

ELECTRICAL PROPERTIES OF AgTlSe_2 SEMICONDUCTOR IN THE LIQUID STATE

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The electrical conductivity and thermoelectric power of AgTlSe_2 have been investigated as a function of temperature from 390 °C up to 508 °C. The experimental data are analyzed in terms of a model developed for the density of states and electrical transport in solid amorphous semiconductors (Mott 1970). 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

Much time and research have been devoted to understand the properties of liquid semiconductors. The physical character of liquid semiconductors puts them in an intermediate position between several other classes of materials: liquid metals, molten salts and amorphous solids. Various models were suggested for liquid semiconductors¹⁻³, and the most comprehensive attack on the theoretical problems posed by the existence of liquid semiconductors has been made by Mott^{1,2}. Mott² and Cutler³ have shown that liquid semiconductors have a special relationship to solid amorphous semiconductors, the fact that there is a liquid rather than a solid has no significance in many aspects of electronic behaviour, since the time scale for many types of electronic motion is much faster than for atomic motion, and the same concepts or theories are applicable.

Of all the physical properties, the electronic transport parameters are the most distinctive ones for liquid semiconductors. The aim of the present contribution is to investigate the electrical conductivity and the thermoelectric power of AgTlSe_2 ternary semiconductor in the liquid state. AgTlSe_2 possesses the chalcopyrite struc-

ture^{9,10}), and its melting point is 328 °C. Recently ternary chalcopyrite semiconductors have attracted great deal of attention because of their possible applications in electro-optical devices¹¹) and infrared detection and generation.

2. Experimental techniques

AgTlSe₂ samples were prepared by melting the proper amounts of highly pure component elements (99.999%) obtained from Goodfellow metals Co. The material was sealed in evacuated quartz tubes at 10⁻³ Pa and heated at 1200 °C for 12 hours with frequent rocking to ensure homogenization of the melt. Then the tubes were quenched in ice to obtain the sample in the amorphous state. The solid material is then heated in inert atmosphere until it melts and then transferred to the measuring cell (Fig. 1).

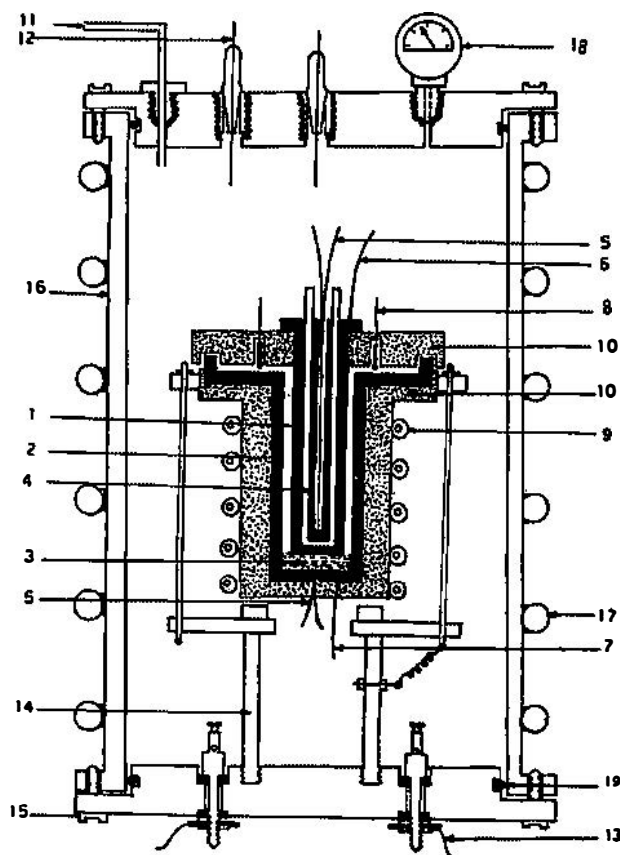


Fig. 1. Cell holder and apparatus:

1. Inner graphite electrode.
2. Outer graphite electrode.
3. Sample.
4. Aluminium radiator.
5. Thermocouples.
- 6, 7. Leads.
8. Guard ring electrode.
9. Heaters.
10. Ceramic tube.
11. Nitrogen gas inlet.
12. Insulated connecting pins.
13. Insulated connecting plugs.
14. Cell holder.
15. Joining rivets.
16. Iron cylinder.
17. Copper tubing for cooling.
18. Pressure manometer.
19. Rubber O-sealing.

