Phase transition in $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ solid solutions and related transport phenomena

2001 J. Phys.: Condens. Matter 13 43

(http://iopscience.iop.org/0953-8984/13/1/305)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 43–49 www.iop.org/Journals/cm PII: S0953-8984(01)17185-7

Phase transition in $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ solid solutions and related transport phenomena

I A Avramova and S K Plachkova

Faculty of Physics, University of Sofia, 5 James Bourchier Blvd, BG-1164 Sofia, Republic of Bulgaria

Received 15 September 2000

Abstract

The experimentally observed anomalies in temperature dependences of the Hall coefficients and the electrical resistivities for hot-pressed samples of $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ with $0.095 < x < 0.333$, due to the ferroelectric lattice instabilities in the phase transition region, are discussed.

The Landau–Lifschitz type criterion for these phenomena shows that the phase transition is of second order. According to the soft-mode conception the main part of the anomalous increase in the resistivity is due to the soft-TO phonon scattering and the curvature caused by the soft-TO phonon near zero wavevector is accelerated with increasing $AgBiTe_2$ content.

1. Introduction

The IV–VI compound GeTe and the solid solutions (SSs) based upon it form the narrow gap semiconductors of p-type conductivity which is due to the presence of vacancies in the cation sublattice. They are the most essential thermoelectric materials operating at temperatures about 700 K. One of them, the so called 'TAGS-85' (i.e. 85% GeTe + 15% $AgSbTe_2$), is successfully applied for direct conversion of heat energy into electricity by radio isotopic thermoelectric generators for space [1, 2]. The replacing of Sb (atomic weight 121.17) with heavier Bi (atomic weight 208.08) will lead to a decrease of thermal conductivity and to an increase of thermoelectric figure of merit. This determines the practical interest of GeTe-rich $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ SSs.

Germanium telluride possesses three polymorphic forms. The high temperature paraelectric form is cubic (β-GeTe), space group of symmetry O_h^5. Below the phase transition (PT) temperature T_c, which varies from 700 K to 650 K depending on composition, the crystal lattice of the ferroelectric GeTe is rhombohedral (α-GeTe, C_{3v}^5) at Te content smaller than 50.4 at.% Te—the ferroelectric phase. It is orthorhombic (γ-GeTe, D_{2h}^{16}) at more than 50.4 at.% Te—the antiferroelectric phase [3]. Theoretically it was shown that the cubic $\leftrightarrow$ rhombohedral PT in GeTe must be of the second order [4].

In the system $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ above 773 K a continuous series of SSs exists [5]. Similarly to the Ge-rich GeTe these SSs undergo a cubic $\leftrightarrow$ rhombohedral PT [6]. The $\beta \leftrightarrow \alpha$ PT is accompanied by a relative shift $\langle u \rangle$ of the cation (Ge, Ag, Bi) and anion (Te) sublattices

