Transport Phenomena in Mixed Layered Tetradymite-like Compounds in the GeTe–Bi$_2$Te$_3$ System

P. P. Konstantinov,* L. E. Shelimova,†,1 E. S. Avilov,† M. A. Kretova,† and J.-P. Fleurial‡

*A. F. Ioffe Physical-Technical Institute of Russian Academy of Science, Politekhnicheskaya 26, 194021 St-Petersburg, Russia;
†A. A. Baikov Institute of Metallurgy of Russian Academy of Sciences, Leninskii Prospect 49, 117911 Moscow, Russia; and
‡Jet Propulsion Laboratory/California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109

The electrical transport properties of the GeBi$_2$Te$_4$-, Ge$_3$Bi$_2$Te$_6$-, and GeBi$_4$Te$_7$-layered compounds were characterized as a function of temperature and for samples with various stoichiometric deviations. The Hall coefficient and electrical resistivity were measured from 77 to 800 K, and the Seebeck coefficient was determined in the 90−450 K temperature range. The onset of intrinsic conductivity behavior was observed in these ternary compounds at fairly low temperatures. On the basis of the variation of the electrical conductivity at elevated temperatures, energy gap values of 0.24, 0.20, and 0.22 eV were calculated at 0 K for the Ge$_3$Bi$_2$Te$_6$, GeBi$_2$Te$_4$, and GeBi$_4$Te$_7$ compounds, respectively. To explain the carrier mobility temperature dependence, a mixed carrier scattering mechanism on acoustic phonons and point defects is proposed at low temperatures. It is found that the contribution of scattering by acoustic phonons increases with temperature. The analysis of experimental data for the GeBi$_4$Te$_7$ compound in the 150−200 K temperature range demonstrated the need for an additional carrier scattering mechanism, probably connected to the order–disorder phenomena in the cation layers. An anomalous temperature dependence of the Hall coefficient was discovered for the "stoichiometric" GeBi$_2$Te$_4$ compound. It is explained by mixed carrier conduction effects due to fluctuations of the composition and the existence of p- and n-type conductivity domains in the GeBi$_2$Te$_4$ crystal. © 1999 Academic Press

1. INTRODUCTION

One of the new promising approaches in the search for effective thermoelectric materials consists of the preparation of semiconductor alloys with multinary compositions and long-period complex structures (1). Such materials may offer the potential for "engineering" complex electronic structures with a high density of states near the Fermi energy, leading to enhanced Seebeck coefficient values. At the same time, these structures with large unit cells and heavy atomic elements are expected to possess low lattice thermal conductivity due to effective scattering of phonons that are responsible for the transfer of heat in the materials.

The nGeTe $\cdot$ mBi$_2$Te$_3$ homologous series of mixed-layered (ML) compounds (2, 3) are particularly attractive because novel structurally and compositionally more complex analogs of solid solutions based on the state-of-the-art Bi$_2$Te$_3$ thermoelectric compound can be synthesized. Using electron diffraction and high-resolution electron microscopy, the (GeTe)$_n$ $\cdot$ Bi$_2$Te$_3$ (n = 1 to, at least, 9 or even greater) ML compounds were identified after annealing the samples at 570–620 K for 300–500 h (2). In addition to the above-mentioned (GeTe)$_n$ $\cdot$ Bi$_2$Te$_3$ compounds, crystals of (Bi$_2$Te$_3$)$_m$GeTe-layered compounds (m = 1–4) have also been prepared (3). It has been suggested (2) that the ML compound structures are analogous to the (GeTe)$_n$As$_2$Te$_3$ compounds (4) which were characterized by ordering alternatively n layers of GeTe with a single lamellae of As$_2$Te$_3$ along the c hexagonal axis.

The Ge$_3$Bi$_2$Te$_6$ (A), GeBi$_2$Te$_4$ (B), and GeBi$_4$Te$_7$ (C) compounds are apparently the most stable members of the homologous series of compounds and are formed by peritectic reactions at 923, 857, and 837 K, respectively (5). Limited stoichiometric deviations (0.2–0.5 at.%) along the Bi–Ge axis of the ternary phase diagram are observed for all three compounds.

Single crystals and powders of the A, B, and C compounds have been investigated by X-ray diffraction (7). The ML crystal structure can be represented by a stacking of close-packed Te layers according to ccp. The Ge and Bi atoms are distributed in octahedral interstices, filling only a fraction of the cation positions. The GeBi$_2$Te$_4$ unit cell (a = 0.4322(5) nm, c = 4.127(2) nm, and the space group is $R\bar{3}m$) consists of three 7-layer packets: TeBiTeGeTeBiTe, with N = 21, where N is the number of layers per unit cell. The Ge$_3$Bi$_2$Te$_6$ unit cell (a = 0.4268(1) nm, c = 6.264(2) nm, and the space group is $R3m$) consists of three 11-layer packets: TeGeTeBiTeBiTeGeTeGeTe (N = 33). The

---

¹To whom correspondence should be addressed.

GeBi$_4$Te$_7$ unit cell ($a = 0.4348(2)$ nm, $c = 2.392(2)$ nm, and the space group is $P\bar{3}m1$) contains the packets of two types: one 5-layer and one 7-layer packet ($N = 12$). In these three layered structures, the bonding within the multilayered packets has ionic–covalent character, while bonds between the packets are preferentially achieved by weak van der Waals forces.

A full determination of the GeBi$_2$Te$_4$ structure, performed by an automatic four-circle diffractometer "Syntex $P\bar{1}$," provided data for the atomic coordinates, occupation factors, and temperature parameters with a reliability index of $R = 3.3\%$ for the 60 reflections (7). Results indicated that the Ge and Bi atoms were statistically distributed in the octahedral interstices to create mixed-cation layers. In addition to this cation sublattice disorder, antistructure defects were also identified, with Te atoms partially located on Bi sites and Bi atoms partially occupying Te sites.

