

well with the experimental relation. It should be noted that the band-band transitions with absorption of nonequilibrium phonons [1], as shown by calculation, are less intense and produce no maximum on the $\Delta K(\hbar\omega)$ curve. The energy deficit incurred upon absorption of light with $\hbar\omega < \epsilon_g$ can occur both as a result of the interaction of the electron-hole pair with the electron gas heated by the strong electric field [7]. However, as shown by calculation, this effect is weaker by more than one order of magnitude than the one described above in the case of transitions to a final exciton state with $n = 1$ via an intermediate state with $n = 1$ in interactions with free hot electrons, and cannot result in a maximum on the $\Delta K(\hbar\omega)$ curve.

It should be noted in conclusion that the observed effect is quite sensitive to the band structure near small values of K , of the order of $\sqrt{2m_e^*k_p\theta}/\hbar$. For this reason, it can be used as a method of investigating the band structure of III-V semiconductors in the vicinity of the Γ point when a more exact theory is constructed. In addition, this phenomenon can be used to determine the lifetimes of long-wave longitudinal optical phonons.

- [1] W. P. Dumke, Phys. Rev. 108, 1419 (1957).
- [2] B. Segall, Phys. Rev. 150, 734 (1966).
- [3] L. E. Vorobyov, V. I. Stafeev, and A. V. Sturbin, Phys. Stat. Sol. (B) 53, 47 (1972).
- [4] R. P. Seisyan, M. A. Abdullaev, and B. P. Zakharchenya, Fiz. Tekh. Poluprov. 6, 408 (1972) [Sov. Phys.-Semicond. 6, 351 (1972)].
- [5] R. J. Elliott, Phys. Rev. 108, 1384 (1957).
- [6] E. O. Kane, J. Phys. Chem. Solids 1, 249 (1957).
- [7] S. M. Ryvkin, Fiz. Tverd. Tela 7, 1278 (1965) [Sov. Phys.-Solid State 7, 1038 (1965)].

ANISOTROPIZATION OF THE ELECTRIC CONDUCTIVITY IN ORIENTED SAMPLES OF VITREOUS SEMICONDUCTORS

B. T. Kolomiets, V. M. Lyubin, and V. P. Shilo
A. F. Ioffe Physico-technical Institute, USSR Academy of Sciences

Submitted 13 April 1973

ZhETF Pis. Red. 17, No. 10, 577 - 580 (20 May 1973)

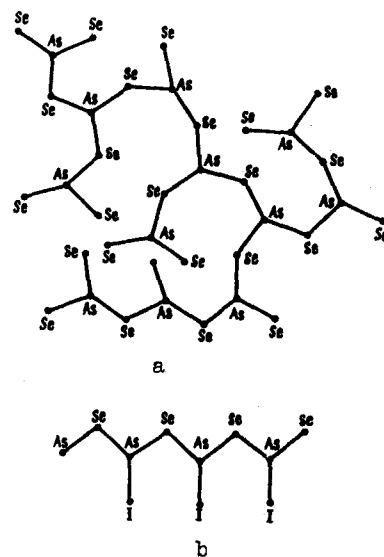
An appreciable anisotropy of the electric conductivity, attributed to orientation of the macromolecules, was observed in oriented samples of vitreous semiconductors of the As-Se-I system. The result proves the influence of the polymer structure on the conduction mechanism of vitreous chalcogenide semiconductors

The question whether chalcogenide glasses are inorganic polymers has been discussed in the literature many times [1 - 4]. An influence of changes of the polymer structure (joining or destruction of the macromolecules) on the electric and acoustic properties, and also on the energy spectrum of the local states in chalcogenide vitreous semiconductors of the As_2Se_3 type having branched two-dimensional frames (Fig. a) was noted in [5, 6]. From the point of view of establishing a correlation between the structure and the properties, it is of considerable interest to investigate chalcogenide vitreous semiconductors, for example the material AsSeI, which has a one-dimensional structure [7, 8] and is the analog of linear organic polymers (Fig. b).

We performed experiments on the orientation of chalcogenide glasses of the As-Se-I system and report here the first results on the electric properties of oriented samples. Glasses with composition $AsSeI_x$ with $0.1 \leq x \leq 0.1$ were synthesized by the known method of fusing the components in vacuum. Oriented samples in the form of strips 0.5 - 2.0 mm wide and 0.05 - 0.2 mm thick were prepared by drawing from a melt of reduced viscosity. The long strips were cut into pieces 1 - cm long, which were fastened on teflon plates and equipped with electrodes of silver paste, so that the resistance of the samples could be measured both along and across the drawing direction (resistances $r_{||}$ and r_{\perp} , respectively).

