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Transport properties of the pressure-induced amorphous semiconductor state of $Al_{32}Ge_{68}$

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Abstract

The temperature dependences of the dc conductivity and thermopower of the bulk amorphous alloy $Al_{32}Ge_{68}$ were investigated at 6–420 K and at 80–370 K, respectively. The samples were prepared by solid-state amorphization of a quenched crystalline high-pressure phase while heating from 77 to 400 K at ambient pressure. Amorphous $Al_{32}Ge_{68}$ was found to be a p-type semiconductor with an unusual combination of transport properties. The behaviour of the properties was described semi-quantitatively in terms of a modified Mott–Davis model assuming that the Fermi level lies inside the valence band tail.

1. Introduction

Spontaneous amorphization of quenched high-pressure phases during their heating at ambient pressure allows production of bulk homogeneous amorphous samples. At the present time, the electric properties have been studied for only two amorphous (a-) semiconductors prepared in this way, a-$Zn_{41}Sb_{59}$ [1] and a-GaSb [2]. The a-$Zn_{41}Sb_{59}$ alloy was found to be a typical amorphous semiconductor with an activated behaviour of the electrical conductivity $\sigma(T)$ and a linear increase in the thermopower S with increasing $1/T$. By contrast, the a-GaSb alloy showed a combination of $\sigma(T)$ and $S(T)$ dependences never observed in a-semiconductors and inconsistent with the conventional Mott–Davis model [3].

The present paper reports on the conductivity and thermopower of the bulk amorphous semiconductor $Al_{32}Ge_{68}$ measured over wide temperature ranges. The samples were prepared by amorphization of a quenched crystalline high-pressure phase. The structure of the amorphous a-$Al_{32}Ge_{68}$ phase was studied by neutron diffraction [4], transmission electron microscopy and x-ray diffraction [5].

2. Experimental details

At ambient pressure, the Al–Ge system has a eutectic at 424 °C and about 30 at.% Ge [6]. The components form no intermediate equilibrium phases. At a pressure of 10 GPa, a new

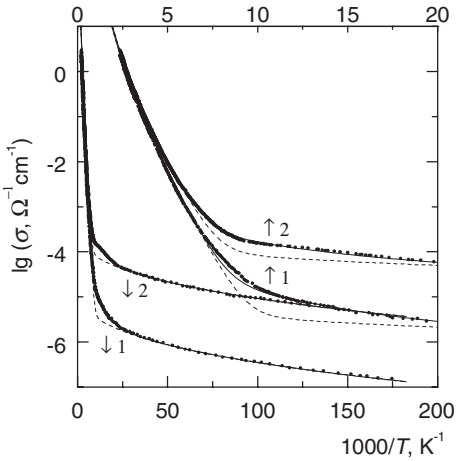

Figure 1. Temperature dependences of the dc conductivity σ for two samples of a-$Al_{32}Ge_{68}$ drawn with two different T-scales. The dashed curves represent the sums of $\sigma_1(T)$ from equation (1) and $\sigma_2(T)$ from equation (3) with the corresponding fitting coefficients. The solid curves show the sums of $\sigma_1(T) + \sigma_2(T) + \sigma_3(T)$, where $\sigma_3(T)$ is given by equation (5).

crystalline metallic γ-phase with a simple hexagonal structure is formed within a narrow concentration range around 68 at.% Ge [7]. Pellets of γ-phase were obtained in a metastable state at ambient pressure by cooling to liquid nitrogen temperature at high pressure. The recovered pellets were transformed to the amorphous state by heating to 130 °C [5].

The samples, $1 \times 1 \times 5\,\mathrm{mm}^3$ in size, were cut out of different a-pellets. The dc conductivity, σ, and the thermoelectric power, S, were measured at temperatures from 6 to 420 K and from 80 to 370 K, respectively.