X-ray diffraction analyses of Ge$_3$Bi$_2$Te$_6$–Ge (A–Ge), GeBi$_2$Te$_4$–Ge (B–Ge), and GeBi$_4$Te$_7$–Ge (C–Ge) alloys determined that structural modifications take place in ML phases with increasing Ge excess (6). They are related to the change in the number of layers N per unit cell that occurs when a cation-to-anion ratio corresponding to that in the nGeTe·mBi$_2$Te$_3$ compound with the next greater n/m-ratio value is reached. For example, 21-layer and 9-layer structures coexist in Ge$_{1+\delta}$Bi$_2$Te$_4$ single crystals when $0 < \delta < 0.2$. The 9-layer structure is inherent to the next member in the series of homologous compounds with $n = 2$ and $m = 1$, i.e., Ge$_2$Bi$_2$Te$_5$ (phase D). For such two-phase (B + D) alloys, domains of the layered phases coexist in the crystal and alternate along the c-axis direction.

The room temperature transport properties of the A, B, and C compounds have been studied as a function of stoichiometric deviations (8, 9). Only p-type conductivity samples were obtained for Ge$_3$Bi$_2$Te$_6$ while GeBi$_4$Te$_7$ samples exhibited only n-type conductivity. However, with variation in the stoichiometry of GeBi$_2$Te$_4$ samples, both n-type (excess Bi or Ge) and p-type (excess Te or Ge deficiency) conductions were observed. All three compounds are characterized by a low lattice thermal conductivity (8) that is probably related to the high degree of sublattice disorder.

In this paper we report on calculated values for the energy gap and carrier effective masses in the Ge$_3$Bi$_2$Te$_6$, GeBi$_2$Te$_4$, and GeBi$_4$Te$_7$ ML compounds on the basis of our analysis of carrier scattering mechanisms. For this purpose, samples with different carrier concentration levels due to stoichiometric deviations were synthesized and their electrical transport properties were measured in a wide temperature range.

2. EXPERIMENTAL

The starting materials, i.e., Bi, Te of 5 N purity, and Ge of 40 Ω-cm specific resistivity, were loaded in quartz ampules, subsequently evacuated and sealed off, and melted at 1073 K for 5 h. After the synthesis, the ampules were air-quenched. The maximum error in composition (± 0.02 at. %) due to the loss of material to the vapor phase at 1073 K was evaluated, taking into account the GeTe, Bi$_2$Te$_3$, and Te$_2$ vapor pressure and the volume of the vapor phase. The resulting polycrystalline ingots were heat-treated using a two-step process of 770 K for 1000 h and then 570 K for 1500 h. The homogeneity in composition of the samples were verified by metallographic study and microhardness measurements. The ML compounds were analyzed by X-ray diffraction using a DRON-3M automatic diffractometer (graphite-monochromated Fe$K\alpha$ radiation). By identifying the number of layers per unit cell, N, one can determine the composition of the alloys as N is directly related to the GeTe-to-Bi$_2$Te$_3$ ratio (7). Additional details about the sample preparation method were given elsewhere (6, 7).

The transport coefficients were measured with the samples representing rectangular $(15 \times 5 \times 1.5)$-mm^3 plates. The Hall coefficient measurements were performed from 77 to 800 K using an automated setup (10) with a two-frequency technique (current of 0.2 A or less with a frequency of 72 Hz; magnetic field of 0.2 T with a frequency of 50 Hz). The electrical resistivity was measured in a four-probe ac arrangement at 72 Hz simultaneously with the determination of the Hall coefficient. The error in the measurement of the Hall coefficient and electrical resistivity is about 2%. The thermoelectric power was determined from 90 to 450 K using a differential thermocouple technique, with a temperature drop between the probes not exceeding 10 K. The error in the Seebeck coefficient measurement does not exceed 3%.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The GeBi$_2$Te$_4$ Compound

Nominal atomic compositions of the GeBi$_2$Te$_4$ alloys with different deviations from stoichiometry and Hall carrier concentrations are reported in Table 1. p-Type conduction is obtained for samples with excess Te or Ge deficiency, and the temperature dependence of the Hall coefficient R_H and electrical resistivity ρ for p-type samples are presented in Fig. 1. As seen from Fig. 1a, the Hall coefficient is practically constant at low temperatures but sharply decreases for temperatures higher than 300–350 K. The electrical resistivity increases with temperature at low temperatures and then decreases at $T > 300$–350 K, corresponding to the onset of intrinsic conductivity behavior (Fig. 1b). An energy gap value of 0.20 eV (at 0 K) was calculated from the dependence of the electrical conductivity, $\sigma = 1/\rho$, on the reciprocal temperature, $1/T$, a value in good agreement with previously published results (5).

The variations of the Hall mobility, $\mu_H = R_H\sigma$, of p-type samples with temperature are presented in Fig. 2. The

TABLE 1
The Nominal Atomic Compositions, Experimental Conductivity Type, and Room Temperature Carrier Concentration of nGeTe·mBi₂Te₃ ML Compounds Prepared with Various Deviations from Stoichiometry

