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Electric properties of bulk amorphous semiconductor Zn₄₁Sb₅₉

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Abstract

The electric conductivity of amorphous $Zn_{41}Sb_{59}$ was shown to be of a nearly activation type with $E_{\sigma} \approx 0.28$ eV at $125 \le T \le 360$ K. It displayed no frequency dependence at $220 \le T \le 300$ K and $f \le 5$ MHz. The thermoelectric power, S, was positive and increased nearly linearly with reciprocal temperature at $186 \le T \le 364$ K; $E_S \approx 0.19$ eV. The Hall coefficient measured at 300 K was negative.

1. Introduction

Amorphous Zn–Sb alloy containing about 60 at.% Sb was one of the first amorphous (a-) substances produced in a solid state reaction – spontaneous amorphization of a crystalline high-pressure phase [1]. A recent high-pressure study [2] has revealed unique features of this material which make it an interesting material for a detailed investigation–two first-order transitions between different amorphous semiconducting states of $a - Zn_{41}Sb_{59}$ were observed at room temperature and approximately at 20 and 49 kbar; the 20 kbar transition was shown to be reversible.

A possibility of 'a-semiconductor \rightarrow a-metal' first-order phase transitions has been discussed and studied for many years [3,4], but the transitions between amorphous semiconducting states, like those found in a $- Zn_{41}Sb_{59}$, has never been considered to our knowledge. The reversibility of the transition occurring in $a - Zn_{41}Sb_{59}$ at 20 kbar suggests that this is a transition between thermodynamically individual states, i.e. the phases corresponding to (local) minima of the free energy.

As for the electric properties, only the temperature and pressure dependences of the $a - Zn_{41}Sb_{59}$ conductivity, σ , have been studied [2]. The roomtemperature σ at 7 GPa was shown to decrease by approximately five orders of magnitude from its atmospheric value. An activation character of the $\sigma(T)$ dependence at atmospheric pressure changed to that typical of conduction by variable-range hopping at 3.5 GPa and then to a semimetal at 7 GPa.

The present work was aimed at characterizing the semiconducting properties of $a - Zn_{41}Sb_{59}$ at atmospheric pressure by measuring the temperature and frequency dependences of the electric conductivity, σ , the temperature dependence of the thermoelectric power, *S*, and the Hall coefficient at room temperature. Note also that these properties had not been measured for any amorphous semiconductor produced via a solid state transformation of a high-pressure phase (Ga-Sb, Cd-Sb, Al-Ge [5]), so it was interesting to know whether or not they would differ

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from those of amorphous substances produced by other means.

2. Sample preparation and experimental details

At P > 6.5 GPa only one intermediate phase, a crystalline metallic δ -phase with compositions in a narrow interval around Zn₄₁Sb₅₉, is in equilibrium in the Zn-Sb system [6]. As was shown in Refs. [1,2], the δ -phase cooled to 100 K is retained after decreasing the pressure to atmospheric. On subsequent heating to room temperature, the phase transforms into an amorphous semiconductor which remains amorphous under room conditions for an indefinitely long time (years at least). The amorphization is accompanied by an approximately 20% increase in the sample volume [2]. Further heating to approximately 425 K results in an irreversible increase in the volume of the amorphous sample by another 5%. At higher temperatures crystallization takes place, and the sample transforms into a mixture of crystalline antimony and ZnSb semiconducting compound in thermodynamic equilibrium at atmospheric pressure.

In the present work, an ingot of the $Zn_{41}Sb_{59}$ two-phase alloy (ZnSb + Sb) was melted from zinc (99.95 wt% Zn) and antimony (99.9 wt% Sb) in an evacuated quartz capsule. To produce $\delta - Zn_{41}Sb_{50}$ samples, part of the ingot was powdered in a mortar to get a more homogeneous (ZnSb + Sb) mixture, the powder was pressed into pellets 7 mm in diameter and 2 mm thick which were then placed in a Teflon container and exposed to P = 7 GPa and T = 623 K for 24 h with subsequent rapid cooling under pressure to 100 K in a Toroid type high-pressure chamber. Then the chamber was unloaded and the pellets were X-rayed at 100 K (a DRON-2.0 diffractometer, Cu K α radiation, phototechnique) in order to be sure that they had completely transformed into the δ -state.