0953-8984/01/010043+07$30.00

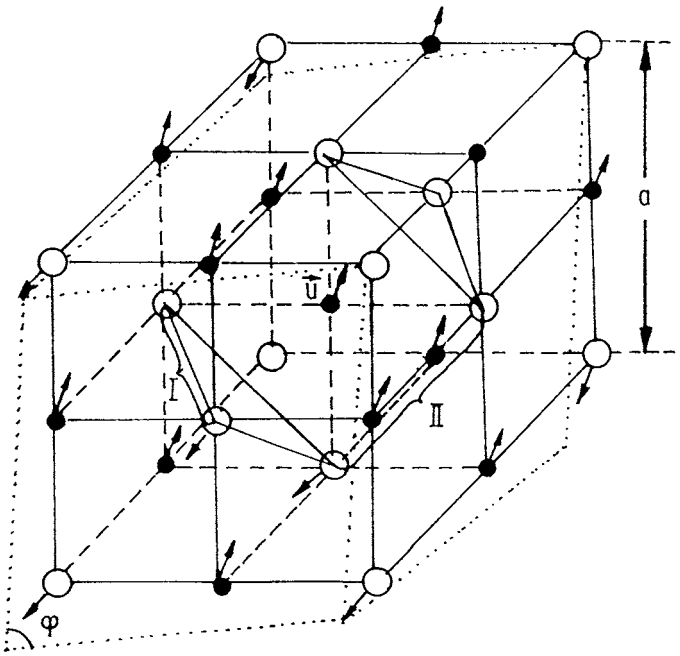

Figure 1. High-temperature rocksalt structure (full and broken lines) and its rhombohedral distortion (dotted lines) at the reversible cubic–rhombohedral phase transition of GeTe and GeTe-rich $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ SSs. Full circles—Ge, Ag or Bi cations; open circles—Te anions. Arrows indicate the directions of the movements of the atoms at the phase transition. I and II show the distances between the Te atoms (d_{Te-Te}) in the layer (intralayer Te–Te distances) and between the layer (interlayer Te–Te distances) respectively in the layered rhombohedral structure. The rhombohedral distortion is characterized by the change in the interaxial angle φ, the lattice constant a and the order parameter $\langle u\rangle^2$.

along one of the eight cubic $\langle 111\rangle$ directions. It becomes a rhombohedral 'c' axis and the crystal becomes uniaxial ferroelectric. The unit cell is stretched in the perpendicular direction (see figure 1). The rhombohedral distortion is characterized by the changes in the interaxial angle $\varphi(\Delta\varphi = \pi/2 - \varphi)$, the lattice constant a and the order parameter $\langle u\rangle^2$. The temperature dependence of the homogeneous rhombohedral shear strain $\varepsilon_s = \frac{1}{2}\Delta\varphi$ is given by [3]

$$2\varepsilon_s = \Delta\varphi \sim \Delta \sim \left(\frac{T_c - T}{T_c}\right)^{\beta} \tag{1}$$

where β is the critical index of the secondary order parameter and $\Delta = \langle u\rangle^2$ is the primary order parameter.

In the case of GeTe and GeTe-rich $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ SSs the rhombohedral shear strain at the $\beta \leftrightarrow \alpha$ PT rises continuously and the value of $\beta \sim 0.5$ characterizes the second order phase transition [7]. It is well known that in the PT region the transport coefficients of IV–VI compounds such as the electrical resistivity ρ and the Hall coefficient R as a result of critical scattering of the carriers show anomalies, due to the order parameter fluctuations [3, 8, 9].

The scope of the present study is the experimentally observed anomalies in temperature dependences of ρ and R in the PT region for hot-pressed samples of $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ with $x = 0.095$, 0.181, 0.260 and 0.333, due to the ferroelectric lattice instabilities.

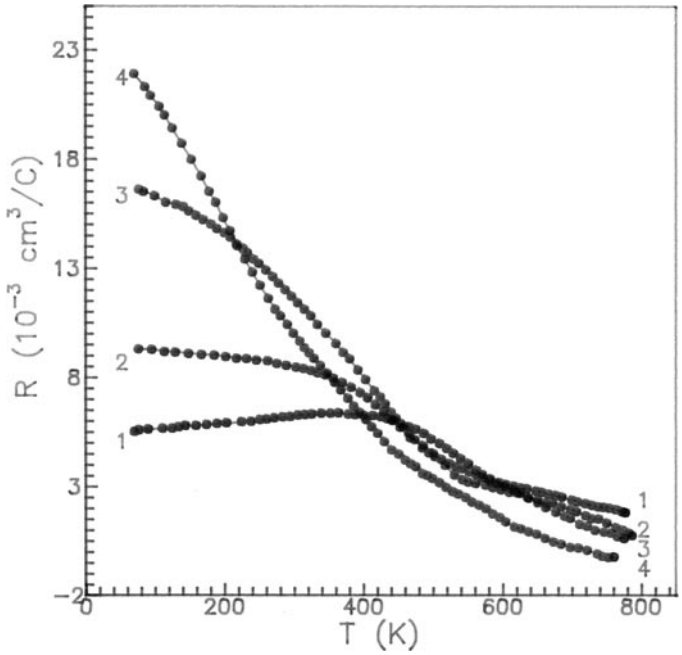

Figure 2. The Hall coefficient R versus temperature of $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ SSs: 1—$x = 0.095$; 2—$x = 0.181$; 3—$x = 0.260$; 4—$x = 0.333$.