Nominal composition	Type of conductivity	$p, n \times 10^{-19}$ (cm^{-3})	Nominal composition	Type of conductivity	$p, n \times 10^{-20}$ (cm^{-3})
$Ge_{0.98}Bi_2Te_4$	p	3.14	$GeBi_{2.025}Te_4$	n	1.53
$Ge_{0.96}Bi_2Te_4$	p	2.50	$GeBi_{2.04}Te_4$	n	1.29
$Ge_{0.94}Bi_2Te_4$	p	2.22	$GeBi_2Te_4$	p	5.34
$GeBi_2Te_{4.015}$	p	6.50	$Ge_{1.02}Bi_2Te_4$	n	2.06
$GeBi_{2.015}Te_4$	p	8.97			
$GeBi_4Te_7$	n	2.12	$Ge_{2.94}Bi_2Te_6$	p	2.90
$Ge_{0.96}Bi_4Te_7$	n	1.88	$Ge_{3.06}Bi_2Te_6$	p	2.01
$Ge_{1.03}Bi_4Te_7$	n	7.17	$Ge_3Bi_{2.025}Te_6$	p	1.78
$GeBi_{4.03}Te_7$	n	1.97	$Ge_3Bi_{2.04}Te_6$	p	1.72
$GeBi_4Te_{7.05}$	n	1.74	$Ge_3Bi_2Te_{6.025}$	p	1.92

$GeBi_2Te_4$ shows that fluctuations in the composition are possible in the crystal. Apparently, Ge-poor and Ge-rich domains coexist in the crystal, although its average composition may correspond to the stoichiometric composition. As reported in Table 1, $Ge_{1-\delta}Bi_2Te_4$ samples have p-type conductivity, whereas the D phase has n-type conductivity with a carrier concentration value of 8.3×10^{19} cm^{-3} (11). This means that p- and n-type crystalline domains alternate in the $GeBi_2Te_4$ multilayered sample and are responsible for the mixed conduction effects and anomalous temperature dependence of the electrical transport properties.

The Seebeck coefficient values for stoichiometric $GeBi_2Te_4$ and the p- and n-type samples are presented in Fig. 4 as a function of temperature. The temperature dependence of the Seebeck coefficient for stoichiometric
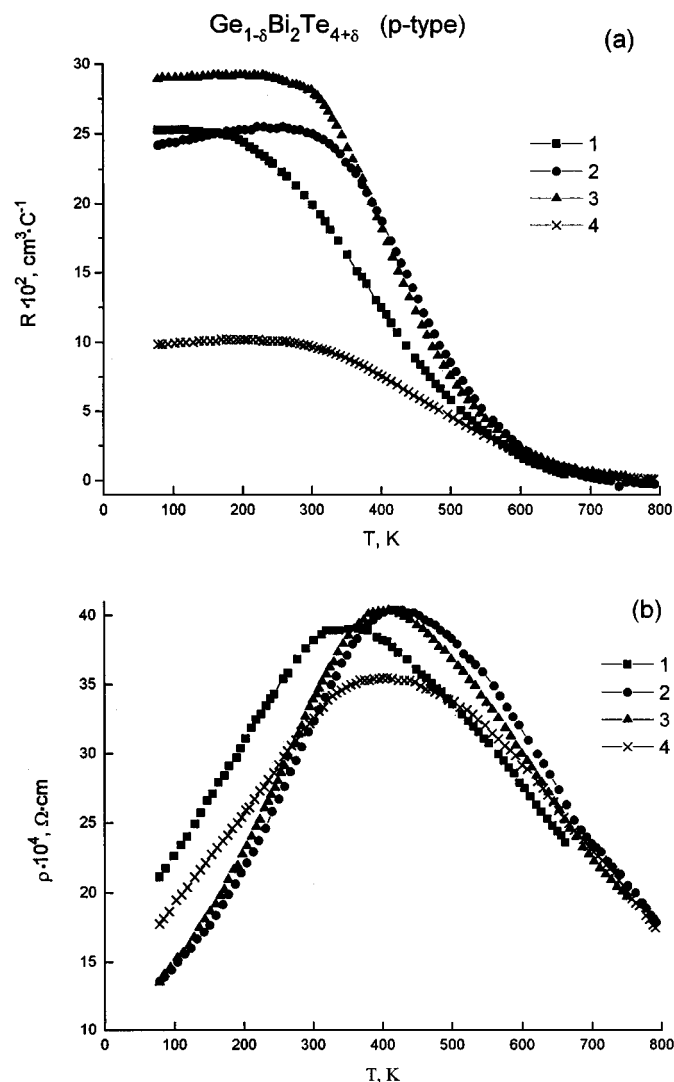
temperature dependence follows a power law $\mu_H \propto T^n$ with n being markedly dependent on the temperature range. At low temperatures, the carrier mobility dependence is relatively weak and can be expressed as $\mu_H \propto T^{-1/2}$. However, the temperature dependence of the carrier mobility rapidly increases with increasing temperature, and at $T > 450$ K, it can be expressed as $\mu_H \propto T^{-6}$. This can be explained by mixed conduction effects as intrinsic behavior develops.

Results for the nominally "stoichiometric" $GeBi_2Te_4$ compound and Ge-rich or Bi-rich compositions are presented in Fig. 3. A transition from p-type conductivity ($GeBi_{2.015}Te_4$) to n-type conductivity ($GeBi_{2.025}Te_4$) is observed for samples with excess Bi as the concentration of Bi atoms increases.

As seen from Fig. 3, an anomalous temperature dependence of the Hall coefficient takes place in the stoichiometric $GeBi_2Te_4$ compound. A sharp decrease is observed in the 77–150 K temperature range while almost constant R_H values are measured in the 200–500 K range. At higher temperatures, the Hall coefficient decreases anew. It is worth noting that this alloy has a high room temperature hole concentration (Table 1) and low hole mobility 7 cm²/V s). Combined with the electrical resistivity measurement data, this anomalous behavior can be interpreted as being due to mixed conduction effects. As a result, Hall mobility values are strongly underestimated because of the compensating effect of electrons.

