ELSEVIER

Journal of Non-Crystalline Solids 289 (2001) 30–36

JOURNAL OF NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrysol

Transport properties of bulk amorphous semiconductor $Al_{32}Ge_{68}$

A.I. Kolyubakin *, V.E. Antonov, O.I. Barkalov, A.F. Gurov, A.I. Harkunov

Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow, Russia

Received 17 May 2000; received in revised form 30 May 2001

Abstract

Temperature dependences of the dc conductivity and thermopower of 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 amorphisation of a quenched crystalline high-pressure phase while heating from 77 to 400 K at ambient pressure. Amorphous $Al_{32}Ge_{62}$ was found to be p-type semiconductor with an unusual combination of transport properties. The change of properties was described semi-quantitatively in terms of a modified Mott–Davis model assuming that the Fermi level lies inside the valence band tail.

PACS: 71.23.Cq; 72.80.Ng

1. Introduction

Among the methods of solid-state amorphisation, spontaneous amorphisation of quenched high-pressure phases during their heating at ambient pressure is one of the most advantageous for producing bulk homogeneous samples [1–3]. Today, the transport properties have been studied only for two amorphous (a-) semiconductors prepared in this way, a-$Zn_{41}Sb_{59}$ [4] and a-GaSb [5]. 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 reciprocal temperature. By contrast, the a-GaSb alloy showed a combination of the $\sigma(T)$ and $S(T)$ dependences never observed in amorphous semiconductors. An explanation of the transport properties of a-GaSb [5] required a modification of the conventional Mott–Davis model [6] by allowing the Fermi level to be positioned inside the band tail.

The present paper is aimed at studying the $\sigma(T)$ and $S(T)$ dependences of bulk a-$Al_{32}Ge_{68}$ samples produced by spontaneous amorphisation of the crystalline high-pressure γ-$Al_{32}Ge_{68}$ phase. The structure of the amorphous a-$Al_{32}Ge_{68}$ phase was studied earlier by neutron diffraction [7] and transmission electron microscopy [8]. The transport properties of amorphous Al–Ge alloys are presented here.

2. Experimental procedure

At ambient pressure, the Al–Ge system has a eutectic at 424°C and about 30 at.% Ge [9]. Both components show limited solid solubility in each

* Corresponding author. Fax: +7-096 676 4111.
E-mail address: kolyubak@issp.ac.ru (A.I. Kolyubakin).

0022-3093/01/$ - see front matter
PII: S0022-3093(01)00645-7

other and form no intermediate equilibrium phases. At a pressure of 10 GPa, a new crystalline metallic γ-phase is formed within a narrow concentration range around 68 at.% Ge [3]. The γ-$Al_{32}G_{68}$ phase can be obtained in a metastable state at ambient pressure if cooled previously to liquid nitrogen temperature at high pressure. The recovered γ-$Al_{32}G_{68}$ phase has a simple hexagonal structure and it transforms to the amorphous state on heating to 130°C [8].

To prepare amorphous a-$Al_{32}Ge_{68}$ in the present work, a 20 g ingot was first melted out of the appropriate amounts of 99.999 wt% pure Al and Ge in a levitation inductance furnace in vacuum. The central part of the ingot was then powdered in an agate mortar to obtain a more homogeneous mixture of the Al(Ge) and Ge(Al) primary solid solutions and the powder was pressed into 5 pellets, 7 mm in diameter and 2 mm thick. Each pellet was put in a Teflon container, exposed to 10 GPa and 325°C for 24 h in a toroid-type high-pressure chamber and cooled to 100 K together with the chamber before the pressure was released. The X-ray examination at 100 K and ambient pressure (DRON-2.0 diffractometer, Cu Kα radiation) showed the complete transformation of the pellets to the high-pressure γ-phase. The pellets were then brought to the amorphous state by heating at 20 K min^{-1} to 130°C. The X-ray examination of the resulting amorphous pellets at room temperature revealed no traces of crystalline phases.