2. Sample preparation and measurements

The different compositions were synthesizes by melting the respective stoichiometric quantities from elements (Ag, Bi Te) with 99.999% purity and 50 Ω cm Ge in quartz ampoules sealed under high vacuum (1.3×10^{-4} Pa). The ampoules were cleaned and outgassed beforehand. The spetial technique was used to minimize the free volume over the melt to ensure the constant composition of every alloy during the synthesis. The temperature of the furnace was elevated to ∼1200 K to 5 h and was kept constant for about 48 h. With synthesis the ampoules were mechanically shaken to ensure a good homogenization of the melt. At the end of synthesis the ampoules were annealed for about 1000 h in order to reach the equilibrium state. Then the alloys were quenched in ice water.

According to practical requirements, especially for thermoelectric applications, materials with various shapes and sizes are needed. This calls for a new preparation technology, so called hot-pressing. That technology consists of the following. The materials which were synthesized in ampoules were powdered to grain sizes lower than 0.16 mm; after that they were pressed at the temperature 300 K and under 5000 kg cm^{-2} pressure for 3 min. The process was repeated for the same pressure and time at the temperature 673 K. Then the materials were annealed in argon atmosphere for about 100 h at 773 K. The parallelepipedic samples were prepared with dimensions in proportion 1:3:9.

The temperature dependences of the Hall coefficients R for hot-pressed samples of $Ge_{1-x}Ag_{x/2}Bi_{x/2}Te$ with $x = 0.095$, 0.181, 0.260 and 0.333 measured by the alternating current and variable magnetic field method [10] are presented in figure 2. The accuracy was about 5%. As seen for samples with $x = 0.095$ and 0.181 (curves 1 and 2 respectively) from 80 K up to a definite temperature the Hall coefficient is approximately constant and over this

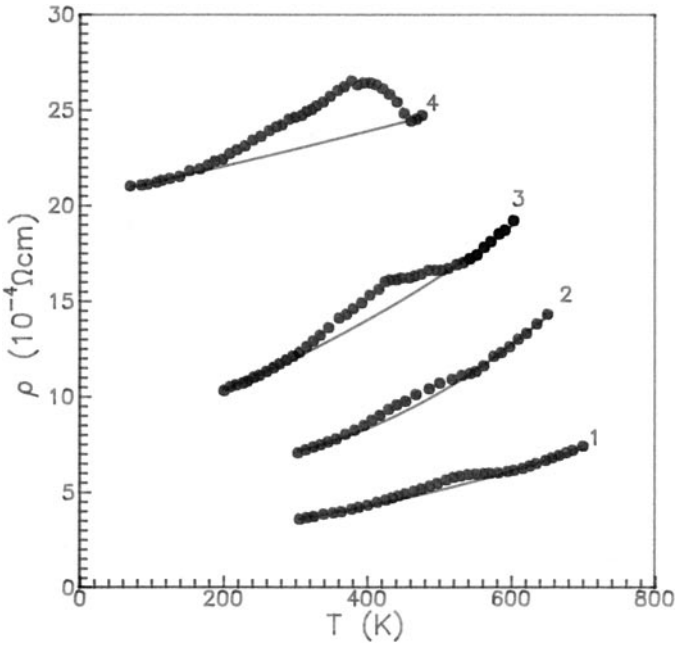

Figure 3. The temperature dependences of the electrical resistivity ρ in the phase transition region of GeTe–$AgBiTe_2$ SSs. The compositions are marked as in figure 2.

temperature it begins to decrease. For compositions with $x = 0.260$ and 0.333 (curves 3 and 4 respectively) it decreases in the whole temperature interval.

The temperature dependences of electrical resistivity ρ for the same compositions were measured using the alternative current van der Pauw method and the four probe method [10]. The maximal error was 3%. The temperature dependences of ρ for different compositions, only in the PT region, are presented in figure 3. Each curve exhibits an anomalous increase of a few per cent in the vicinity of the PT temperature. The electrical resistivity increases with temperature and composition. The last behaviour is typical for a metals. It is established in [11] that at higher temperatures ρ begins to decrease as in semiconductors.