The origin of mixed conductivity for $GeBi_2Te_4$ samples can be explained from X-ray diffraction data (6) for the B–Ge compositional section. In stoichiometric $GeBi_2Te_4$, 21-layer structure crystalline domains (B phase) coexist in the crystal with 9-layer lattice (D phase) crystal domains, alternating along the c axis (6). The presence of two types of X-ray diffraction reflections i the pattern for stoichiometric

FIG. 1. The temperature dependence of the Hall coefficient (a) and electrical resistivity (b) for p-type $GeBi_2Te_4$ samples. 1, $Ge_{0.98}Bi_2Te_4$; 2, $Ge_{0.96}Bi_2Te_4$; 3, $Ge_{0.94}Bi_2Te_4$; 4, $GeBi_2Te_{4.015}$.

FIG. 2. Hall mobility $[\log(R_H\sigma)]$ as a function of temperature $[\log(T)]$. 1, $Ge_{0.98}Bi_2Te_4$; 2, $Ge_{0.96}Bi_2Te_4$; 3, $Ge_{0.94}Bi_2Te_4$; 4, $GeBi_2Te_{4.015}$.

increase is much smaller for extrinsic n-type samples with excess Ge (from 45 cm²/Vs at 300 K to 87 cm²/Vs at 77 K). This interpretation assumes that carrier concentrations remain constant in the temperature range of interest, with no anomalous variations in the Seebeck coefficient of each domain and no significant carrier scattering effects due to potential barriers at the domain interfaces. This last factor is not taken into account because of the high carrier concentration values. The assumption of nearly constant carrier concentration values is rather justified because of the typical extrinsic temperature dependence of the Hall coefficient for other samples of p- and n-type at low temperatures (Figs. 1 and 3). Finally the variations of the Seebeck coefficient of these same samples with temperature are typical of very
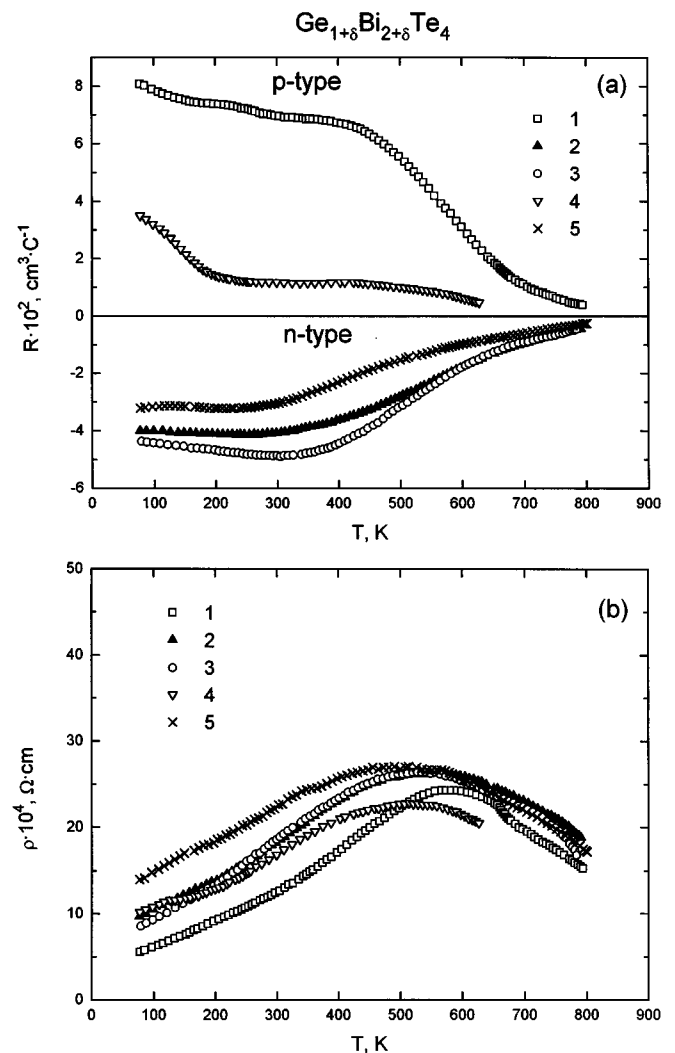
$GeBi_2Te_4$ has an anomalous character in agreement with the variations of the Hall coefficient and electrical resistivity. At low temperatures, the Seebeck coefficient is positive and slowly decreases with increasing temperature. At temperatures higher than 200 K, the Seebeck coefficient becomes negative, whereas the Hall coefficient is still positive (Fig. 3).

The Seebeck coefficient for a two-phase mixture consisting of p- and n-type domains was analyzed in Ref. (12) for the $AgSbTe_2$ compound. The analysis is based on theoretical consideration of transport phenomena in inhomogenous semiconductors using a model of spheres of each phase imbedded in an infinite medium with average properties (13–15). According to (15), the effective Seebeck coefficient of the mixture is given by

$$S = \sum S_i\sigma_i\gamma_i/(1 - 2\sigma\sum\gamma_i), \qquad [1]$$

where

$$\gamma_I = 3\kappa V_i/(2\sigma + \sigma_i)(2\kappa + \kappa_i) \qquad [2]$$

and σ and κ are the effective electrical and thermal conductivities of the mixture, respectively; σ_i and κ_i are the partial electrical and thermal conductivities, respectively, of an i domain having a V_i volume fraction.

