

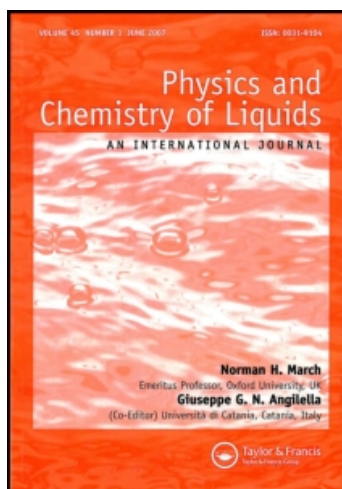
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## Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

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### Viscosity of Liquid $\text{CuBiSe}_2$ and $\text{CuSbSe}_2$ Semiconductors

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**To cite this Article** Sharaf, K. A. H. , Abdelmohsen, N. , Abdelghany, A. , Ela, A. H. Abou El and Abdelwahab, D. M.(1990) 'Viscosity of Liquid  $\text{CuBiSe}_2$  and  $\text{CuSbSe}_2$  Semiconductors', *Physics and Chemistry of Liquids*, 21: 2, 81 – 86

**To link to this Article:** DOI: 10.1080/00319109008028468

**URL:** <http://dx.doi.org/10.1080/00319109008028468>

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## VISCOSITY OF LIQUID $\text{CuBiSe}_2$ AND $\text{CuSbSe}_2$ SEMICONDUCTORS

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*(Received 5 April 1989)*

The viscosity and density of  $\text{CuSbSe}_2$  and  $\text{CuBiSe}_2$  have been studied in the liquid state. The rotating cylinder method was used. Experimental measurements show that  $\log(\text{viscosity})$  of liquid  $\text{CuSbSe}_2$  and  $\text{CuBiSe}_2$  decreases linearly with  $1000/T$ . The results were explained on the basis of the free volume model.

**KEY WORDS:** Rotational molten, Free volume model.

### INTRODUCTION

Viscosity measurements have yielded some information about changes in the short-range order on heating liquid compounds.

A close relationship between the viscosity and the structure of a liquid was first pointed out by Banchinskii<sup>1</sup>, who found that the free volume plays a decisive role in the process of viscosity flow. Moreover, Stewart<sup>2</sup> has shown that the viscosity of a liquid falls when the degree of order in the distribution of molecules decreases. Golik and Karlikov<sup>3</sup> have demonstrated the relationship between the viscosity and the structure of a liquid by a direct comparison of the diffraction patterns of melts of the same viscosity. They have found that the isoviscous liquids have identical diffraction patterns, and consequently identical short-range order.

The aim of the present contribution is to study the viscosity and density of some ternary chalcopyrite semiconductors, namely  $\text{CuBiSe}_2$  and  $\text{CuSbSe}_2$  in a wide range of temperatures in amorphous and liquid states.

Ternary chalcopyrite semiconductors have attracted recently a great deal of attention because of their possible applications in electro-optical devices<sup>4</sup> and infrared generation and detection. They can be regarded as valence analogs of the III-V and II-VI semiconductors respectively<sup>5</sup>, and they crystallize in the chalcopyrite structure<sup>6,7</sup> which is closely related to zinc blende.

### EXPERIMENTAL

$\text{CuBiSe}_2$  and  $\text{CuSbSe}_2$  samples were prepared by melting the proper amount of highly pure component elements (99.999%). The material was sealed in evacuated quartz

tubes at  $10^{-4}$  Pa and heated at  $1200^{\circ}\text{C}$  for 12 hrs with frequent rocking to ensure homogenization of the melt. Then the tubes were quenched in ice to obtain the sample in a glassy state. The solid glassy material is then heated in an inert atmosphere until it melts, then transferred to the measuring apparatus.