In most samples with appreciable iodine content ($0.25 \leq x \leq 1.0$), we observed a noticeable anisotropy of the electric conductivity ($r_{\perp}/r_{||} \gg 1$), which increased with increasing iodine content. The resistances of some typical oriented samples with various compositions are listed in the table together with the data on the softening temperature T_g , obtained by the method described in [9]. In samples prepared by drawing from the low-viscosity melt, no noticeable anisotropy of the electric conductivity was observed ($r_{\perp}/r_{||} = 1$).

Состав	$T_g, ^\circ\text{C}$	Resistance before annealing		Resistance after annealing	
		$r_{ }, \text{ohms}$	r_{\perp}, ohms	$r_{ }, \text{ohms}$	r_{\perp}, ohms
AsSeI	70 ± 2	$8 \cdot 10^{10}$	$1 \cdot 10^{12}$	$1 \cdot 10^{12}$	$1 \cdot 10^{12}$
AsSeI	70 ± 2	$3 \cdot 10^{10}$	$1 \cdot 10^{12}$	$8 \cdot 10^{11}$	$1 \cdot 10^{12}$
AsSeI	70 ± 2	$5 \cdot 10^8$	$2 \cdot 10^{12}$	—	—
AsSeI	70 ± 2	$6 \cdot 10^{10}$	$1 \cdot 10^{12}$	$2 \cdot 10^{12}$	$1,5 \cdot 10^{12}$
AsSeI _{0,8}	80 ± 2	$1,5 \cdot 10^{10}$	$1,5 \cdot 10^{12}$	—	—
AsSeI _{0,8}	80 ± 2	$2 \cdot 10^{10}$	$1 \cdot 10^{12}$	$1 \cdot 10^{12}$	$1,2 \cdot 10^{12}$
AsSeI _{0,5}	107 ± 2	$1 \cdot 10^{11}$	$1,5 \cdot 10^{12}$	$1,6 \cdot 10^{12}$	$1,5 \cdot 10^{12}$
AsSeI _{0,5}	107 ± 2	$2 \cdot 10^{11}$	$2 \cdot 10^{12}$	$2 \cdot 10^{12}$	$2 \cdot 10^{12}$
AsSeI _{0,5}	107 ± 2	$5 \cdot 10^{11}$	$1,5 \cdot 10^{12}$	$2 \cdot 10^{12}$	$1,5 \cdot 10^{12}$
AsSeI _{0,5}	107 ± 2	$5 \cdot 10^{10}$	$2 \cdot 10^{12}$	$1,5 \cdot 10^{12}$	$2 \cdot 10^{12}$



Schematic structures of the vitreous semiconductors As_2Se_3 (a) and AsSeI (b).

That the observed conductivity anisotropy is due to the orientation of the macromolecules and not to some other cause is proved by the following fact. When the oriented samples were annealed at temperatures $T_g - \Delta T$, where $\Delta T = 10 - 20^\circ\text{C}$, for two hours the conductivity anisotropy vanished completely with $r_{||}$ increasing and with r_{\perp} remaining constant (or even decreasing).

It should be noted that the low values of $r_{||}$ in many samples were not stable enough and had a tendency to increase, particularly in samples with large iodine contents, characterized by small values of T_g .

In our opinion, the results show clearly that the carrier motion in vitreous semiconductors must be subdivided into motion over the macromolecule and intermolecular hopping, and the difficulty in realizing the latter increases the resistance of the samples. Orientation leads, obviously, to an appreciable decrease of the number of intermolecular hops when the carriers move along the drawing direction, and annealing the samples causes a rolling up of the macromolecules, which is accompanied by vanishing of the anisotropy of the conductivity.

We note here that it is precisely the hopping of the carriers between the molecules which may be the cause of the anomalous temperature-frequency characteristics of the conductivity of chalcogenide vitreous semiconductors [10 - 12], which is frequently connected with hops over the impurity states.

Contemporary models of amorphous semiconductors [13 - 16] do not take into account the singularities in their molecular structure, and can therefore hardly describe completely and with sufficient detail the electric properties, particularly the transport and the energy spectrum of those amorphous materials that are polymers, and especially many chalcogenide vitreous semiconductors.

