

# Doping Effects of Ga And Te On The Kinetic Coefficients of Rhombohedral And Cubic Phases Of $\text{Ge}_{1-x}\text{Ga}_x\text{Te}$ Solid Solution Alloys

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## Abstract

In this study Ga and Te doping effects on the kinetic parameters (thermo e.m.f., electrical conductivity, heat conductivity, Hall and Nernst-Ettingshausen coefficients) of the rhombohedral and cubic phases of  $\text{Ge}_{1-x}\text{Ga}_x\text{Te}$  ( $0 < x \leq 0,06$ ) solid solutions has been investigated between 77-900 K temperature intervals. Increase in the amount of Te increases hole concentration and reduces lattice constant, whereas rhombohedral properties of GeTe rises with increase of Ga concentration.

The observed anomalies on the kinetic parameters may be explained qualitatively by the complexity of the Fermi surface shape and the zone model of GeTe which involves the separation of the L extremums that is same for “ $\alpha$ ”, “ $\beta$ ” and “ $\gamma$ ” phases of the compound.

## Introduction

GeTe and its solid solvation derivatives are degenerate semiconductors with high hole concentration ( $\approx 10^{20} - 10^{21} \text{cm}^{-3}$ ) whose stoichiometric deviation depends on Te amount in GeTe and are quite promising materials for the p branch of thermoelectric converters which work at 500-900 K temperature range [1-3].

GeTe alloys pass from high temperature cubic  $\beta$  phase to low temperature rhombohedral  $\alpha$  phase or rhombic  $\gamma$  phase by polymorphic phase transition [4-9] for  $T \leq T_s = 630-700$  K temperature range. Phase transition is realized by the exchange of sublattices of Ge and Te and these transitions have ferroelectric ( $\beta \rightarrow \alpha$ ) or antiferromagnetic ( $\beta \rightarrow \gamma$ ) character [10].  $\alpha \rightarrow \gamma$  transition can be observed when Te concentration is increased

( $x > 0,504$ ) in the  $\text{Ge}_{1-x}\text{Te}_x$  alloys [2,3].

The temperature dependence of homogen zone boundaries of GeTe and the existence of three polymorphic modifications in the homogen zone boundaries show that structural and physical properties of these alloys are complex functions of temperature, composition and thermal treatments [3].

The effects of polymorphic phase transition in the GeTe were observed as some anomalies on the concentration and temperature characteristics of the kinetic parameters. At first, anomalies on the temperature and concentration characteristics of the GeTe and its derivatives were explained by a complex valence band model. According to this model the valence band has two parabolic sub zone regions which is separated by  $\Delta \approx 0,027$  eV energy gap. In one of them, holes have light effective mass ( $m^* = 1,2 m_0$ ) and heavy effective mass ( $m^* = 3 m_0$ ) in the other [11-13].

In the following years, consideration of the band structure of GeTe changed and the light hole zone of GeTe has been accepted as non-parabolic [12]. The non-parabolic light hole zone depends on 4  $L_p$  extremums whereas a heavy hole zone depends on 12  $\Sigma_p$  extremums.  $\Sigma_p$  extremums are separated from  $L_p$  extremums by an energy band of more than 0,6 eV in GeTe and this energy gap does not affect electrical conductivity of the materials. According to [14-16], the role of light and heavy hole zones are realized by  $L_p$  extremum groups, which separate with energy scales in ratios 1:3 or 2:2. These extremum groups are separated because the crystal lattice deformation takes place during the phase transition from high temperature  $\beta$  cubic phase to low temperature  $\alpha$  rhombic phase. However, investigations have showed that most theoretical works about band structure of GeTe are related to  $\beta$  cubic modification.

Since today's methods for calculation of the zone structure of the  $\alpha$  and  $\gamma$  phases with low symmetry is very difficult, experimental results will be interpreted qualitatively.

GeTe system has been widely investigated [16-24, 28,31]. According to these reports, the dissolution ratio of GeTe is 6% mole and this dissolution occurs when Ge is replaced by Ga. Investigation of thermoelectric properties of solid solutions showed that GaTe does not radically affect the energy spectrum of current carriers in GeTe.