As seen from Eqs. [1] and [2], and assuming mixed conductivity domains in the $GeBi_2Te_4$ compound, the behavior of S and R_H at low temperatures can best be understood if hole mobility values are substantially larger than electron mobility values. For example, carrier mobility values increase sharply with decreasing temperatures for extrinsic p-type samples with Ge deficiency (from 83 cm²/Vs at 300 K to 200 cm²/Vs at 77 K), while the

FIG. 3. The temperature dependence of the Hall coefficient (a) and electrical resistivity (b) for $GeBi_2Te_4$ samples with excess Ge or Bi. 1, $GeBi_{2.015}Te_4$; 2, $GeBi_{2.025}Te_4$; 3, $GeBi_{2.04}Te_4$; 4, $GeBi_2Te_4$; 5, $Ge_{1.02}Bi_2Te_4$.
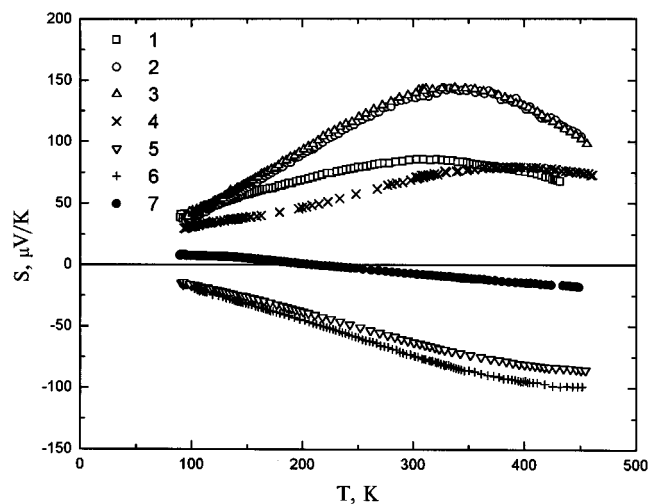
FIG. 4. The temperature dependence of the Seebeck coefficient for GeBi$_2$Te$_4$ samples with different stoichiometric deviations. 1, Ge$_{0.98}$Bi$_2$Te$_4$; 2, Ge$_{0.96}$Bi$_2$Te$_4$; 3, Ge$_{0.94}$Bi$_2$Te$_4$; 4, GeBi$_2$Te$_{4.015}$; 5, GeBi$_{2.025}$Te$_4$; 6, GeBi$_{2.04}$Te$_4$; 7, GeBi$_2$Te$_4$.

heavily doped materials, where values decrease linearly with decreasing temperatures (Fig. 4).

The Ge$_3$Bi$_2$Te$_6$ Compound

Regardless of the type of stoichiometric deviations, Ge deficiency or excess Ge, Bi or Te, Ge$_3$Bi$_2$Te$_6$ samples always possessed p-type conductivity. The nominal compositions of the samples under study are presented in Table 1. The Hall coefficient and electrical resistivity data as functions of temperature are plotted in Fig. 5a and 5b. Compared to the GeBi$_2$Te$_4$ and GeBi$_4$Te$_7$ compounds, Ge$_3$Bi$_2$Te$_6$ is characterized by a greater concentration of native point defects (11) and consequently a high carrier concentration, over 1.7×10^{20} cm^{-3} (300 K). The highest hole concentration value (2.9×10^{20} cm^{-3}) was achieved for a composition with Ge deficiency. Due to these high carrier concentrations, relatively low hole mobility values are obtained not exceeding 70 cm^2/V s at 100 K.

A sharp decrease in the Hall coefficient and electrical resistivity takes place in Fig. 5 for temperatures above 500 K. This behavior can probably be attributed to the onset of intrinsic conductivity, similar to that observed for the GeBi$_2$Te$_4$ compound. On the basis of the temperature dependence of the electrical conductivity, an energy gap value of 0.24 eV (at 0 K) was determined for the Ge$_3$Bi$_2$Te$_6$ compound. Mixed conduction effects are thus responsible for the strong decrease in hole mobility with temperatures above 500 K ($\mu_H \propto T^{-6}$), as shown in Fig. 6. At low temperatures, the Hall mobility obeys a $\mu_H \propto T^{-1/2}$ law, and in a 300–500 K temperature range, μ_H is proportional to T^{-1} (Fig. 6).

If nearly constant Hall coefficient values are observed in the 250–450 K temperature range, R_H values increase substantially with decreasing temperatures below 200 K. This increase cannot be explained by the near-linear variation of the electrical resistivity in the temperature range of interest. Instead, we suggest that higher Hall coefficient values could result from a strong scattering of the charge carriers. This effect may be related to the complex shape of the Fermi surface, which can lead to a considerable dispersion of the carrier velocities and relaxation times.

The GeBi$_4$Te$_7$ Compound

Only n-type conductivity samples were obtained for GeBi$_4$Te$_7$, regardless of the type of stoichiometric deviations,
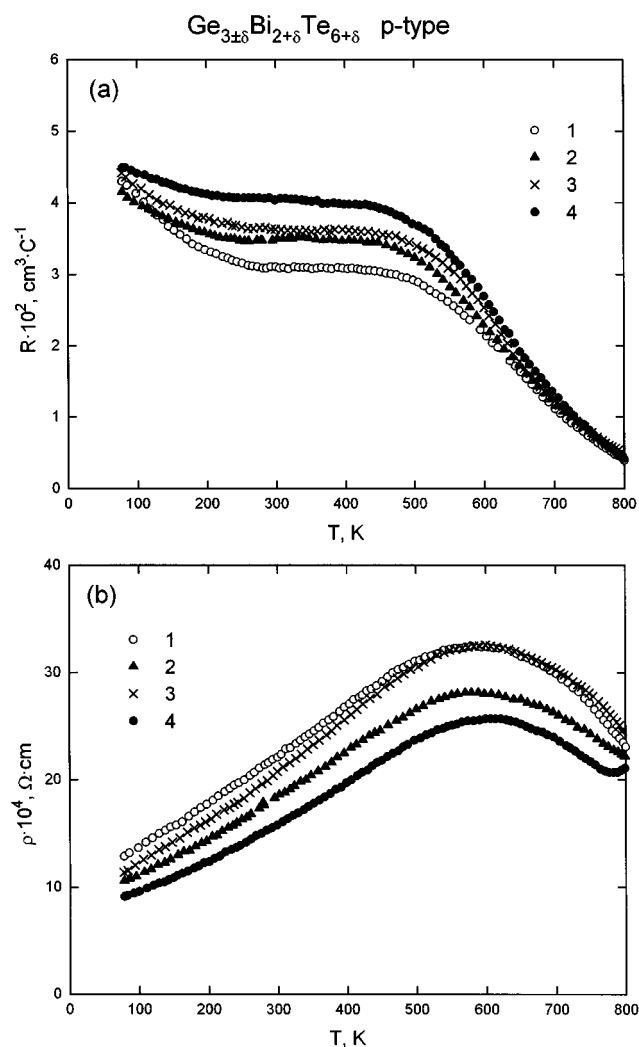