The next step was amorphization of the obtained pellets by warming to 300 K at 5 K/min. Twenty samples in the form of bars $1 \times 1 \times 5$ mm³ were then cut out of the amorphous pellets with an abrasive wire saw (WS-20A).

Copper electrodes 0.05 mm in diameter were stuck to each sample with silver paste and σ measured at $T \leq 300$ K. Four samples were then successively annealed at 353, 373, 403, 423, 443 and 453 K for 30 min at each temperature. The electrodes to these samples were soldered with $In_{23}Bi_{77}$ alloy at 350 K using an ultrasonic soldering iron, and the $\sigma(T)$ dependences of the samples were measured at $T \le 350$ K.

The pasted electrodes permitted a reliable measurement of the dc conductivity at $\sigma \ge 10^{-8}$ (Ω cm)⁻¹ and the soldered ones at $\sigma \ge 10^{-9}$ (Ω cm)⁻¹. Both types of electrodes made it possible to reliably measure the thermoelectric power and ac conductivity at $\sigma \ge 10^{-5}$ to 10^{-6} (Ω cm)⁻¹.

After each measurement the sample was X-rayed at room temperature to make sure that no crystallization had taken place.

3. Experimental results

The $\sigma(T)$ dependences of the a-Zn₄₁Sb₅₉ measured in Ref. [2] at $205 \le T \le 328$ K were of nearly activation type,

$$\sigma = \sigma_0 \exp\left(-E_{\sigma}/kT\right),\tag{1}$$

with both E_{σ} and σ_0 varying noticeably from sample to sample. The results of the present measurements in wider temperature intervals were in line with these observations.

A representative $1g(\sigma)$ versus T^{-1} dependence is shown in Fig. 1, curve 1. For all the studied samples, deviation of such dependences from straight lines became clearly detectable only at lower temperatures, for $\sigma < 10^{-8} (\Omega \text{ cm})^{-1}$. Fitting of the measured dependences at higher temperatures by straight lines gave $0.27 \le E_{\sigma} \le 0.30$ eV and $50 \le \sigma_0 \le 1500$ $(\Omega \text{ cm})^{-1}$. This scatter in the values of E_{σ} and σ_0 for different samples seemed to be an intrinsic property of the a-Zn₄₁Sb₅₉ prepared by our procedure.

Of the four a-Zn₄₁Sb₅₉ samples additionally annealed at temperatures up to 443 K, two samples exhibited an increase in the values of E_{σ} and σ_0 (within the above limits) with annealing temperature that agreed with the data in Ref. [2]. The $\sigma(T)$ dependences of another two samples, however, remained unchanged after the same treatments. We conclude that the conductivity of the a-Zn₄₁Sb₅₉ is nearly unaffected by relaxation processes occurring



Fig. 1. Temperature dependences of the electric conductivity, σ , (1) and thermopower, S, (2) of amorphous Zn₄₁Sb₅₉ after annealing for 30 min at 373 K, and electric conductivity (3) of the same sample after crystallization at 453 K.

in the internal $300 \le T \le 443$ K and the underlying 5% volume increase [2].

A 30 min annealing of the a-Zn₄₁Sb₅₉ samples at 453 K resulted in crystallization. The conductivity of the crystallized samples was nearly temperature independent in the range $5 \le T \le 250$ K (curve 3 in Fig. 1 represents a higher-temperature part of the data), significantly exceeded the conductivity of the amorphous samples and was close to that of the starting crystalline two-phase (ZnSb + Sb) alloy.

The ac conductivity of three a-Zn₄₁Sb₅₉ samples was investigated. Two of them had not been heated above 300 K and the third one had been annealed at 403 K. The measurements at 300, 260 and 220 K revealed no frequency dependence of their σ at frequencies $f \le 5$ MHz.

