

ELECTRONIC PROPERTIES OF MOLTEN CuSbTe_2

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The electrical conductivity and thermoelectric power of CuSbTe_2 have been measured both in the solid and liquid states. The observed conductivity values of this compound just above its respective melting points and increase with increasing temperature. The contact method was used in our investigations. The experimental data were explained on the basis of a model developed for the density of states and electrical transport in solid amorphous semiconductors (Mott). The data for CuSbTe_2 were fitted to the model with $E_g = 0.035$ eV and $E_g = 0.11$ eV in solid state and liquid state. Positive thermoelectric power suggests a large predominance of holes in electrical conduction. It appears that the conduction is due to holes in localized states near the band edge.

1. Introduction

The electrical conductivity is one of the most sensitive indicators of changes in the nature of the chemical bonding. In general, the electrical conductivity is governed by the product of the carrier density and the carrier mobility.

Much time and research have been devoted to understand the physical properties and the electronic transport phenomena of amorphous and liquid semiconductors. Of all the physical properties, the electronic transport properties are the most distinctive one for amorphous and liquid semiconductors. Various models²⁻⁹ have been proposed for amorphous and liquid semiconductors and it was established that the semiconducting behaviour in the amorphous and liquid state is connected with the existence of covalent bonds.

The ternary compound CuSbTe_2 belongs to the I-III-VI₂ family of semiconductors which have a chalcopyrite structure¹⁰. It has been suggested that this compound and other members of this family whose energy gap varies between 0.9 and 3.5 eV have great potential for the manufacturing of electro-optical devices¹⁰. 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 point¹⁰. The aim of the present contribution is to investigate the electrical conductivity and thermoelectric power of CuSbTe_2 ternary semiconductor in a wide range of temperatures in the solid and liquid states.

2. Experimental methods

CuSbTe_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^{-5} Pa and heated at 1200 °C for 48 h with frequent rocking to ensure homogenization of the melt. Then the tubes were quenched in ice to obtain the samples in the amorphous state. The solid material is then heated in inert atmosphere until it melts and then transferred to the measuring cell.

Measurements of the electrical conductivity and thermoelectric power were carried out in the measuring cell which was made from a ceramic material and was fitted with graphite electrodes, heaters, and thermocouples for accurate measurements of temperature up to 0.2 °C. The working space between the electrodes was made highly homogeneous and spacing between the electrodes was 1 mm. A highly stabilized power supply, a sensitive voltmeter, and a sensitive galvanometer capable of measuring currents as low as 10^{-9} A were used.

3. Experimental results and discussion

The dc conductivity, σ , was calculated from the contact point method using the equation:

$$\sigma(T) = i(T)/EA \quad (1)$$

where E is the field applied, A is the electrode area, and $i(T)$ is the current. The activation energy for dc conductivity, E_σ , was determined from:

$$\sigma = \sigma_0 \exp\left(-\frac{E_\sigma}{KT}\right) \quad (2)$$

where σ_0 is the pre-exponential factor, T is the absolute temperature and K is the Boltzmann constant. E_σ and σ_0 were determined from the slope of $\log \sigma$ versus $1/T$ in Fig. 1.

The temperature dependence of Seebeck coefficient S for semiconductors¹⁾, can be expressed in the following form:

$$S = \pm \frac{K}{e} (E_s / KT + A)$$

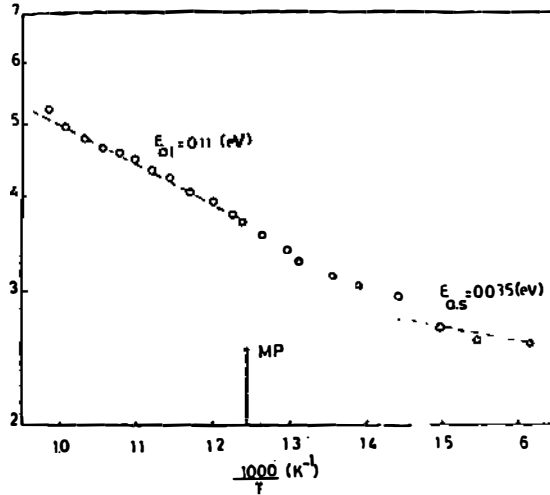


Fig. 1. Temperature dependence of the electrical conductivity of CuSbTe_2 in the solid and liquid states.