Five samples in the form of bars $1 \times 1 \times 5$ mm^3 were cut out of different amorphous pellets with an abrasive wire saw. Copper electrodes were stuck to the samples with silver paste. 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

Representative temperature dependences of σ and S for two a-$Al_{32}Ge_{68}$ samples are shown in Figs. 1 and 2. As seen from Fig. 1, the $\sigma(T)$ curves are of an approximately activated character at $T > 150$ K and exhibit rather large activation

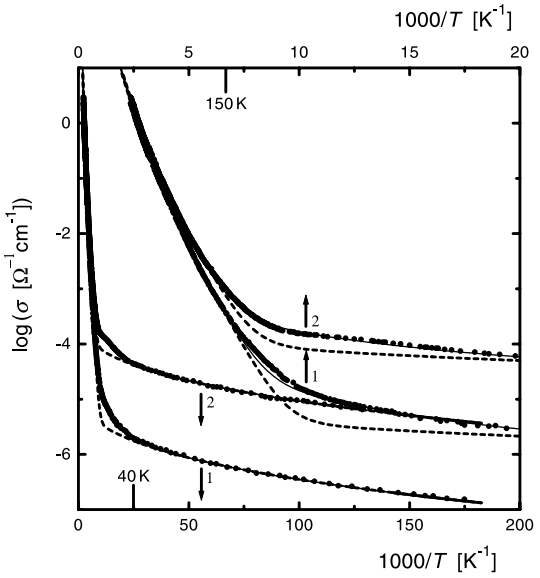

Fig. 1. Temperature dependences of the dc conductivity σ for two samples of amorphous $Al_{32}Ge_{68}$ drawn with two different temperature scales. The dashed curves represent the sums of $\sigma_1(T)$ from Eq. (1) and $\sigma_2(T)$ from Eq. (4) with the corresponding fitting coefficients. The solid curves show the sums of $\sigma_1(T) + \sigma_2(T) + \sigma_3(T)$, where $\sigma_3(T)$ is given by Eq. (7).

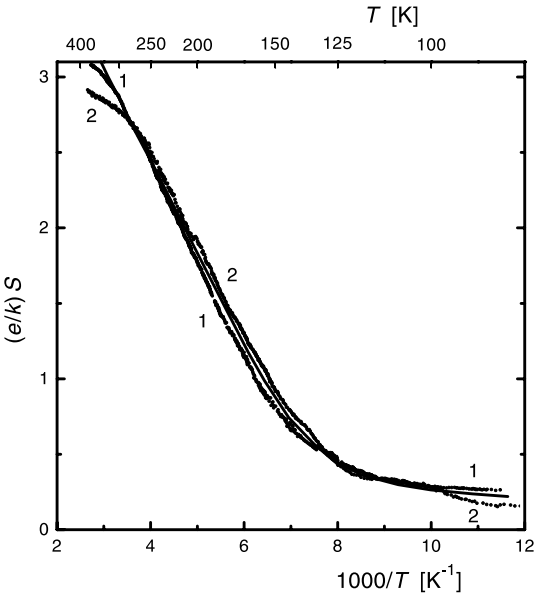

Fig. 2. Temperature dependences of the thermopower S for the same two samples of amorphous $Al_{32}Ge_{68}$ as in Fig. 1. e is the elementary charge, k is the Boltzmann constant. The solid curve represents $S(T)$ from Eq. (8) including the contributions from all the three mechanisms of conduction involved.

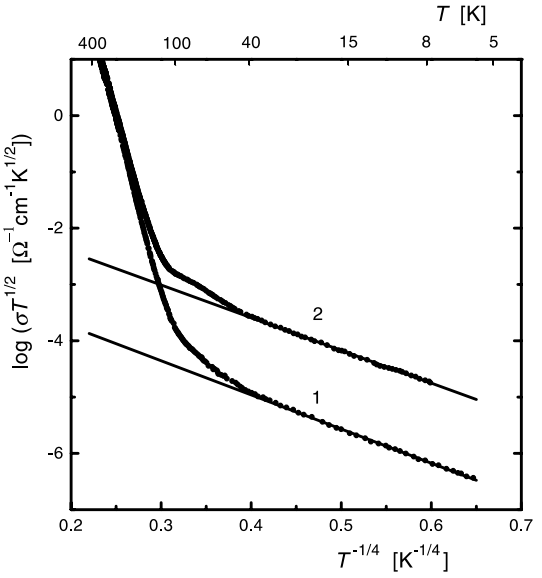

Fig. 3. Mott's plot for the data in Fig. 1.

energies $E_{act}(T) = -d(\ln \sigma)/d(1/kT)$ exceeding 0.1 eV. At lower temperatures, $E_{act}(T)$ gradually decreases and at $T < 40$ K, as one can see from Fig. 3, the $\sigma(T)$ dependences well obey the formula $\sigma_1 = B_1 T^{-1/2} \exp[-(T_0/T)^{1/4}]$ typical of variable-range hopping conductivity [6]. 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 sample 1 and 2, respectively.