- [1] R. L. Myuller, in: *Stekloobraznoe sostoyanie (The Vitreous State)*, AN SSSR, 1960, p. 61.
- [2] V. A. Romanovskii, V. V. Tarasov, *ibid.*, p. 474.
- [3] V. V. Tarasov, G. M. Bartenev, A. S. Eremeeva, V. A. Ratobyl'skaya, *ibid.* 1965, p. 167.
- [4] B. T. Kolomiets, V. M. Lyubin, and V. P. Shilo, *Dokl. Akad. Nauk SSSR* **201**, 988 (1971).
- [5] B. T. Kolomiets, V. M. Lyubin, V. P. Shilo, and V. L. Averyanov, *J. Noncryst. Sol.* **8 - 10**, 1017 (1972).
- [6] Yu. A. Bozhko, B. T. Kolomiets, V. M. Lyubin, V. A. Ratobyl'skaya, L. A. Simonova, and V. P. Shilo, *Proc. Internat. Conf. on Amorphous, Liquid, and Vitreous Semiconductors*, Part 1, Sofia, 1972, p. 59.
- [7] S. A. Dembovskii and A. P. Chernov, *Neorganicheskie materialy* **4**, 1229 (1968).
- [8] T. E. Hopkins, R. A. Pasternak, E. B. Bould, and I. R. Herdon, *J. Phys. Chem.* **66**, 733 (1962).
- [9] B. T. Kolomiets, V. M. Lyubin, and V. P. Shilo, *Izv. AN SSSR, ser. neorgan. materialy* **7**, 733 (1971).

- [10] A. E. Owen and J. M. Robertson, *J. Noncryst. Sol.* 2, 40 (1970).
 [11] E. B. Ivkin and B. T. Kolomiets, *ibid.* 3, 41 (1970).
 [12] H. K. Rockstad, *Sol. St. Comm.* 9, 2233 (1971).
 [13] A. I. Gubanov, *Kvantovo-elektronnaya teoriya amorfnykh poluprovodnikov* (Quantum Electronics Theory of Amorphous Semiconductors), AN SSSR, 1963.
 [14] N. F. Mott, *Phil. Mag.* 13, 989 (1966); 17, 1259 (1968), 19, 835 (1969); 22, 7 (1970).
 [15] M. H. Cohen, H. Fritsche, and S. R. Ovshinsky, *Phys. Rev. Lett.* 22, 1065 (1969).
 [16] M. H. Cohen, *J. Noncryst. Sol.* 4, 391 (1970).

INVESTIGATION OF CHOLESTERYL VALERATE UNDER PRESSURE

V. Ya. Baskakov and V. K. Semenchenko

Moscow State University

Submitted 17 April 17 1973

ZhETF Pis. Red. 17, No. 10, 580 - 583 (20 May 1973)

We report the results of an experimental study of the specific volume of liquid-crystal matter (cholesteryl valerate) at a pressure up to 1000 atm and in the temperature interval 80 - 129°C, including the phase transitions: plots of the isotherms and the P-T diagram are presented.

Interest in liquid crystals is due to their applications in electronics [1], medicine [2], and other fields [3, 4], and the temperature interval in which the mesophases exist is of considerable practical interest.

We have investigated experimentally the behavior of the mesophases under pressure, and also the nature of the phase transitions between different phases of this class of substances. We note that in spite of the great theoretical interest there are no published experimental data on the specific volume of liquid crystals under pressure.

The first such investigations were performed by us on paraazoxyanisole [4], a homolog of the dialoxyazoxybenzene series, in which only one liquid-crystal (nematic) phase, whereas cholesteryl valerate has two phases, cholesteric and smectic [5]. The investigation of the cholesteryl valerate was carried out at pressures up to 1000 atm on 32 isotherms (80 - 129°C), five of which are shown in Fig. 1 (the 111, 109, 103, and 99°C isotherms are raised in the figure 0.04, 0.04, 0.06, and 0.07 cm³/g, respectively).

As follows from the figure, with increasing pressure the volume of the isotropic phase decreases linearly and goes over into the cholesteric phase without any noticeable effect, apart from an insignificant change of slope. Such a behavior is observed on the majority of the isotherms, and the transition points shown on the T-P diagram lie on a straight line given by the expression (Fig. 2a)

$$t^{\circ}\text{C} = 102 + 0.0715P.$$

We note that the behavior of the cholesteric phase under pressure differs little from the isotropic phase, although under normal conditions this difference is more noticeable [3]. Such transitions are apparently closed phase transitions [6].

Further increase of the pressure transforms the cholesteric phase into the smectic one. The transition occurs in some range of pressure (not at a single point), and is well noticed on all the isotherms (starting with 94°C upwards). The transition temperature increases with increasing pressure linearly (Fig. 2b) and is described by the expression

$$t^{\circ}\text{C} = 93 + 0.0565P.$$

The sensitivity of the employed setup [3] has enabled us to measure several points within the limits of the transition (isotherms 119 and 103°C of Fig. 1).

Finally, we measured the specific volume of the smectic phase, whose variation under pressure is patently nonlinear. When temperatures given by the relation (Fig. 2c)

$$t^{\circ}\text{C} = 79.6 + 0.0396P$$

are reached, a transition to the solid-crystal phase sets in and is accompanied by a jump in the volume. The volumes given for the solid-crystal phase should be regarded as tentative, since the apparatus was not intended for measurements of solid phases.