The thermopower of five $a-Zn_{41}Sb_{59}$ samples, including those annealed at $T \le 443$ K, was measured. For all the samples S was positive (corresponding to conduction by holes) and increased approximately linearly with the reciprocal temperature; a representative dependence is shown in Fig. 1, curve 2. Supposing the measured dependences to obey [4,7]

$$S = (k/e)([E_s/kT] + C), \qquad (2)$$

where e is the electron charge, the fitting parameters $E_s = 0.19 \pm 0.01$ eV and $C = 1 \pm 0.5$ were obtained.

No distinct effect of heat treatment of the samples on their thermopower was observed.

The Hall coefficient at 300 K measured on the same five a- $Zn_{41}Sb_{59}$ samples was negative and fell in the range from -10^2 to -10^3 cm³/°C.

4. Discussion

The measured properties of a-Zn₄₁Sb₅₉ are characteristic of a classic amorphous semiconductor [7]: (i) negative sign of the Hall coefficient along with a positive sign of the thermopower; (ii) nearly activation type of conduction with E_{σ} close to half of the band gap, E_g , in the crystalline semiconductor of the nearest composition (in our case, a ZnSb compound with $E_g/2 \approx 0.3$ eV at 4.2 K [8]); (iii) a nearly linear increase of the thermopower with T^{-1} , the value of E_s being less than E_{σ} . This allows an interpretation of our experimental results within the framework of the conventional Davis–Mott model for amorphous semiconductors [3].

According to the model, the Fermi level, $E_{\rm F}$, is assumed to be pinned close to the middle of the mobility gap, $E_{\rm mg}$, (usually close to $E_{\rm g}$ of the related crystalline semiconductor [7]) where a maximum of partly filled localized states is situated. The positive sign and rather large value of the thermopower indicate that conduction is due to the states in the vicinity of the mobility edge, $E_{\rm V}$, of the valence band. As a matter of fact, the magnitude of S is determined by the average distance, $\delta E_{\rm avr}$, between $E_{\rm F}$ and the conducting levels [9]:

$$S = \frac{k}{e} \int \frac{E_{\rm F} - E}{kT} \frac{\sigma(E)}{\sigma} dE = \frac{k}{e} \frac{\delta E_{\rm avr}}{kT}.$$

The value of δE_{avr} of a-Zn₄₁Sb₅₉ thus estimated varied from 0.21 eV at 180 K to 0.24 eV at 370 K and was therefore of the order of $E_{mg}/2$.

If conduction is due to holes excited into extended states beyond E_V , then $E_{\sigma} = E_F - E_V$; $E_S = E_{\sigma}$ [3,7], and $\delta E_{avr} > E_{\sigma}$ is to be observed. The fact that δE_{avr} and E_s are noticeably less than E_{σ} indicates that conduction is dominated by thermally activated hopping of the carriers in the localized states of the valence band tail with the mobility [3,7]:

$$\mu_{\rm hop} = \mu_o \, \exp(-W/kT). \tag{3}$$

In this case the thermopower is given by

$$S = \frac{k}{e} \left(\frac{E_{\rm F} - E_{\rm A}}{kT} + C \right),\tag{4}$$

where E_A is the edge of the tail and the value of C depends on the energy distribution of the density, N(E), of the localized states. If N(E) is assumed to behave as some power, r, of E in the interval from E_A to approximately $E_A + 3kT$,

$$N(E) = K(E_{\rm A} - E)',$$

then the value of C in Eq. (4) is almost independent of T but depends on r; in particular, C = 2 for r = 1and C = 3 for r = 2 [7].

Comparing the theoretical and experimental dependences, (4) and (2), one can deduce that the edge of the valence band tail is by $E_{\rm F} - E_{\rm A} \approx E_{\rm S} \approx 0.19$ eV below the Fermi level. Though the experiment yielded C < 2, we think that $r \approx 1$ is most likely since, as with many other semiconductors, some decrease in C may take place due to a decrease in the band gap with temperature. For example, if $E_{\rm mg}(T)$ of a-Zn₄₁Sb₅₉ is close to $E_{\rm g}(T)$ of crystalline ZnSb [8], then the temperature coefficient, $\gamma_{\rm FA}$, of $E_{\rm F} - E_{\rm A}$ (constituting approximately one third of $E_{\rm mg}$) can be estimated as $\gamma_{\rm mg}/3 \approx 1.3 \times 10^{-4}$ eV/K. This would decrease the theoretical estimate for C by $\gamma_{\rm FA}/k \approx 1.5$.