The measuring cell was made from a ceramic material and was fitted with graphite electrodes, heater and thermocouples for accurate measurements of temperature. The working space between the electrodes was made highly homogenous and the spacing between the electrodes is 10^{-4} m. Measurements of the electrical conductivity were carried out using a highly stabilized power supply, a sensitive voltmeter and a sensitive galvanometer capable of measuring currents as low as 10^{-9} Ampere.

3. Results and discussion

Figures 2 and 3 show the temperature dependence of the electrical conductivity and thermoelectric power in the liquid state from 390 °C up to 508 °C. $\ln \sigma$ and S are found to be linear with $1/T$ only at low temperatures, and the activation energy determined from the slope of $\ln \sigma$ versus $1/T$ in the low temperature region is found to be $E_\sigma = 0.54$ eV. For higher temperatures the activation energy becomes temperature dependent and decreases with temperature. The temperature dependence of the thermopower which is positive yields a slightly lower value for the activation energy $E_s = 0.5$ eV. Positive values of thermoelectric power indicate a large predominance of holes in electrical transport.

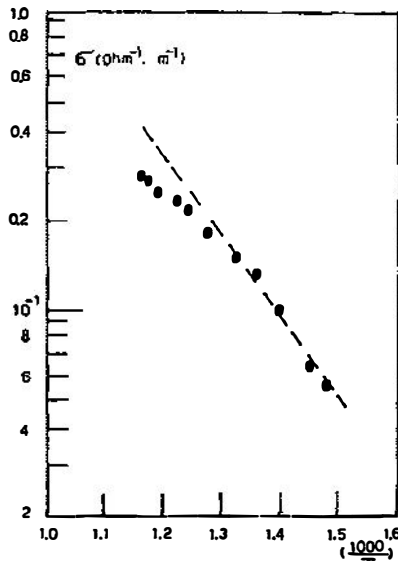


Fig. 2. Temperature dependence of the electrical conductivity for AgTlSe_2 in the liquid state.

The measured transport data can be interpreted in terms of the model developed by Mott^{1,2)} and Davis and Mott^{1,3)} for a solid amorphous semiconductor. According to this model, the electronic structure of energy bands is not significantly different from that in the corresponding crystal. The difference is that the electronic

states at the band edges are tailed in the forbidden gap and become localized. Therefore, the conduction mechanism changes radically from crystalline to amorphous structure. 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.

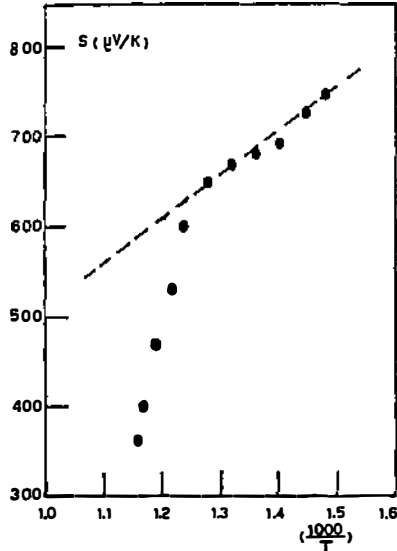


Fig. 3. Temperature dependence of the thermoelectric power for AgTlSe₂ in the liquid state.

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. In the later case the activation energy of the electrical conductivity (E_σ) must be slightly higher than one of the thermopower (E_S). Indeed, the activation energy of the conductivity is composed of two terms: the activation energy for carrier creation and for carrier hopping, while the activation energy of thermopower only includes the one for carrier creation¹⁴⁾.