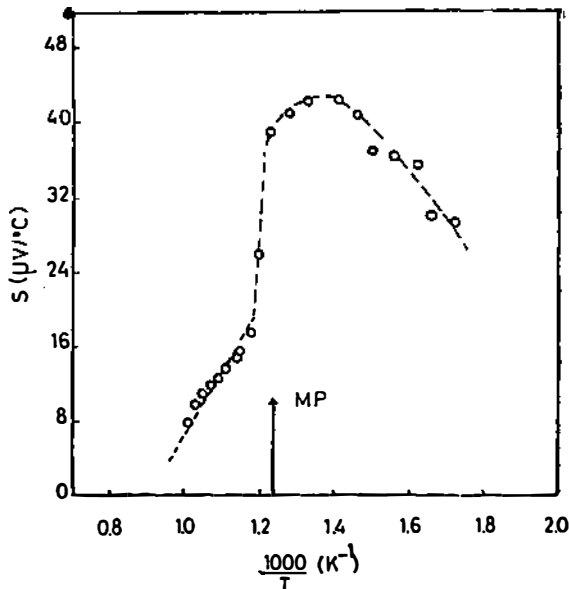


Fig. 2. Temperature dependence of the thermoelectric power of CuSbTe_2 in the solid and liquid states.

where e is the electronic charge, K is the Boltzmann constant, T is the absolute temperature, E_a is the activation energy for thermoelectric power and A is a constant which is dependent on the mechanism of the electrical transport. The positive and negative signs represent p -type and n -type conductions, respectively.

Figs. 1 and 2 show the temperature dependence of the electrical conductivity and thermoelectric power in the solid and liquid states, $\ln \sigma$ is found to be linear with $1/T$ in both solid and liquid states, the activation energy determined from the slope of $\ln \sigma$ versus $1/T$ in low temperature region is found to be $E_a = 0.035$ eV, while increases to 0.11 eV at high temperature after melting (Fig. 1). The temperature dependence of the thermoelectric power is positive in both solid and liquid states. It can be observed from the figure that in the solid state the thermoelectric power increases as temperature increases. It reaches its maximum value just before the melting point at which a sudden decrease in thermoelectric power occurs. In the liquid state the thermoelectric power decreases as the temperature increases in a nearly linear fashion, while the electrical conductivity increases with temperature. Positive values of thermoelectric power indicate that holes largely predominate in electrical transport, and increase of both S and σ with temperature in the solid state just before melting may be attributed to the increase of carrier mobility with temperature.

A sudden decrease in the thermoelectric power at the melting point (530°C) is observed which may be attributed to changes in the short range order at melting and the subsequent decrease in carrier mobility. The increase of the activation energy in the liquid state indicates a weakening of the influence of impurities and change from extrinsic to intrinsic conduction in the liquid state. Moreover, it appears that in the liquid state the energy gap becomes wider than in the solid state.

Mott¹⁾ and Cutler¹¹⁾ had shown that when the energy for the hole mobility is small compared with the energy gap, the electrical conductivity can be expressed as:

$$\sigma = \sigma_0 \exp \frac{E_f - E_v}{KT} \quad (3)$$

The value of the constant σ_0 varies strongly with the conduction process and can be obtained from the intercept of $\log \sigma$ curve at $1/T = 0$, which is equal in the present case to $17.6 (\Omega \cdot \text{cm})^{-1}$. Moreover, $(E_f - E_v)$ depends on the temperature and is given by¹⁾:

$$E_f - E_v = E(0) - \gamma T \quad (4)$$

where γ is the coefficient of linear decrease of the energy gap with the temperature.