FIG. 5. The temperature dependence of the Hall coefficient (a) and electrical resistivity (b) for Ge$_3$Bi$_2$Te$_6$ samples with different stoichiometric deviations. 1, Ge$_{3.06}$Bi$_2$Te$_6$; 2, Ge$_3$Bi$_{2.025}$Te$_6$; 3, Ge$_3$Bi$_{2.04}$Te$_6$; 4, Ge$_3$Bi$_2$Te$_{6.025}$.
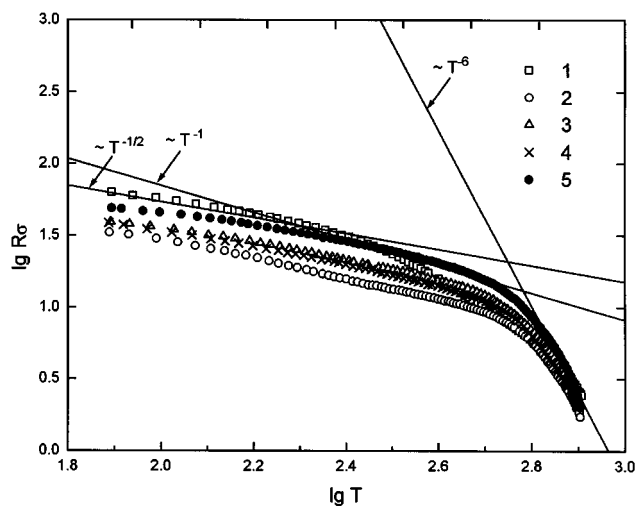
FIG. 6. Hall mobility $[\log(R_H\sigma)]$ as a function of temperature $[\log(T)]$. 1, $Ge_{2.94}Bi_2Te_6$; 2, $Ge_{3.06}Bi_2Te_6$; 3, $Ge_3Bi_{2.025}Te_6$; 4, $Ge_3Bi_{2.04}Te_6$; 5, $Ge_3Bi_2Te_{6.025}$.

i.e., excess Bi. Te, or Ge as well as Ge deficiency. These compositions are reported in Table 1. The electron concentration for the stoichiometric $GeBi_4Te_7$ compound is $\sim 2 \times 10^{19}$ cm^{-3}. Significant changes in carrier concentration were only achieved by excess Ge doping ($\sim 7 \times 10^{19}$ cm^{-3}) and could be explained by the incorporation of Ge atoms into the van der Waals gaps in the multilayered structure (8).

The variations of the Hall coefficient, electrical resistivity, and Seebeck coefficient of $GeBi_4Te_7$ samples with temperature are presented in Figs. 7a, 7b, and 9, respectively. The onset of intrinsic conductivity appears for all samples at temperatures near 300 K, as both the electrical resistivity and Hall coefficient decrease with increasing temperature. On the basis of the temperature dependence of the electrical resistivity, an energy gap of 0.22 eV (at 0 K) was calculated for $GeBi_4Te_7$ (Fig. 8), a value in good agreement with prior work (5).

Humplike anomalies are observed in the temperature dependence of electrical resistivity near 150 K. Because both Hall and Seebeck coefficients do not exhibit comparable anomalies near this temperature, these anomalies are probably not related to a change in carrier concentration. Such behavior could be instead related to the contribution of an additional charge carrier scattering mechanism at low temperatures or more likely to some order–disorder phenomena in the cation layers. It is worth noting that these low-temperature electrical resistivity anomalies disappear after heating the samples to 800 K.

Charge Carrier Scattering Mechanisms

The main scattering mechanisms for electrical transport in the ML compounds can be identified by analyzing the temperature dependence of the carrier mobility (Figs. 2 and 6), electrical resistivity and Seebeck coefficient. It is found that the mobility dependence obeys a $\sim T^{-1/2}$ law in the 77–200 K interval for $Ge_3Bi_2Te_6$ and $GeBi_2Te_4$ and in the 77–120 K range for $GeBi_4Te_7$. An appreciable residual resistivity was found by extrapolating the $\rho = f(T)$ dependence to absolute zero temperature, which indicates strong point defect scattering of the charge carriers. If this mechanism is predominant in such a degenerate semiconductor, the carrier mobility is expected to be temperature independent, i.e., $\mu_H \propto T^0$ (16). At the same time, a linear $\rho = f(T)$ dependence at a constant carrier concentration at low temperatures, i.e., in the temperature range where extrinsic conduction occurs, points to the contribution of acoustic phonons to the scattering of charge carriers. For this
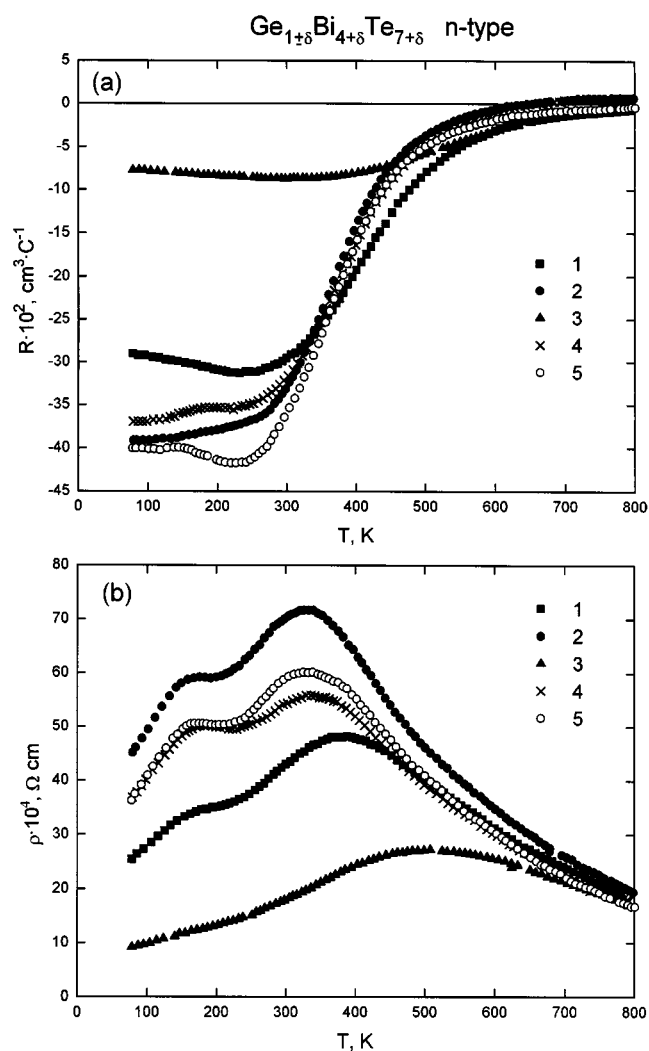