As seen from Fig. 2, the thermopower of a-$Al_{32}Ge_{68}$ is positive that points to the p-type of its conductivity, which is characteristic of most amorphous semiconductors. However, the $S(T)$ dependences of the a-$Al_{32}Ge_{68}$ samples look rather unusual. At 300 K $> T >$ 150 K, the thermopower decreases approximately linearly with increasing reciprocal temperature, $Se/k \approx 5 - 0.05$ [eV]$/kT$, while at $T < 150$ K the dependence becomes much less steep and the thermopower remains positive and small, $Se/k \approx 0.4$ or less.

4. Discussion

4.1. Low temperatures

According to the conventional Mott–Davis model [6], the Fermi level E_F in amorphous semiconductors is pinned in the mobility gap at a relatively narrow peak in the density of states $N(E)$ for charge carriers. The peak is positioned near the middle of the gap, see Fig. 4(a), and originates from defects in the random network, such as dangling bonds, vacancies, etc.

In the framework of this model, 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. The carriers can move between such states via a phonon-assisted tunnelling process and they tend to hop to larger distances with decreasing T in order to find sites which are energetically closer than the nearest neighbours. This mechanism gives a small value of thermo-

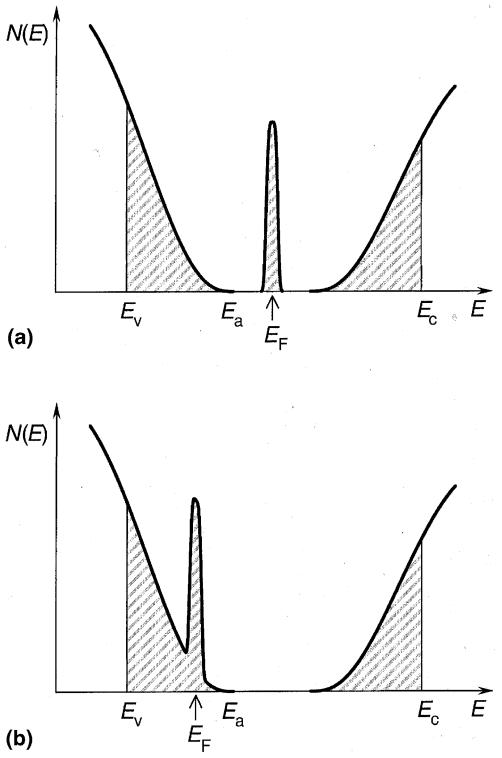

Fig. 4. Schematic density of states diagrams for amorphous semiconductors. (a) The conventional Mott–Davis model showing a narrow band near the middle of the gap. (b) The modified Mott–Davis model with a narrow band positioned inside the valence band tail. E_F is the Fermi energy; E_a is the valence band tail edge; E_v and E_c are the mobility edges for the valence and the conduction band, respectively.

electric power $|S_1 e/k| < 1$ and usually leads to Mott's equation for conductivity [6,10]:

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

The behaviour of the experimental $\sigma(T)$ dependences of the a-$Al_{32}Ge_{68}$ samples is described well with Eq. (1) at $T < 40$ K (see Fig. 3) and their Se/k values fall below 1 already at $T < 150$ K (Fig. 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 principle, Mott's treatment of variable-range hopping also predicts [6,10] that $T_0 \approx 16\alpha^3/kN(E_F)$ and $B_1 \approx 0.1e^2 v_{ph}[N(E_F)/\alpha k]^{1/2}$, where $N(E_F)$ is the density of states at the Fermi energy E_F, α is the parameter characterising the decay of the wave function of a charge carrier with $E = E_F$ and v_{ph} is the frequency of the order of the maximum phonon frequency. However, these expressions do not describe the conductivity in a quantitative way and, in particular, often give unreasonable values for $N(E_F)$ [6]. In the case of a-$Al_{32}Ge_{68}$ these expressions do not seem to work either and yield inconsistent results: substituting experimental values of T_0 and B_1 for samples 1 and 2 from Section 2, and the values of $v_{ph} = 10^{12}$ s^{-1} and $\alpha^{-1} = 1$ nm typical of amorphous semiconductors [6], one gets $N(E_F) \approx 10^{22}$ cm^{-3} eV^{-1} from the equation for T_0 and $N(E_F) \approx 10^{13}$–10^{16} cm^{-3} eV^{-1} from the equation for B_1.