For the given type of N(E) dependence, the temperature dependence of σ is of almost activation character [7], and for r = 1

$$\sigma = \sigma_1 \exp\left[-(E_{\rm F} - E_{\rm A} + W)/kT\right], \qquad (5)$$

where σ_1 is proportional to *T*. Because of *T* entering the pre-exponentional factor, fitting of the experimental $\sigma(T)$ for a-Zn₄₁Sb₅₉ by Eq. (5) instead of Eq. (1) leads to values of $E_F - E_A + W$ less than E_σ by approximately 0.02 eV. This allows an estimation of $W \approx E_\sigma - (E_F - E_A) - 0.02 \approx E_\sigma - E_S - 0.02 =$ 0.07 ± 0.02 eV. The factor σ_1 from Eq. (5) estimated under this assumption, is of the order of $\sigma_0/3$ at 250 K.

The factors σ_1 and μ_0 entering Eqs. (5) and (3) can be written as $\sigma_1 = \frac{1}{6}K\nu_{\rm ph}e^2kT \exp(-2\alpha R + \gamma_{\rm FA}/k)$ and $\mu_0 = \frac{1}{6}\nu_{\rm ph}eR^2/kT \exp(-2\alpha R)$, where $\nu_{\rm ph}$ is a characteristic phonon frequency, R is the distance covered in one hop and α is the rate at which the atomic wave functions fall off with distance [3,7]. For typical $\nu_{\rm ph} \approx 10^{13} \text{ S}^{-1}$, $R \approx 0.5 \text{ nm}$ and $\alpha R \approx 1$ these yield $\mu_{\rm hop} \approx 0.02 \text{ cm}^2/\text{V}$ s at room temperature, which is a reasonable value for an amorphous semiconductor [7].

As for the large scatter in σ_1 for different samples (about 30 times), it may be caused by relatively small differences in R due to an exponential dependence on R. In fact, $K \alpha R^{-3}$ and thus $\sigma_1 \alpha R^{-1} \exp(-2\alpha R)$.

The observed deviation of the $\sigma(T)$ dependence from the activation behaviour at lower temperatures (Fig. 1, curve 1) may be due to a contribution of conduction by hopping amongst the localized states near the Fermi level.

The negative sign of the Hall effect typical for most amorphous semiconductors is usually attributed to the geometrical peculiarities of thermally activated hopping of the holes [7].

For the given mechanism of conduction, the frequency dependence of the $a-Zn_{41}Sb_{59}$ conduction should follow [7,10]

$$\sigma(\omega,T) - \sigma(0,T)$$
$$= A \omega \left[\ln \left(\frac{\nu_{\rm ph}}{\omega} \right) \right]^4 \exp \left(-\frac{E_{\rm F} - E_{\rm A}}{kT} \right),$$

where the factor A, however, could not be calculated theoretically. As the experiment has shown that $\sigma(\omega,T) - \sigma(0,T) \ll \sigma(0,T)$ at temperatures down to 220 K, one can find that $A < 10^{-12}$ s/ $\Omega \cdot$ cm.

5. Conclusions

The measured electric properties of bulk amorphous $Zn_{41}Sb_{59}$ can be interpreted in the framework of a conventional model [3] often used for amorphous semiconductors. The characteristic features of $a-Zn_{41}Sb_{59}$ are:

(1) the Fermi level is pinned close to the middle of the mobility gap approximately 0.6 eV wide;

(2) conduction is dominated by thermally activated hopping of holes excited into the tail of the

valence band, the activation energy being of the order of 0.07 eV;

(3) the edge of this tail is 0.19 eV below the Fermi level;

(4) the above parameters refer to T = 0 and are only slightly affected by the relaxation processes occurring in a-Zn₄₁Sb₅₉ at temperatures up to the crystallization temperature.

Note in conclusion that, from its measured properties, $a-Zn_{41}Sb_{59}$ proved to be a classic amorphous semiconductor, so it can be used as a bulk model material with relatively high thermal stability for investigations into other interesting aspects of the nature of the amorphous state.

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