It should also be noted that the above reports had also investigated the direct effects of Ga on the kinetic parameters of the solid solutions and, according to Korshuev [3], the increase of Te or Ge vacancies highly affect the alloying processes and energy spectrum of current carriers and crystal structure at the same time.

The aim of this report is to investigate the kinetic parameters of rhombohedral and cubic phases of  $\text{Ge}_{1-x}\text{Ga}_x\text{Te}$  solid solutions between 77-900 K temperature interval. These kinetic parameters depends on Ga and Te doping amounts.

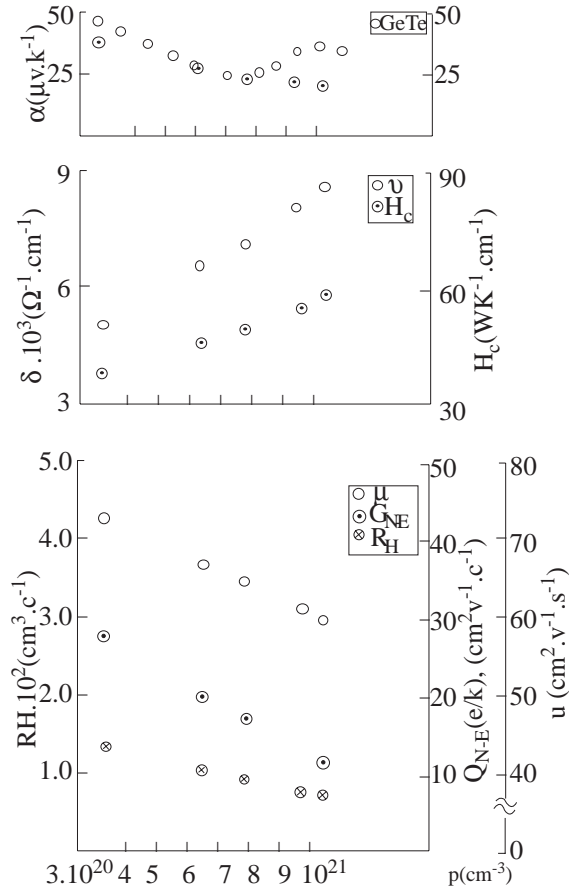
## Experimental Details

For the research of the rhombohedral and cubic modifications of kinetic parameters of the  $(\text{Ge}_{1-x}\text{Ga}_x)_{1-y}\text{Te}$  ( $0 \leq x \leq 0,06; 0 \leq y \leq 0,06$ ) parameters such as thermo e.m.f. ( $\alpha$ ), electrical conductivity ( $\sigma$ ), heat conductivity ( $H_c$ ), Hall coefficient ( $R_H$ ) and Nernst-Ettingshausen coefficient ( $Q_{N-E}$ ) were measured.

Polycrystalline samples were prepared by metal-ceramic method. Samples were annealed at 450 C for 250 hours and then slowly cooled to the room temperature.

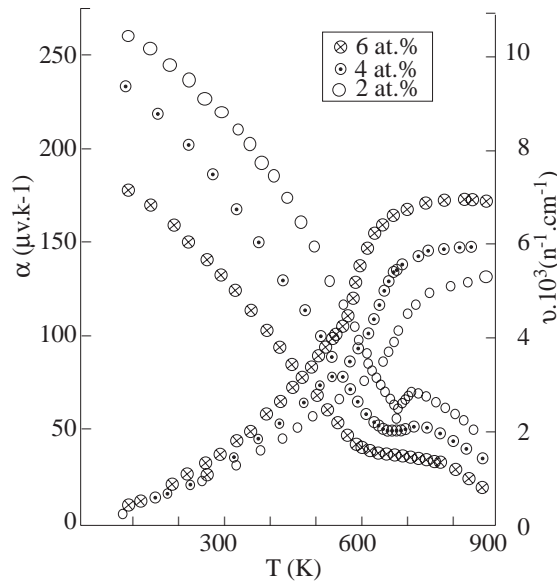
Concentration dependence of  $\alpha$ ,  $\sigma$ ,  $H_c$ ,  $R_H$  and  $Q_{N-E}$  are shown in Fig. 1 (the change in the amount of Te and Ge leads to a change in the hole concentration). In Fig. 2., Fig. 3. and Fig. 4. temperature dependence of  $\alpha$ ,  $\sigma$ ,  $R_H$  and  $Q_{N-E}$  are shown, respectively.