4.2. High temperatures

In the framework of the Mott–Davis model, the transport properties of amorphous semiconductors at high temperatures are mainly determined by hopping conductivity of carriers thermally excited into the band tails. The tails originate from the absence of the long-range order in amorphous substances and are assumed not to overlap with the Fermi-peak, see Fig. 4(a). The basic parameter of the model is

$$\Delta E = E_F - E_a,$$

where E_a is the tail edge energy. In the p-type semiconductors like a-$Al_{32}Ge_{68}$, this is the valence band tail and therefore $\Delta E > 0$. The density of states in the valence band tail can be approximated as $N(E) \propto (E_a - E)^n$ [6,10] that leads to conductivity of the 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 [6,10]

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

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

As seen from Figs. 1 and 2, at $T > 150$ K amorphous $Al_{32}Ge_{68}$ demonstrates an activated character of conductivity with a rather large activation energy $E_{act}(T) > 0.1$ eV this also happens for $Se/k > 1$. However, the thermopower of a-$Al_{32}Ge_{68}$ steeply decreases with reciprocal temperature that 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 [6,10].

The anomalous behaviour of σ and S at high temperatures similar to that found for a-$Al_{32}Ge_{68}$ was earlier observed for amorphous GaSb semiconductor [5]. The effects were explained assuming that $\Delta E < 0$ is possible for the p-type amorphous materials. The negative value of ΔE suggests that the Fermi level pinned to the peak of the density of states is positioned inside the tail of the valence band, as schematically shown in Fig. 4(a). New features in the behaviour of the $\sigma(T)$ and $S(T)$ dependences resulting from the Mott–Davis model modified in this way were briefly discussed in [6] and will be described in more detail further.

According to [10], the transport properties of the p-type amorphous semiconductors are governed by the holes located near the maximum of the $N(E)f(E)[1 - f(E)]$ product, where $f(E) = (1 + \exp[(E_F - E)/kT])^{-1}$ is the Fermi–Dirac distribution 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 [6,10] the resulting 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 $E_F > E_a$ (Fig. 4(a)) imposes no additional limitations on the temperature region where Eq. (2) is valid. With $E_F < E_a$ (Fig. 4(b)), this equation is true only in the non-degenerate case when $(E_F - E_m)/kT > 1$, that is, at sufficiently high temperatures

$$T > (E_a - E_F)/(n-1)k = -\Delta E/(n-1)k. \tag{3}$$

According to [6,10], $Se/k \approx (E_F - E_m)/kT$ and $\sigma \approx e\mu kTN(E_m)\exp[(E_m - E_F)/kT]$, where the mobility μ has a thermally activated nature, $\mu \propto T^{-1}\exp(-W/kT)$. Substituting E_m from Eq. (2) one gets $Se/k \approx (E_F - E_a)/kT + n$ and $\sigma \propto T^n \exp[(E_a - E_F - W)/kT] = T^n \exp[-(\Delta E + W)/kT]$. More rigorous evaluation [10] gives $Se/k = \Delta E/kT + n + 1$.

At high temperatures (typically, at $T > 100$ K), the value of ΔE as well as the mobility gap E_g vary approximately linearly with temperature in most amorphous semiconductors: $\Delta E(T)/\Delta E_0 \approx E_g(T)/E_{0g} \approx 1 - \gamma T$, where ΔE_0 and E_{0g} refer to $T = 0$ K [10]. Correspondingly, the expressions for the temperature dependences of conductivity and thermopower can be written as

$$\sigma_2 \propto T^n \exp[-(\Delta E + W)/kT] \propto AT^n \exp[-(\Delta E_0 + W)/kT], \tag{4}$$

$$S_2 e/k \approx \Delta E/kT + n + 1 \approx \Delta E_0/kT + C, \tag{5}$$

where

$$C = n + 1 - \gamma \Delta E_0/k. \tag{6}$$

The obtained expressions (4)–(6) 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 $T > |\Delta E|/(n-1)k$.