FIG. 7. The temperature dependence of the Hall coefficient (a) and electrical resistivity (b) for $GeBi_4Te_7$ with different deviations from stoichiometry. 1, $GeBi_4Te_7$; 2, $Ge_{0.96}Bi_4Te_7$; 3, $Ge_{1.03}Bi_4Te_7$; 4, $GeBi_{4.03}Te_7$; 5, $GeBi_4Te_{7.05}$.

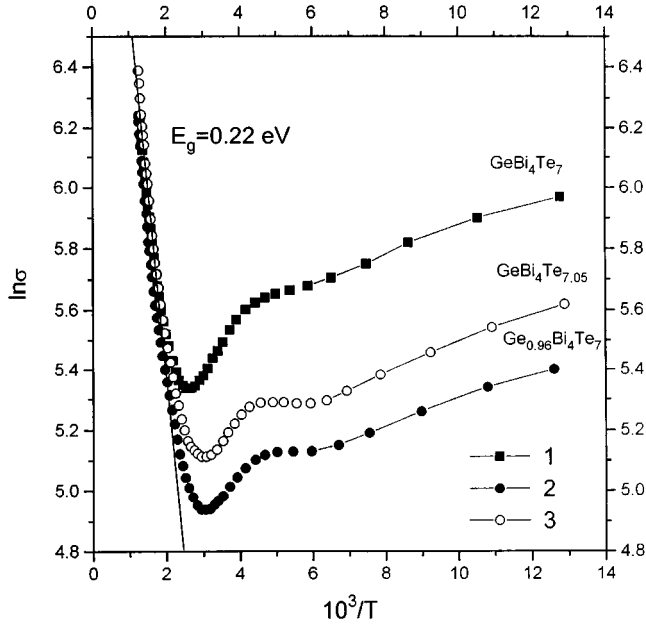**FIG. 8.** Electrical conductivity $[\ln(\sigma)]$ as a function of reciprocal temperature for $GeBi_4Te_7$ samples.

scattering mechanism, the energy dependence of the relaxation time (τ) is expressed as

$$\tau = \tau_0 \varepsilon^{r-1/2}, \quad [3]$$

where the scattering index $r = 0$. The temperature dependence of carrier mobility in this case is governed by a $\mu_H \propto T^{-1}$ law (16). The experimental $T^{-1/2}$ carrier mobil-
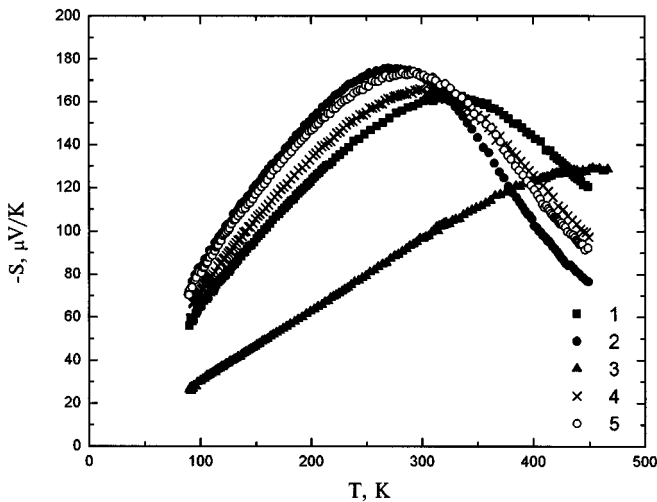

FIG. 9. The temperature dependence of the Seebeck coefficient for $GeBi_4Te_7$ samples with different stoichiometric deviations. 1, $GeBi_4Te_7$; 2, $Ge_{0.96}Bi_4Te_7$; 3, $Ge_{1.03}Bi_4Te_7$; 4, $GeBi_{4.03}Te_7$; 5, $GeBi_4Te_{7.05}$.

ity dependence observed in the present work can thus be explained by mixed point defect and acoustic phonon scattering mechanisms of charge carriers at low temperatures.