3. Results and discussion

Representative temperature dependences of σ and S for two a-$Al_{32}Ge_{68}$ samples are shown in figures 1 and 2. As seen from figure 1, the $\sigma(T)$ curves are of an approximately activated character at $T > 150$ K and exhibit rather large activation energies E_{act} exceeding 0.1 eV. At lower temperatures, $E_{\mathrm{act}}(T)$ gradually decreases and at $T < 40$ K, the $\sigma(T)$ dependences obey well the formula $\sigma_1 = B_1 T^{-1/2} \exp[-(T_0/T)^{1/4}]$ typical of variable-range hopping conductivity [3]. The fitting parameters are $B_1 = 0.0029$ and 0.054 Ω^{-1} cm^{-1} K$^{1/2}$ and $T_0 = 38\,000$ and 32 000 K for samples 1 and 2, respectively. As seen from figure 2, the thermopower is positive, which points to the p-type conductivity of a-$Al_{32}Ge_{68}$, which is characteristic of most amorphous semiconductors.

However, the $S(T)$ dependences look rather unusual. At $300 > T > 150$ K, S decreases approximately linearly with increasing $1/T$, $Se/k \approx 5$–0.05 [eV]$/kT$, while at $T < 150$ K the dependence becomes much less steep and S remains positive and small, $Se/k \approx 0.4$ or less.

According to the conventional Mott–Davis model, the Fermi level E_{F} in amorphous semiconductors is pinned in the mobility gap at a relatively narrow peak of the density of states $N(E)$ for charge carriers, usually near the middle of the gap; see figure 3(a).

The low-temperature transport properties of amorphous semiconductors can be described in terms of variable-range hopping conductivity due to the states near the Fermi level. This

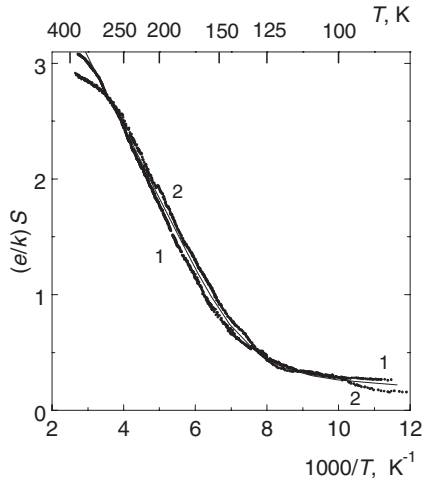

Figure 2. Temperature dependences of the thermopower S for the same two samples of a-$Al_{32}Ge_{68}$ as in figure 1. The solid curve represents $S(T)$ from equation (6).

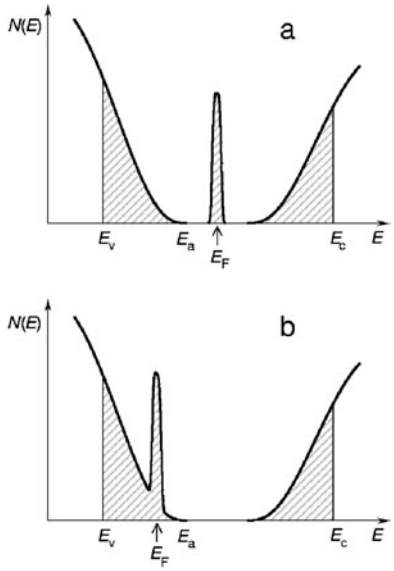

Figure 3. Schematic density of states diagrams for amorphous semiconductors: (a) the conventional Mott–Davis model, (b) the modified Mott–Davis model with a narrow band positioned inside the valence band tail. E_F is the Fermi energy; E_a is the valence band tail edge; E_v and E_c are the mobility edges for the valence and the conduction band.

mechanism gives a small value of thermoelectric power $|S_1 e/k| < 1$ and usually leads to Mott's equation for conductivity [3, 8]:

$$\sigma_1 = B_1 T^{-1/2} \exp[-(T_0/T)^{1/4}]. \tag{1}$$

The behaviour of the experimental $\sigma(T)$ is described well with equation (1) at $T < 40$ K and their Se/k values already fall below 1 at $T < 150$ K (figure 2). One can therefore conclude that the transport properties of a-$Al_{32}Ge_{68}$ at $T < 40$ K are mainly determined by the variable-range hopping mechanism.