Eqs. (5) and (6) allow an estimation of the ΔE_0 and n values for a-$Al_{32}Ge_{68}$. A linear approximation at $T > 130$ K of the $S(1/T)$ dependences presented in Fig. 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 amorphous semiconductors [10], one gets $\gamma \Delta E_0/k < 0.1$ and, correspondingly, $n \approx C - 1 \approx 4$.

As seen from Fig. 5, at $T > 190$ K the experimental $\sigma(T)$ dependences for a-$Al_{32}Ge_{68}$ are well described by Eq. (4) with $n = 4$ resulting from the analysis of the $S(T)$ dependences. The fitting parameters are $A = 1.03 \times 10^{-9}$ and 0.93×10^{-9} Ω^{-1} cm^{-1} K^{-4} and $\Delta E_0 + W = 0.097$ and 0.087 eV for sample 1 and 2, respectively. With $\Delta E_0 = -0.05$ eV derived from the thermopower measurement, this gives a value of $W \approx 0.14$–0.15 eV for the activation energy of hopping mobility in the band tail of a-$Al_{32}Ge_{68}$.

With the values of ΔE_0 and n thus determined, the condition (3) of applicability of non-degenerate Boltzmann statistics used to obtain Eq. (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, however, that the transport properties of amorphous semiconductors at high temperatures will also be affected by conduction due to holes excited into the extended states below the mobility edge E_v. One could ex-

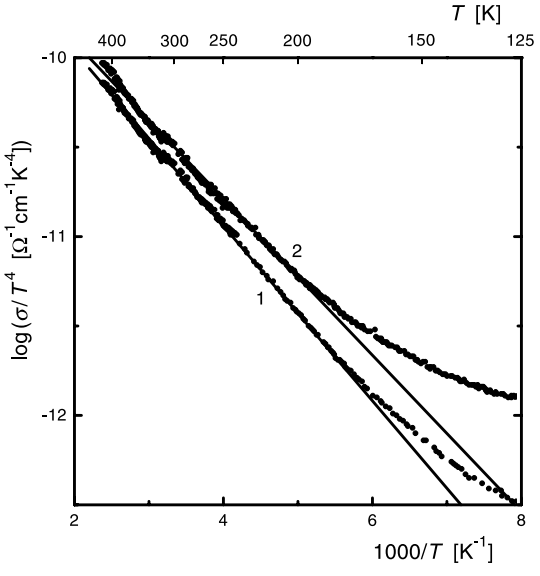

Fig. 5. The plot illustrating the applicability of Eq. (4) with $n = 4$ to the data from Fig. 1.

pect in this connection that the deviation of the $S(T^{-1})$ dependences for a-$Al_{32}Ge_{68}$ from the straight line observed at $T > 300$ K (Fig. 2) might be due to the growing contribution from this very conduction mechanism.

4.3. Intermediate temperatures

The dashed curves in Fig. 1 show the sum of $\sigma_1(T)$ and $\sigma_2(T)$ given by Eqs. (1) and (4), respectively. One can see that these curves fit the experimental points at $T > 150$ K and $T < 40$ K. However, within a rather large temperature interval from 40 to 150 K the calculated curves differ significantly from the experimental ones. The difference might be due to the contribution from another, 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 temperatures should change to the constant-range regime with increasing temperature because the hopping distance will reach its minimum possible value when the carriers jump between the nearest neighbour sites [6]. The conductivity resulting from constant-range hopping is usually written as

$$\sigma_3 \approx B_3 \exp(-w_3/kT), \tag{7}$$

where w_3 is the energy of the order of the half-width of the peak at the Fermi energy [6]. The value of S remains less than k/e.

The contribution to conductivity from this mechanism can rarely be observed because other types of conduction usually prevail. However, in the case of a-$Al_{32}Ge_{68}$ this contribution seems to be significant within a large temperature interval that 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 sample 1 and 2, respectively, and $w_3 \approx 0.02$ eV for both samples.