Viscosity measurements were carried out using the rotating cylinder method<sup>8</sup> in which the damped oscillations of a cylinder filled with liquid sample and suspended by an elastic filament were recorded. The viscosity was calculated by the method of successive approximations using Shvidkovskii equation<sup>9</sup>:

$$\eta = \frac{0.8225MR^2R^2\sigma}{2\tau[(I + MR^2/2)\delta - I(\tau/\tau_0)\delta_0]} d.$$

where  $M$  is the mass of the liquid,  $I$  is the moment of inertia of the empty cylinder,  $R$  is the radius of the cylinder,  $\delta$  and  $\delta_0$  are the logarithmic decrements of the damped

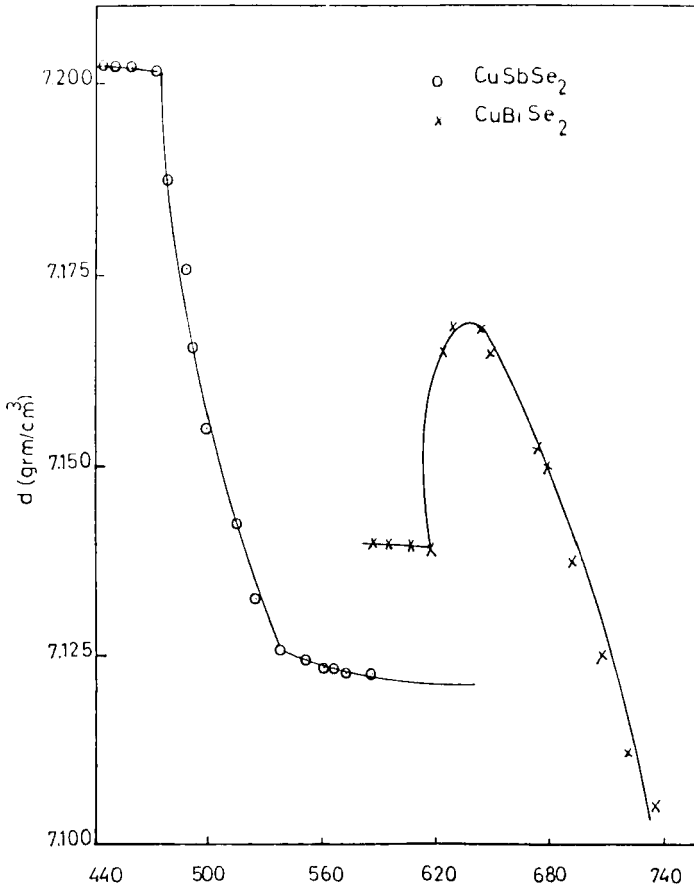


Figure 1 Temperature dependence of the density for  $\text{CuBiSe}_2$  and  $\text{CuSbSe}_2$  systems.

oscillations of the filled and empty cylinders,  $\tau$  and  $\tau_0$  are the oscillation periods of the filled and empty cylinders and  $d$  is the density.

Density measurements were carried out using the thermometer method<sup>8</sup> where a certain mass of the liquid sample was placed in a calibrated pycnometer, a specially shaped silica ampoule whose middle part is capillary with a scale allowing for measurements of volume at different temperatures.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the density for  $\text{CuBiSe}_2$  and  $\text{CuSbSe}_2$  systems. The increase of the density in the temperature interval between  $585^\circ\text{C}$  and  $630^\circ\text{C}$  for  $\text{CuBiSe}_2$  may be attributed to the increase of the coordination number, (number of nearest neighbor atoms) with temperature whose rate is larger than the rate of increase of interatomic spacing (note that the increase of interatomic spacing increases the volume and decreases the density). For temperature higher than  $630^\circ\text{C}$ , the decrease of density with temperature may be attributed to a large thermal expansion coefficient, and the increase of the interatomic spacing which causes a net increase in volume.

For  $\text{CuSbSe}_2$ , the decrease of density with temperature may be attributed to a large thermal expansion coefficient and a large rate of increase of interatomic spacing.

From our previous work on electrical conductivity<sup>9,10</sup>, we had calculated the activation energy and we found:

$$E_a \text{ for liquid } \text{CuSbSe}_2 = 0.2 \text{ eV}$$

and

$$E_a \text{ for liquid } \text{CuBiSe}_2 = 0.15 \text{ eV.}$$

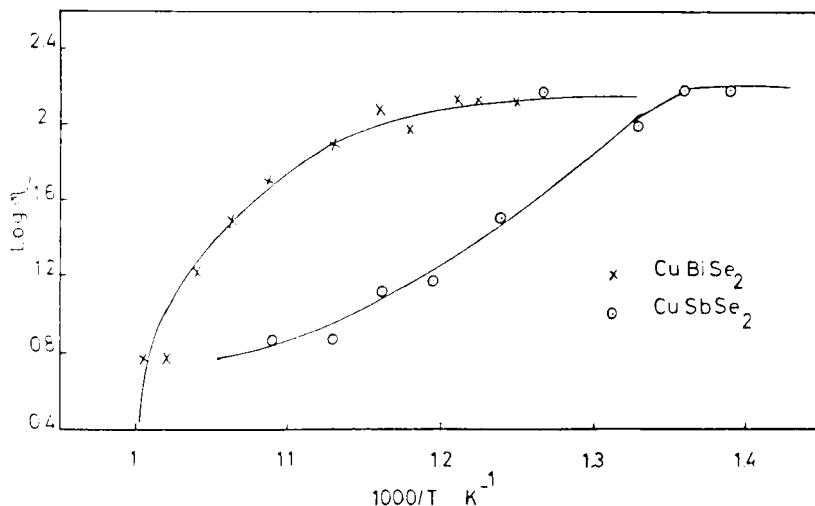


Figure 2 Relation between the dynamic viscosity versus 1000/T.

Figure 2 shows the relation between the dynamic viscosity ( $\eta = \gamma\rho$  where  $\rho$  is the density) plotted in logarithmic coordinates versus  $1000/T$ .

The values of the activation energy of viscous flow have been calculated using the empirical relation  $\eta = \eta_0 e^{E_\eta/KT}$  and were found to be  $E_\eta = 1.7$  eV for  $\text{CuBiSe}_2$ ;  $E_\eta = 1.12$  eV for  $\text{CuSbSe}_2$ .

The flow behaviour for  $\text{CuBiSe}_2$  and  $\text{CuSbSe}_2$  in the liquid state may be discussed in the standard models for viscosity<sup>12-18</sup>. The marked curvature of  $\log \eta$  vs.  $1/T$  relation indicates that the flow process is not simply activated and the simple absolute rate theory<sup>17</sup> does not provide an appropriate description of the data. The flow process behaves differently near the melting point and at high temperatures. It appears that the free volume model is more adequate for representing the flow behaviour in the high temperature region.

Bueche<sup>18</sup>, on the assumption of freely orienting chain consisting of 2 freely orienting segments, has found that the viscosity is proportional to the molecule length and segmental friction factor (the force required to pull a single molecule through its surroundings at unit speed). The molecules are confined to a cage bounded by their intermediate neighbours, occasionally there is a fluctuation in density which opens up a hole within a cage large enough to permit a considerable displacement of the molecules contained by it. The diffusive motion occurs as a result of the translation of a molecule across the void in its cage and diffusion occurs not as a result of redistribution of free volume within the liquid<sup>13,19</sup>.

The free volume of a given molecule is the volume within its cage less than the volume of the molecule, and it should exceed a critical volume  $V^*$  just large enough to permit another molecule to jump in after the displacement. The free volume in the material can arise in two ways; either of which will increase with the temperature.

Firstly the inter-atomic spacing can increase with temperature leading to an excess volume which is uniformly distributed among the atoms or molecules. Secondly, the increasing atomic vibrations can produce a nonuniform distribution of excess volume due to the localized formation of holes with volumes.

Comparable to the atomic or molecular volume. At temperatures above the glass transition extensive molecular transport can occur and this implies the presence of a considerable number of holes, and the magnitude of the free volume is determined by the excess volume arising from holes. The free volume can be approximately obtained from the expression:

$$V_f = \alpha \bar{V}_m(T - T_0), \quad (1)$$

where  $\alpha$  is the coefficient of thermal expansion,  $\bar{V}_m$  is the mean molecular volume, and  $T_0$  is the temperature at which the free volume disappears.

$$T_0 = T_g \text{ glass transition temperature.}$$

The viscosity can be written as<sup>19</sup>

$$\eta = CT^{1/2} \exp\left(\frac{\gamma V^*}{\alpha \bar{V}_m(T - T_g)}\right) \quad (2)$$