3. Discussion

For magnetic systems with strong electron–phonon interaction the following relation is obtained [12]:

$$\frac{R - R_c}{R_c} \sim b\Delta^2 \tag{2}$$

where R is the Hall coefficient at $T < T_c$, R_c is the one at T_c. Δ the primary order parameter and b is a constant.

Taking into account (1) the relation (2) may be written as

$$\frac{R - R_c}{R_c} \sim b\left(\frac{T_c - T}{T_c}\right)^{2\beta}. \tag{3}$$

The values of T_c for each composition are derived from the observed kinks in the temperature dependences of electrical resistivity (figure 3) after its theoretical interpretation which is given below.

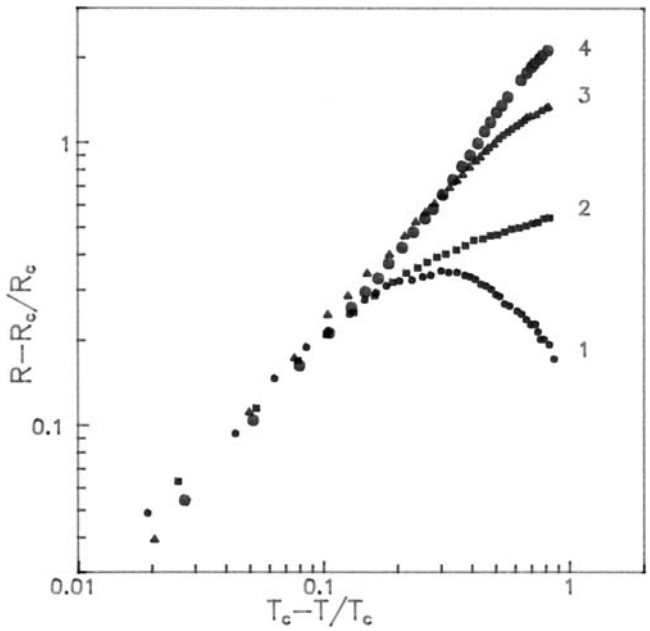

Figure 4. The plot of $\ln[(R - R_c)/R_c]$ versus $\ln[(T_c - T)/T_c]$ for GeTe–$AgBiTe_2$ SSs illustrating the relation (3). The compositions are marked as in figure 2.

In figure 4 are presented the values of $\ln[(R - R_c)/R_c]$ against $\ln[(T_c - T)/T_c]$. The dependences are linear at temperatures lower by about 100 K than T_c. From the linear part of these dependences it is established that the critical index of the secondary order parameter is equal to 0.50 ± 0.05. This value corresponds to $\beta = 0.5$ found from the phenomenological Landau theory for a second order PT [13].

The observed anomaly in $\rho(T)$ dependences near T_c for IV–VI compounds was interpreted by assuming that scattering of free carriers by phonons and other mechanisms causes a smooth background while the resistivity increment observed at the critical temperature is attributed to the carrier–soft-TO phonon interaction [9, 14]. This interaction becomes particularly strong for $T \cong T_c$ due to the increase in phonon population as $\omega_{TO} \to 0$ (ω_{TO} being the frequency of the transversal optical phonons). This problem is treated more thoroughly by taking into account also the anomalous scattering by the acoustic TA, LA and LO phonons [15]. It was pointed out that variation in the shape of the resistivity anomaly for different samples may be associated with the formation of ferroelectric domains in the rhombohedral phase and additional scattering by domain walls [16].