From Fig.1. we can see that when Ga concentration is increased  $\alpha(p)$  changes slowly and this curve fits the curve of GeTe. In this situation, while  $\sigma(p)$  and  $H_c(p)$  decrease,  $R_H(p)$  and  $Q_{N-E}(p)$  increase. Lattice component of the heat conduction and mobility increases with Ga contents (Fig.1). As shown in Fig. 2., at the beginning thermo e.m.f. increases with temperature, and the rate of increase is proportional to Ga concentration. A bending can be observed at a certain temperature range after which the curve reaches a maximum. This maximum moves to a lower temperature with rise of Ga concentration.



**Figure 1.** Changes of coefficients  $\alpha$ ,  $\sigma$ ,  $H_c$ ,  $\mu$ ,  $Q_{N-E}$  and  $R_H$  With concentration of Ga at 300K

( $y=0.03$ ; 2,3,4,5,6 at. % Ga)



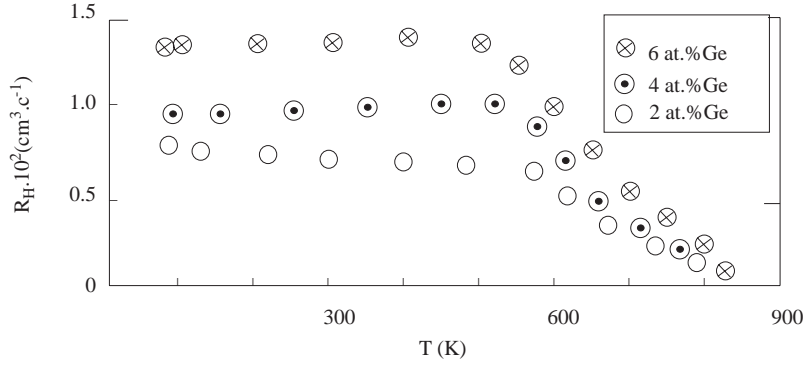
**Figure 2.** Temperature dependences of coefficients of  $\alpha$  and  $\sigma$  ( $y=0.03$ ) as a function of Gallium.

$\sigma$  decreases with Ga at low temperatures, but an abrupt conductivity hopping can be observed at low Ga concentration at high temperatures. Sharpness of this hopping decreases with Ga concentration [Fig.2].

Temperature dependence of electrical conductivity changes in correlation to  $T^{-S}$ . The concentration and temperature dependence of S is slow. For example, S is approximately 0,7-0,9 for  $T < 200$  K and is approximately 1,1-1,4 for  $T > 300$  K

Temperature dependence of  $R_H$  shows that [Fig.3.] a change in the  $R_H$  is not important for low concentrations of Ga; but for higher concentrations the rate of increase for  $R_H$  goes up and then it decreases at the narrow temperature interval 480-520 K for all samples. Thus, maximums in Fig.2. move strongly towards low temperatures with the rise of Ga concentration. If Te concentration goes up, the fall in the  $R_H(T)$  becomes more clear.

The temperature dependence of the Nernst-Ettingshausen coefficient, like the temperature dependence of  $R_H$  and  $Q_{N-E}$ , maintains negative sign in the investigated temperature range.



**Figure 3.** Temperature dependences of  $R_H$  coefficient ( $y=0.03$ )

## Discussion

As mentioned above, some authors [3,14,25,26] attribute the electrophysical properties of GeTe alloys to the separated bands of the L extremums, which are same for  $\alpha$ ,  $\beta$  and  $\gamma$  phases.  $\alpha$  and  $\beta$  phase crystal structure can be considered to occur with little deformation of  $\beta$  phase crystal structure during phase transition [3,10,27-31]. Thus the  $\beta \leftrightarrow \gamma$  phase transition may be realized either suddenly or slowly; however,  $\beta \leftrightarrow \alpha$  and  $\beta \leftrightarrow \gamma$  must be abrupt.