5. Conclusions

Amorphous $Al_{32}Ge_{68}$ is the p-type semiconductor. Its $\sigma(T)$ and $S(T)$ dependences calculated as the sum of the contributions from the three different conduction mechanisms considered above are plotted in Figs. 1 and 2 with the solid lines:

$$\begin{aligned}\sigma(T) &= \sigma_1 + \sigma_3 + \sigma_2 \\ &= B_1 T^{-1/2} \exp[-(T_0/T)^{1/4}] \\ &\quad + B_3 \exp(-w_1/kT) \\ &\quad + AT^4 \exp[-(\Delta E_0 + W)/kT], \\ S(T) &= (S_1\sigma_1 + S_3\sigma_3 + S_2\sigma_2)/\sigma, \end{aligned} \tag{8}$$

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

At $T < 40$ K, variable-range hopping conduction in localized states near the Fermi energy dominates and gives $\sigma_1 \approx B_1 T^{-1/2} \exp[-(T_0/T)^{1/4}]$ and $S_1 e/k \ll 1$. The parameter B_1 varies from 0.003 to 0.06 Ω^{-1} cm^{-1} K$^{1/2}$ for different a-$Al_{32}Ge_{68}$ samples, while $T_0 \approx 35\,000$ K for all the samples.

In the intermediate temperature range from 40 to 150 K, constant-range hopping conduction in localized states near the Fermi energy significantly contributes to the transport properties of a-$Al_{32}Ge_{68}$. This mechanism yields the conductivity $\sigma_3 \approx B_3 \exp(-w_3/kT)$ with a small activation energy of $w_3 \approx 0.02$ eV and the thermopower $S_3 e/k \ll 1$.

At $T > 150$ K, the transport properties of a-$Al_{32}Ge_{68}$ are mainly governed by conduction in the valence band tail. In contrast to all other amorphous semiconductors except a-GaSb [5], amorphous $Al_{32}Ge_{68}$ shows the 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. The Mott–Davis model changed in this way yields a self-consistent description of the transport properties of a-$Al_{32}Ge_{68}$. The high-temperature conductivity is given as $\sigma_2 = AT^n \exp[-(\Delta E_0 + W)/kT]$ and the thermopower as $S_2 e/k = \Delta E_0/kT + n + 1$, where $A \approx 10^{-9}$ Ω^{-1} cm^{-1} K^{-4} and $n \approx 4$. The value of $\Delta E_0 \approx -0.05$ eV is the difference between the Fermi energy and the tail edge energy at $T = 0$ K and $W \approx 0.15$ eV is the activation energy of hopping mobility in the valence band tail.

Acknowledgements

This work was supported by the Grants no. 99-02-17007 and 96-15-96806 from the Russian Foundation for Basic Research and by the Grant no. 34-1997 for young scientists from the Russian Academy of Sciences. The authors are grateful to Professor E.G. Ponyatovsky for helpful discussions.

References

[1] I.T. Belash, E.G. Ponyatovsky, High Temp. High Press. 9 (1977) 651.
[2] E.G. Ponyatovsky, I.T. Belash, O.I. Barkalov, J. Non-Cryst. Solids 117&118 (1990) 679.
[3] E.G. Ponyatovsky, O.I. Barkalov, Mater. Sci. Rep. 8 (1992) 147.
[4] V.E. Antonov, O.I. Barkalov, A.I. Kolyubakin, J. Non-Cryst. Solids 176 (1994) 58.
[5] V.E. Antonov, O.I. Barkalov, A.I. Kolyubakin, E.G. Ponyatovsky, Phys. Status Solidi (b) 198 (1996) 497.
[6] N.F. Mott, E.A. Davis, Electron Process in Non-Crystalline Materials, Clarendon, Oxford, 1979.
[7] A.I. Kolesnikov, U. Dahlborg, M. Calvo-Dahlborg, O.I. Barkalov, E.G. Ponyatovsky, W.S. Howells, A.I. Harkunov, Phys. Rev. B 60 (1999) 12681.
[8] O.I. Barkalov, A.S. Aronin, G.E. Abrosimova, E.G. Ponyatovsky, J. Non-Cryst. Solids 202 (1996) 266.
[9] M. Hansen, Constitution of Binary Alloys, McGraw-Hill, New York, 1958.
[10] P. Nagels, in: M.H. Brodsky (Ed.), Amorphous Semiconductors, Topics in Applied Physics, vol. 37, Springer, New York, 1985.