According to [14] the temperature dependent part of the resistivity due to the scattering of the TO phonon is given by

$$\rho_{TO} = \text{const}\frac{TG(T, k_F)}{\gamma} \tag{4}$$

where

$$G(T, k_F) = 2 - \frac{\omega_{TO}^2(0)}{2A(T)k_F^2}\log\left(1 + \frac{4A(T)k_F^2}{\omega_{TO}^2(0)}\right)$$

T is the temperature, k_F is the Fermi wavevector, $A(T)$ is the dispersion coefficient which is assumed to be temperature independent and $\gamma = 4A(T)k_F/\alpha$ characterizes the curvature in

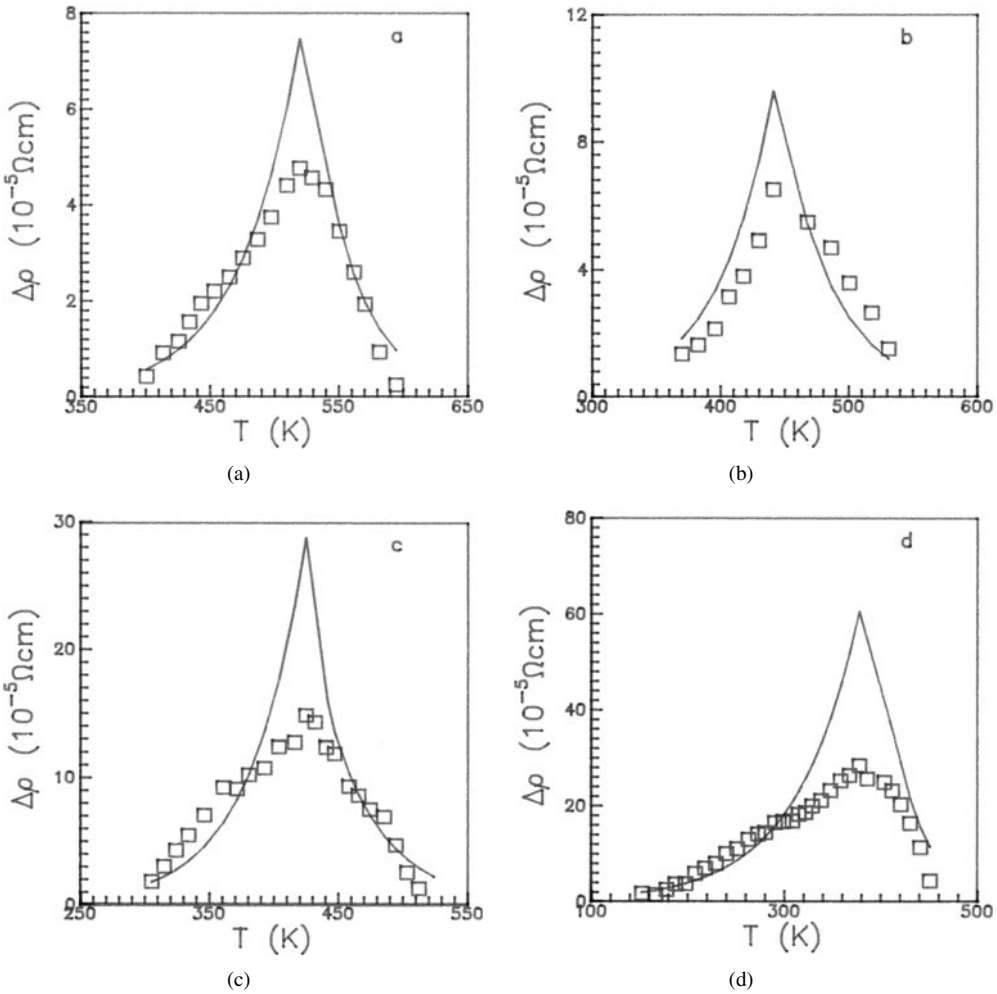

Figure 5. Resistivity increment $\Delta\rho$ as a function of temperature. Points represent experimental data and full curves are data calculated using equation (4). (a) $x = 0.095$, $T_c = 520$ K, $\gamma = 80$; (b) $x = 0.181$, $T_c = 441.3$ K, $\gamma = 50$; (c) $x = 0.260$, $T_c = 424.9$ K, $\gamma = 20$; (d) $x = 0.333$, $T_c = 378.3$ K, $\gamma = 5$.

the resistivity caused by the soft-TO phonon near zero wavevector. The Landau theory for the second order phase transitions [13] based on a phenomenological expansion of the free energy up to fourth order in a local order parameter describes the temperature dependence of the soft mode by

$$\omega_{TO}^2 = \alpha(T - T_c) \qquad \text{for } T > T_c$$
$$\omega_{TO}^2 = 2\alpha(T - T_c) \qquad \text{for } T < T_c$$

where α is a constant characteristic of the material.