The present results show that $E_\sigma = 0.54$ eV, is slightly higher than $E_S = 0.5$ eV, therefore, the conduction mechanism may be attributed to holes excited in localized states near the band edges with an activated mobility. Mott¹²⁾ and Cutler¹⁵⁾ had shown that when the activation energy for the hole mobility is small compared with the energy gap, the electrical conductivity may be expressed as

$$\sigma = \sigma_0 \exp\left(-\frac{E_F - E_v}{k T}\right) \tag{1}$$

where the value of σ_0 varies strongly with the conduction process and can be determined from the intercept of $\log \sigma$ curve at $1/T = \text{zero}$, and is equal to $130 (\text{Ohm}^{-1} \cdot \text{m}^{-1})$. Moreover, $(E_F - E_v)$ depends on the temperature and is given by

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

From Eqs. (1) and (2) one obtains

$$\sigma = \sigma_0 \exp(\gamma/k) \exp(-E(0)/kT) \tag{3}$$

with $E_g \simeq E_s$. The temperature coefficient γ , which gives the temperature dependence of the energy gap, may be calculated directly from the thermopower which is given by

$$S = \frac{k}{e} \left(\frac{E_F - E_v}{kT} + A \right) = \frac{k}{e} \left(\frac{E(0)}{kT} - \frac{\gamma}{k} + A \right) \tag{4}$$

where the average energy of the transported hole is kTA measured with respect to E_v and the value of A depends on the nature of the scattering process. If A is known, γ can be determined from the intercept on the $1/T = \text{zero}$ axis of a plot of S versus $1/T$. From Eqs. 1 and 4, one obtains the relation between σ and S

$$\sigma = \sigma_0 \exp\left(-\frac{eS}{k} + A\right). \tag{5}$$

It is clear from Figs. 2 and 3 that $\log \sigma$ and S vary linearly with $1/T$, in the low temperature range, in accordance with Eqs. 3 and 4. The straight line extrapolated to $1/T = \text{zero}$ yields $S_0 = (-\gamma + kA)/e$. Mott and Davis¹⁴⁾ and Cutler and Mott¹⁵⁾ had shown that the kinetic term A is of the order unity for disordered structures. In the present discussion, we assume $A = 1$, then the value of γ for liquid AgTlSe_2 is found to be 0.56×10^{-4} eV/K. Mott¹⁴⁾ 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.

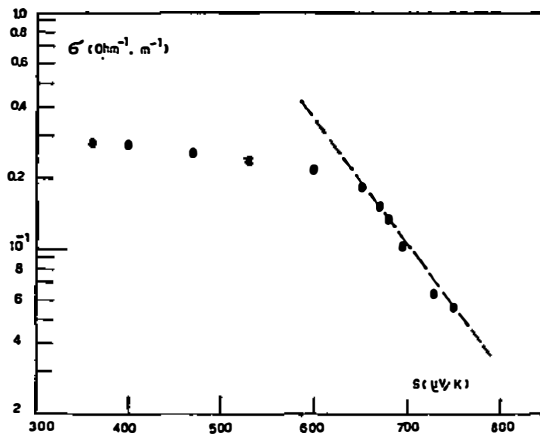


Fig. 4. \log (electrical conductivity) versus thermoelectric power for liquid AgTlSe_2 .

Fig. 4 shows that the dependence of $\log \sigma$ versus S is linear in the low temperature range, in accordance with Eq. 5. The behaviour of Figs. 2,3 and 4 at high

temperatures may be attributed to the effect of the temperature on the energy gap. The linear decrease of the gap may give rise to the transition from semiconducting to metallic behaviour expected at higher temperatures^{14, 16}. As the gap contracts with increasing temperature, the tails of the conduction and valence bands become more pronounced and the activation energy is lowered. At sufficiently high temperatures, these tails overlap, leading to a filling in of the gap and the disappearance of localization. Consequently, the electrical conductivity shows a weak temperature dependence and the thermoelectric power should approach zero.

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ELEKTRIČKA SVOJSTVA POLUVODIČA AgTlSe_2 u TEKUĆEM STANJU

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Mjerena je električka vodljivost i termoelektromotorna sila poluvodiča AgTlSe_2 u temperaturnom intervalu od 390° do 508°C . Dobiveni rezultati su analizirani prema modelu Motta (Mott 1970) koji se odnosi na poluvodiče u amorfnom stanju. Pozitivni predznak termoelektromotorne sile sugerira da su šupljine nosioci naboja u električkoj struji. Analiza dobivenih rezultata pokazuje da se gibanje šupljina odvija preko lokaliziranih stanja koja se nalaze u blizini ruba energetskeg procijepa.