It may be concluded from X-ray diffraction analysis and electrical transport property measurements that the lattices of these multilayered compounds are characterized by a high concentration of native point defects such as the $Bi_{Ge}^{\bullet}$, Ge_{Bi}' substitution defects and the Bi_{Te}', $Te_{Bi}^{\bullet}$ antistructure defects exist in the lattices (7). In addition, the formation of ionized Ge (V_{Ge}'') and Te ($V_{Te}^{\bullet\bullet}$) vacancies is very likely, based on prior work on the $Ge_{1-\delta}Te$ (17) and Bi_2Te_3 compounds (18). The p-type conductivity of the $Ge_{3-\delta}Bi_2Te_6$ and $Ge_{1-\delta}Bi_2Te_{4+\gamma}$ samples can be explained by a high concentration of Ge vacanices (V_{Ge}''). The n-type conductivity of $Ge_{1+\delta}Bi_{2+\gamma}Te_4$ samples with excess Bi or Ge may be associated with $Bi_{Ge}^{\bullet}$ substitution defects and vacancies in the anion sublattice. The predominant defects in the $GeBi_4Te_7$ lattice which are responsible for n-type conductivity regardless of the type of stoichiometric deviations are predicted to be $Te_{Bi}^{\bullet}$ antistructure defects and, probably, $Bi_{Ge}^{\bullet}$, $V_{Te}^{\bullet\bullet}$ donor defects.

At temperatures higher than 200 K, when the degree of degeneracy declines (for example, in the case of p-type and n-type $GeBi_2Te_4$ samples) the carrier mobility decreases faster, approaching a $\mu_H \propto T^{-3/2}$ dependence characteristic of charge carrier scattering by acoustic phonons in nondegenerate semiconductors. $Ge_3Bi_2Te_6$ samples remained degenerate up to 300–400 K and the temperature dependence of carrier mobility for this compound obeys a $\sim T^{-1}$ law, i.e. corresponds to the predominance of carrier scattering by acoustic phonons. Based on current experimental data, it is difficult to establish what is the dominant scattering mechanism near 300 K for $GeBi_4Te_7$ samples.

The density-of-states effective mass of electrons and holes is calculated from the experimental values of Seebeck coefficient and carrier concentration, using generalized Fermi–Dirac statistics and the following assumptions: (i) A parabolic band structure approximation is valid and is independent of the small stoichiometric deviations of the samples under study; (ii) transport properties are controlled by one type of prevailing free current carriers; (iii) the relaxation time can be expressed by Eq. [3] suggesting $r = 0$; (iv) all three compounds are degenerate semiconductors. Seebeck coefficient experimental values measured at 100, 200, and 300 K were used for the $GeBi_4Te_7$, $GeBi_2Te_4$, and $Ge_3Bi_2Te_6$ compounds respectively to satisfy this last assumption of extrinsic conductivity. The following effective mass values were obtained:

Compound	$GeBi_4Te_7$	$GeBi_2Te_4$	$Ge_3Bi_2Te_6$
m_d^*/m_0 (electron)	0.79±0.05 (100 K)	0.87±0.05 (200 K)	
m_d^*/m_0 (hole)		0.52±0.05 (200 K)	1.0±0.01 (300 K)

REFERENCES

1. D. Y. Chung, T. Hogan, J. Schindler, L. Iordanidis, P. Brazis, C. R. Kannewurf, B. Chen, C. Uber, and M. G. Kanatzidis, "Proceedings of the 16th International Conference on Thermoelectrics," Dresden, Germany, p. 459. IEEE, Inc., Danvers, 1997.
2. S. Kuypers, G. Van Tendeloo, J. Van Landuyt, and S. Amelinckx, *J. Solid State Chem.* **76,** 102 (1988).
3. N. Frangis, S. Kuypers, C. Manolikas, J. Van Landuyt, and S. Amelinckx, *Solid State Commun.* **69,** 817 (1989).
4. S. Kuypers, G. Van Tendeloo, J. Van Landuyt, and S. Amelinckx, *J. Solid State Chem.* **73,** 192 (1988).
5. N. Kh. Abrikosov and G. T. Danilova-Dobryakova, *Izv. Akad. Nauk. U.S.S.R., Ser. Neorg. Mater.* **1,** 57 (1965).
6. L. E. Shelimova, O. G. Karpinsky, M. A. Kretova, and E. S. Avilov, *J. Alloys Compd.* **243,** 194 (1996).
7. O. G. Karpinsky, L. E. Shelimova, M. A. Kretova, and J.-P. Fleurial, *J. Alloys Compd.* **265,** 170 (1998).
8. L. E. Shelimova, O. G. Karpinsky, M. A. Kretova, E. S. Avilov, and J.-P. Fleurial, "Proceedings of the 16th International Conference on Thermoelectrics," Dresden, Germany, IEEE Catalog No. 97TH8291, p. 481. IEEE Int. Danver, 1997.
9. O. G. Karpinsky, L. E. Shelimova, M. A. Kretova, and E. S. Avilov, *Phys. Status Solidi A* **142,** 307 (1994).
10. B. F. Gruzinov and P. P. Konstantinov, *Sov. Prib. Tekhn. Eksp.* **5,** 225 (1972).
11. L. E. Shelimova, O. G. Karpinsky, E. S. Avilov, M. A. Kretova, and G. U. Lubman, *Russ. Inorg. Mater.* **30,** 1412 (1994).
12. R. Wolfe, J. H. Wernick, and S. Haszko, *J. Appl. Phys.* **31,** 1959 (1960).
13. C. Herring, *J. Appl. Phys.* **31,** 1939 (1960).
14. V. I. Odelevsky, *Zhur. Tekh. Fiz.* **21,** 678 (1951).
15. S. V. Airapetyanz, *Zhur. Tekh. Fiz.* **27,** 478 (1957).
16. F. J. Blatt, "Theory of Mobility of Electrons in Solid," Academic Press Inc., New York, 1957.
17. N. Kh. Abrikosov and L. E. Shelimova, "Poluprovodnikovye Materialy na osnove soedinenii $A^{IV}B^{VI}$," Izd. Nauka, Moskva, 1975.
18. P. Pecheur and G. Toussaint, *J. Phys. Chem. Solids* **55,** 327 (1994).