In the framework of the Mott–Davis model, the transport properties of a-semiconductors at high temperatures are mostly due to hopping conductivity of carriers thermally excited into the band tails. The tails originate from the absence of long-range order in amorphous substances and are assumed not to overlap with the Fermi peak; see figure 3(a).

The basic parameter of the model is $\Delta E = E_F - E_a$, where E_a is the tail edge energy. In p-type semiconductors this is the valence band tail and therefore $\Delta E > 0$.

The density of states in the valence band tail can be approximated as $N(E) \propto (E_a - E)^n$ [3, 8] which leads to conductivity of an almost activated type:

$$\sigma \propto T^n \exp[-(\Delta E + W)/kT],$$

where W is the activation energy for hopping mobility in the band tail. In the same approximation [3, 8],

$$Se/k \approx \Delta E/kT + n + 1.$$

The thermopower is therefore non-degenerate, $Se/k > 1$, and should increase with increasing $1/T$.

As seen from figures 1 and 2, at $T > 160$ K a-$Al_{32}Ge_{68}$ demonstrates an approximately activated character of conductivity and also $Se/k > 1$. However, the S-value of a-$Al_{32}Ge_{68}$ decreases steeply with $1/T$ which is inconsistent with the predictions of the Mott–Davis model for conduction in band tails. At the same time, there must be the conduction in band tails as any mechanism of conduction in localized states near the Fermi energy gives $Se/k < 1$ and small values of $E_{act}(T) \ll 0.1$ eV [3, 8].

Anomalous behaviour of σ and S at high T similar to that found for a-$Al_{32}Ge_{68}$ was observed for a-GaSb semiconductor [2]. The effects were explained assuming $\Delta E < 0$ for the p-type amorphous materials. Negative ΔE suggests that the Fermi level is positioned inside the tail of the valence band, as schematically shown in figure 3(b). The transport properties of p-type a-semiconductors are governed [8] by the holes located near the maximum of the $N(E)f(E)[1-f(E)]$ function, where $f(E)$ is the Fermi–Dirac function. At high temperatures $f(E)[1 - f(E)] \approx \exp[(E - E_F)/kT]$, and with the density of states $N(E) \propto (E_a - E)^n$ in the valence band tail [3, 8] the final product $(E_a - E)^n \exp[(E - E_F)/kT]$ has a maximum at

$$E_m = E_a - nkT, \tag{2}$$

inside the band tail. The conventional model with $E_F > E_a$ (figure 3(a)) imposes no additional limitations on the temperature region where equation (2) is valid. With $E_F < E_a$ (figure 3(b)), this equation is true only in the non-degenerate case when $(E_F - E_m)/kT > 1$, that is, at sufficiently high temperatures $T > (E_a - E_F)/(n - 1)k$.

According to [3, 8], $\sigma \approx e\mu kTN(E_m)\exp[(E_m - E_F)/kT]$ and $Se/k \approx (E_F - E_m)/kT$, where the mobility μ has a thermally activated character, $\mu \propto T^{-1}\exp(-W/kT)$. Substituting E_m from equation (2), one gets $Se/k \approx (E_F - E_a)/kT + n$ and $\sigma \propto T^n \exp[-(\Delta E + W)/kT]$. More rigorous evaluation [8] gives $Se/k = \Delta E/kT + n + 1$.

At high T (typically, at $T > 100$ K), ΔE as well as the mobility gap E_g usually vary approximately linearly with temperature: $\Delta E(T)/\Delta E_0 \approx E_g(T)/E_{0g} \approx 1 - \gamma T$, where ΔE_0 and E_{0g} refer to $T = 0$ K [8]. Correspondingly, $\sigma(T)$ and $S(T)$ can be written as

$$\sigma_2 \approx AT^n \exp[-(\Delta E_0 + W)/kT], \tag{3}$$

$$S_2 e/k \approx \Delta E_0/kT + n + 1 - \gamma\,\Delta E_0/k. \tag{4}$$

The expressions obtained are formally identical to those of the standard Mott–Davis model, but they nevertheless differ significantly in two aspects: (i) ΔE is negative and (ii) the expressions are valid only at high $T > |\Delta E|/(n - 1)k$.