The temperature dependences of the anomalous part $\Delta\rho$ of the resistivity for all investigated compositions are presented in figure 5 (points). It is equal to the difference between the measured and the background resistivity which was drawn smoothly by connecting the experimental curve at a distance from T_c (see figure 3). The temperature at which is obtained

the maximal value of $\Delta\rho$ is the phase transition temperature T_c. The values of T_c determined in this way are 520 K for $x = 0.095$, 441.3 K for $x = 0.181$, 424.9 K for $x = 0.260$ and 378.3 K for $x = 0.333$. The results from the calculation of ρ_{TO} (solid curve) and experimental points are compared in figure 5. A fit to the data is obtained through adjustment of the parameter γ. The observed difference between experimental and calculated curves is a result from assuming at calculation only the soft-TO phonon scattering. The values of γ for the investigated SSs similarly to that for the p-type SnTe [14] are small ($\gamma < 100$). One can see that γ decreases with increasing x (the content of $AgBiTe_2$), i.e. the curvature caused by the soft-TO phonon near zero wavevector is accelerated. This finding leads us to the conclusion that the point of transition temperature is not smeared in the SSs at the statistical distribution of the Ge cations with Ag and Bi ions. The values of T_c given in the caption of figure 5 also correspond to the peaks in calculated curves of ρ_{TO} (the solid curves).

4. Conclusion

In conclusion it may be stated that:

(1) For GeTe-rich GeTe-$AgBiTe_2$ SSs the temperature dependence of the Hall coefficient may be used to describe the local-order parameter for the second-order phase transition in accordance with the phenomenological Landau theory.
(2) The results from calculation of the electrical resistivity due to the soft-TO phonon show that with increasing number of Ag and Bi atoms in the GeTe the curvature of the soft-TO phonon changes rapidly near the zone centre.

References

[1] Scrabec E A and Thrimmer D S 1995 *Properties of General TAGS System (CRC Handbook of Thermoelectrics)* ed D M Rowe (New York: Chemical Rubber Company) p 267
[2] Mahan G D 1997 *Good Thermoelectrics (Solid State Physics vol 51)* (New York: Academic) p 81
[3] Korzhuev M A 1986 *Tellurid Germania i Ego Fisicheskie Svoistva* (Moscow: Nauka)
[4] Birman J L 1968 *J. Physique Coll.* **29** C4 151
[5] Plachkova S K, Odin I N and Novoselova A V 1984 *Izv. Acad. Nauk SSSR, Ser. Neorg. Mater.* **20** 403
[6] Plachkova S K, Shelimova L E and Karpinskii O G 1990 *Phys. Status Solidi* a **117** 155
[7] Halperin B I and Hohenberg P C 1977 *Mod. Phys.* **49** 435
[8] Zhdanova V V, Gruzinov B F, Konstantinov P P, Lev E Ja and Sisoeva L M 1975 *Neorg. Mater.* **11** 365
[9] Kobayashi K L I, Kato Y, Katayama Y and Komatsubara K F 1975 *Solid State Commun.* **17** 875
[10] Pavlov L P 1987 *Methodi Izmerenia Parametrov Poluprovodnikovah Materialov* (Moscow: Vishaia Shkola)
[11] Avramova I A and Plachkova S K 2000 *Phys. Status Solidi* a **179** 171
[12] Takada S 1971 *Prog. Theor. Phys.* **46** 15
[13] Landau L D 1937 *Phys. Z. Sowjun* **11** 26 545
[14] Katayama S 1976 *Solid State Commun.* **19** 381
[15] Katayama S and Milles D L 1980 *Phys. Rev.* B **32** 336
[16] Jantsch W 1983 *Dynamical Properties of IV–VI Compounds (Springer Tracts in Modern Physics vol 99)* (Berlin: Springer)