with increasing temperature to the fact that the difference between the distance from one atom to nearest and next-nearest neighbour decreases.

From Eqs. (1) and (3) one obtains the relation between σ and S:

$$\sigma = \sigma_0 \exp\left(-e\frac{S}{k} + A\right).$$

Fig. 3 shows a plot of the electrical conductivity (log scale) versus the thermoelectric power in liquid state. The value of intercept on the $S = 0$ axis yields $\sigma_0 = 4\,\Omega^{-1}\mathrm{m}^{-1}$.

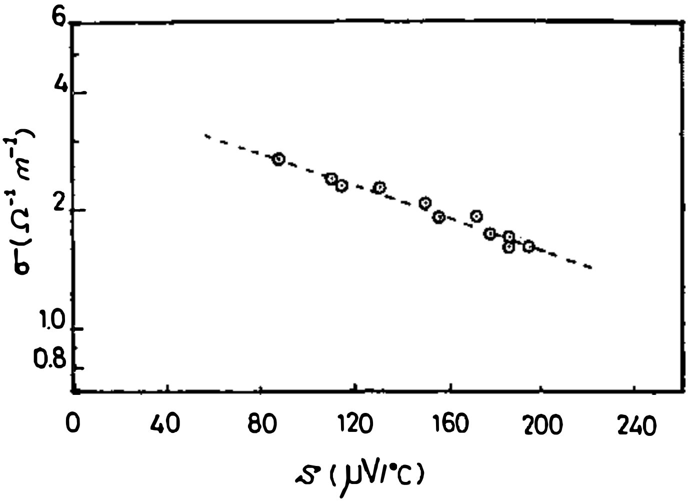

Fig. 3. Electrical conductivity versus thermoelectric power for liquid $CuSbSe_2$.

The low value of σ_0 in the liquid state indicates that holes in localized states near the band edges are responsible for conduction. As the energy gap contracts with rising temperature, the tails of the conduction and valence bands become more pronounced.

References

1) M. J. Thwaites, R. D. Tolinson and M. J. Hamphsire, Solid State Commun. **23** (1977) 905;
2) L. I. Berger and V. D. Prochukan, *Ternary Diamond-Like Semiconductors,* Consultants Bureau Enterprises Inc., New York, p. 47 (1969);
3) V. B. Zhuze, V. M. Sergeeva, E. L. Shtum, Sov. Phys.-Tech. Phys. **3** (1958) 1925;
4) J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors,* Pergamon Press, London (1975);
5) N. F. Mott, Phil. Mag. **13** (1966) 989; **24** (1971) 1;
6) N. F. Mott, Adv. Phys. **16** (1967) 49;
7) M. Cutler and C. E. Mallon, J. Appl. Phys. **36** (1965) 201;
8) A. H. Abou El Ela and N. Abdelmohsen, Appl. Phys. A **29** (1982) 39;
9) M. M. Cohen, H. Fritzsche and S. R Ovshinsky, Phys. Rev. Lett. **22** (1969) 1065;
10) M. Cutler and N. F. Mott, Phys. Rev. **181** (1969) 1336;
11) N. F. Mott, Phil. Mag. **22** (1970) 7;
12) N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials,* 2nd ed. (University Press Oxford) (1979).

ELEKTRIČNA VODLJIVOST I TERMOELEKTROMOTORNA SILA $CuSbSe_2$ U ČVRSTOM I TEKUĆEM STANJU

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UDK 538.93

Originalni znanstveni rad

Izmjerena je električna vodljivost i termoelektromotorna sila čvrstog i tekućeg $CuSbSe_2$ u širokom rasponu temperatura. Eksperimentalni podaci analizirani su uz pomoć modela razvijenog za gustoću stanja i električni transport u čvrstim amorfnim poluvodičima. Pozitivna termoelektromotorna sila sugerira da u električnom transportu dominiraju šupljine.