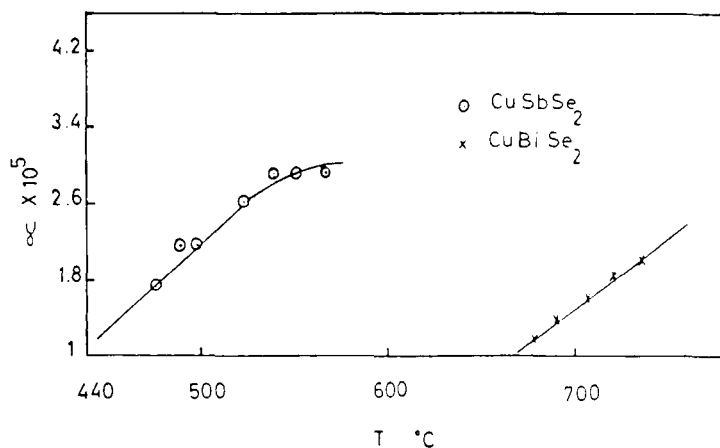


Figure 3 Temperature dependence of the coefficient of thermal expansion  $\alpha_c$ .

where  $Z$  is the number of molecules,

$$C = \left( \frac{8mK}{9\pi^3} \right)^{1/2} \frac{1}{a^2} \tag{3}$$

$m$  is the molecular mass,  $K$  is the Boltzmann's constant, and  $a$  is the molecular diameter.  $\gamma$  is a numerical factor introduced to correct for the overlap of free volume ( $\gamma = 0.5$ ).

Figure 3 shows the temperature dependence of the coefficient of thermal expansion  $\alpha_c$ . It is clear from the figure that  $\alpha_c$  increases with temperature increase. Therefore, the observed decrease of the dynamic viscosity  $\eta$  with temperature, Figure 2, could be attributed to the exponential dependence of  $\eta$  on temperature  $T$  and  $\alpha_c$  according to equation 2.

References

1. A. I. Bachinskii, Selected works IZS. ANSSSR, Moscow, (1960).
2. E. Stewart, *Phys. Rev.*, **9**, 1575 (1957).
3. A. Z. Golik, and D. N. Karlikov, *Dokl. ANSSSR*, **114**, 361 (1957).
4. M. J. Thwaites, R. D. Tolinson and M. J. Hampshirs, *Solid state Commun.*, **23**, 905 (1977).
5. L. I. Berger and V. D. Prochukan, *Ternary Diamond-Like Semiconductors* (Consultants Bureau Enterprises, Inc, New York, 1969, p. 47
6. V. P. Zhuze, V. M. Sergeeva, and E. L. Shtrum, *Soviet Phys. Techn. Phys.*, **3**, 1925, (1958).
7. J. L. Shay and J. H. Wernik, *Ternary Chalcopyrite Semiconductors*.
8. V. H. Glazov, J. N. Chizhevskaya, and N. N. Glagoleva, *Liquid Semiconductors* (Plenum Press, New York, 1969).
9. N. Abdelmohsen, A. Abdelghany, A. Abou El Ela and D. Abdelwahab, Electrical Conductivity and Thermoelectric Power of  $\text{CuSbSe}_2$  in the Solid and Liquid State, *Fizika, Yugoslavia*, In Press.
10. N. Abdelmohsen, A. Abdelghany, A. Abou El Ela and D. Abdelwahab, Electrical Conductivity and Thermoelectric Power of  $\text{CuBiSe}_2$  in the Solid and Liquid State, *Indian Journal of Phys.*, New Delhi, In Press.
11. E. C. Shvidkovskii, *Some Problems in the Viscosity of Molten Metals* (Gosekhteorizdat, Moscow, 1955).
12. J. F. Rialland, and J. C. Perron, Proc. 6th Int. Conf. on Amorphous and Liquid Semiconductors, (Leningrad 1976).

13. M. H. Cohen, D. Turnbull, *J. Chem. Phys.*, **11**, 1164 (1959).
14. P. B. Macido, and Litovitz, *J. Chem. Phys.*, **42**, 3038(1970).
15. Chaussemy G., *J. de Phys. Lett.*, **40**, 347 (1970).
16. A. H. Abou El Ela, K. A. Sharaf and H. H. A. Labib, *Appl. Phys.*, A **26**, 203-306 (1981).
17. S. Classton, K. J. Laidler and H. Eyring, *The Theory of Rate Process* (McGraw-Hill, New York, 1941).
18. F. Bueche, *Physical properties of Polymers* (Interscience Publishers, New York, 1962).
19. M. M. Cohen and D. Turnbull, *J. Chem. Phys.*, **52**, 3038 (1959).