Equations (3) and (4) allow an estimation of the values of ΔE_0 and n for a-$Al_{32}Ge_{68}$. A linear approximation of the $S(1/T)$ dependences at $T > 130$ K (figure 2) yields $C \approx 5.0$ and $\Delta E_0 \approx -0.05$ eV. Taking a value of $\gamma = 10^{-4}$ K^{-1} typical of a-semiconductors [8], one gets $\gamma \Delta E_0/k < 0.1$ and, correspondingly, $n \approx C - 1 \approx 4$.

At $T > 190$ K, the $\sigma(T)$ dependences for samples 1 and 2 are well described by equation (3) with $n = 4$, $A = 1.03 \times 10^{-9}$ and 0.93×10^{-9} Ω^{-1} cm^{-1} K^{-4} and with $\Delta E_0 + W = 0.097$ and 0.087 eV. With $\Delta E_0 = -0.05$ eV this gives $W \approx 0.14$–0.15 eV for the activation energy of mobility in the band tail of a-$Al_{32}Ge_{68}$.

With the values of ΔE_0 and n thus determined, the condition $T > (E_a - E_F)/(n-1)k$ of applicability of non-degenerate Boltzmann statistics used to obtain equation (2) for E_m is valid at $T > 200$ K. All calculations above are therefore self-consistent in this temperature range.

It is worth mentioning that the transport properties of a-semiconductors at high T will also be affected by conduction due to holes excited into the extended states below the mobility edge E_v. One could suspect that the deviation of the $S(T^{-1})$ dependences for a-$Al_{32}Ge_{68}$ from the straight line observed at $T > 300$ K (figure 2) might be due to the growing contribution from this very conduction mechanism.

The dashed curves in figure 1 show the sum of $\sigma_1(T)$ and $\sigma_2(T)$ given by equations (1) and (3), respectively. These curves fit the experimental points at $T > 150$ K and $T < 40$ K. However, at $40 < T < 150$ K the calculated curves differ significantly from the experimental ones. The difference might be due to the contribution from the third conduction mechanism: constant-range hopping conduction in localized states near the Fermi energy.

In fact, the variable-range hopping regime dominating at low T should change to the constant-range regime with increasing T because the hopping distance will reach its minimum possible value when the carriers jump between the nearest-neighbour sites [3]. Constant-range hopping results for $S < k/e$ and σ given by

$$\sigma_3 \approx B_3 \exp(-w_3/kT), \tag{5}$$

where w_3 is the energy of the order of the half-width of the peak at the Fermi energy [3].

In the case of a-$Al_{32}Ge_{68}$ this contribution seems to be significant over a large temperature interval, which allows a rather reliable evaluation of the fitting parameters $B_3 = 1.1 \times 10^{-4}$ and 8×10^{-4} Ω^{-1} cm^{-1} for samples 1 and 2, respectively, and $w_3 \approx 0.02$ eV for both samples.

For the total value of the thermopower we therefore have

$$S = (S_1\sigma_1 + S_2\sigma_2 + S_3\sigma_3)/\sigma \tag{6}$$

where $S_1 e/k \approx S_3 e/k \approx 0.2$ and $S_2 e/k = \Delta E_0/kT + n + 1$.

4. Conclusions

Our results demonstrate that amorphous $Al_{32}Ge_{68}$ is a p-type semiconductor showing three different conductivity mechanisms in different temperature ranges. At $T < 40$ K, the dominating mechanism is variable-range hopping conduction in localized states near the Fermi energy. At $40 < T < 150$ K, constant-range hopping conduction in localized states near the Fermi energy significantly contributes to the transport properties. At $T > 150$ K, these properties are mainly governed by conduction in the valence band tail. In contrast to all other amorphous semiconductors except a-GaSb [2], amorphous $Al_{32}Ge_{68}$ shows a combination of the $\sigma(T)$ and $S(T)$ dependences that cannot be explained in the framework of the conventional Mott–Davis model and requires the assumption that the Fermi energy is less than the edge energy of the valence band tail (see figure 3(b)). The Mott–Davis model changed in this way

yields a self-consistent description of the transport properties of a-$Al_{32}Ge_{68}$ over the entire temperature interval studied.

Acknowledgments

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