The results of X-ray analysis show that the lattice constant decreases because of the rise of vacancies with Te amount. In the same way rhombohedral deformation and the displacement of Ge atoms reduce with increase in Te concentration. Primitive cell volume increases little and the central position of Ge ions moves some with rise of Ga concentration (ion radii of  $\text{Ga}^{3+}$  and  $\text{Ge}^{2+}$  are 0,62 and 0,65 Å, respectively). The degree of rhombohedral deformation determines the splitting energy of the extremums.

The reason for the weak dependence of the thermo e.m.f. coefficient on Ga concentration may be explained qualitatively by the decrease of the overlap of the extremums. This means that the Fermi energy increases but state density decreases.

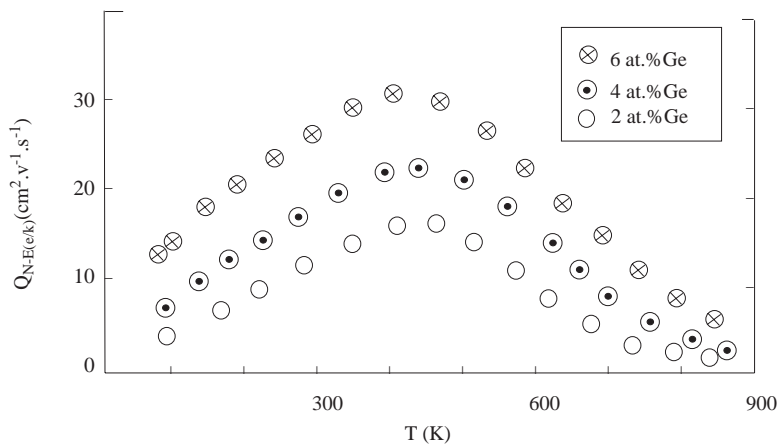
$\alpha$  is small for high hole concentration and is maximal for low hole concentrations (Fig.1). The anomaly observed on the temperature dependence of  $\alpha$  is related to the decrease in Fermi energy  $E_F$  and splitting energy  $\Delta^{\alpha,\gamma}$ . The reason for the decrease in this energy is the change in Fermi surfaces. The energies of extremums become equal after the transition to cubic phase and current carriers are shared by more extremums, while the  $\alpha$  concentration anomaly disappears (Fig. 1) and temperature dependence of  $\alpha$  steepens near the phase transition point. This result is supported by the increase in effective mass in the Fermi level, which is calculated from the quadratic law of dispersion. In this situation, hole mobility decreases with the rise of temperature. With high Ga concentration near the transition point there is reduction of hole mobility dependence on temperatures; for higher temperatures, this rate increases again.

Abrupt changes in the observed temperature dependence of electrical conductivity near phase transition point is related the rise of hole mobility. Thus hole scattering at high temperatures comes from acoustic phonons. In the phase transition, during charge flow, the Fermi energy reduces and mobility rises. A part of this increase may be compensated by the hole scattering contributed by the soft phonon branch [14].

In the cubic phase hole mobility is insensitive to doping materials.

Weak temperature dependence of the Hall coefficient (Fig.3.) at temperatures below the phase transition point and at low Ga concentration may be explained by the multi-zone effect which components the decrease of Hall coefficient during decrease of Fermi level.

Local anomaly in  $R_H(T)$  near phase transition point is related to the change in Fermi surface and multizone effect. The Fermi surface is not spherical and the value of  $R_H$  is not equal to 1 around the L extremum. Acceleration in the temperature dependence of  $R_H$  for high Ga concentration may be explained by the decrease in Fermi energy and increase in the Hall factor A ( $R_H=A/p.e$ ). If Te concentration is rised in the alloy, the shape of Fermi surface becomes more complex and harmonious with the effect Hall factor A decreases and abrupt change in  $R_H$  as a function of temperature occurs.



**Figure 4.** Temperature dependences of  $Q_{N-E}$  coefficient ( $y=0.03$ )

Thus it is understood from the above qualitative analysis that doping effects of Ga and Te on the kinetic parameters of rhombohedral and cubic phase are different in  $(Ge_{1-x}Ga_x)_{1-y}$  Te alloys. The observed anomaly in hole concentration and kinetic parameter as a function of temperature may be explained by the separation of L extremums according to the GeTe zone model.

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