From Eqs. (3) and (4) one obtains:

$$\sigma = \sigma_0 \exp \left(\frac{\gamma}{K} \right) \exp (-E(0)/KT) \quad (5)$$

where $E_\sigma = E_s$. The temperature coefficient, γ , can be calculated directly from the thermoelectric power which is given by:

$$S = \frac{K}{e} \left(\frac{E_f - E_v}{K} + A \right) = \frac{K}{e} \left(\frac{E(0)}{KT} - \frac{\gamma}{K} + A \right) \quad (6)$$

where the average energy of the transported holes in KTA measured with respect to E_v , and the value of A depends on the nature of scattering process and is normally a small constant. If A is known, γ can be determined directly from the intercept on the $1/T = 0$ axis of a plot of S versus $1/T$. From Eqs. (3) and (6) one obtains the relation between σ and S

$$\sigma = \sigma_0 \exp \left(-e \frac{S}{K} + A \right). \quad (7)$$

It is clear from Figs. 1 and 2 that the $\log \sigma$ and S vary linearly with $1/T$ in accordance with Eqs. (5) and (6). If the straight line extrapolated to $1/T = 0$, it would yield $S(0) = \left(-\gamma + \frac{KA}{e} \right)$. Cutler and Mott^{11,3,12} had shown that when the density of states and the mobility are temperature independent, the kinetic term A will be of order unity for conduction in extended states.

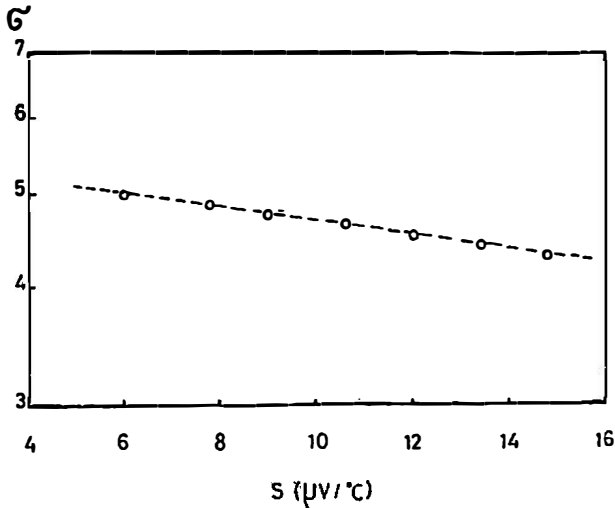


Fig. 3. The electrical conductivity (in the logarithmic coordinate) versus thermoelectric power for liquid CuSbTe_2 .

So, if we assume $A = 1$, the value of the coefficient γ is found to be 1.51×10^{-4} eV/K. This value of γ , which gives the temperature dependence of the energy gap for liquid CuSbTe_2 is of the same order as those found for liquid Te-Se alloys^{13,14}. Mott had attributed the large linear decrease of the gap with increa-

sing temperature to the fact that the difference between the distance from one atom to the nearest and next-nearest neighbours decreases.

Fig. 3 shows the dependence of $\log \sigma$ as a function of S . According to Eq. (7), with the assumption $A = 1$, the value of the intercept on the $S = 0$ axis yields $\sigma_0 = 5.54 (\Omega \text{ m})^{-1}$.

The low value of σ_0 indicates that holes in extended states near the band edges are responsible for conduction. As the energy gap contract with increasing temperature (because of the relation $E(g) = E(0) - \gamma(T)$), the tails of the conduction and valence bands become more pronounced.

4. Conclusion

The electrical conductivity and the thermoelectric power for the compound CuSbTe_2 amorphous semiconductors have been carried out in the both solid and liquid states. In the solid state both (σ) and (S) increase with temperature. But in the liquid state, the electrical conductivity (σ) increases with temperature while the thermoelectric powers (S) decrease. Moreover, it appears that in the liquid state the energy gap becomes wider than in the solid state. Also the thermoelectric power for CuSbTe_2 in both solid and liquid states is positive.

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ELEKTRONSKA SVOJSTVA TEKUĆEG CuSbTe_2

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Električna vodljivost i termoelektrična snaga mjereni su u tekućoj i čvrstoj fazi CuSbTe_2 . Eksperimentalni podaci objašnjeni su na bazi Mottovog modela razvijenog za opis gustoće stanja i električnog transporta u amorfnim poluvodičima. Pokazuje se da vodljivost najvjerojatnije potječe od šupljina u lokaliziranim stanjima blizu ruba vrpce.