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CONCENTRATION ANOMALIES OF PROPERTIES IN $Pb_{1-x}Ge_xTe$ SOLID SOLUTIONS

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The investigation of electrical conductivity, coefficient of thermal electromotive force, Hall coefficient, microhardness and mobility in $Pb_{1-x}Ge_xTe$ ($x = 0 \div 0.1$) alloys in the temperature range of 77–300 K was carried out. Anomalies were detected in isotherms of properties in the vicinity of $x = 0.008$. The anomalies were treated as a manifestation of concentration phase transitions occurring in solid solutions of any kind and associated with existence of critical concentration (percolation threshold) at which the uninterrupted chain of interactions between impurity atoms is formed.

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The detection of non-monotonic character of concentration dependence of properties in the region of small impurity concentrations in a number of solid solutions, including those based on $A^{IV}B^{VI}$ compounds (see, for example [1, 2]) stimulates systematical investigations in this direction.

The objects of the present investigation are solid solutions based on PbTe in $Pb_{1-x}Ge_xTe$ system ($x = 0 \div 0.1$). The solubility of GeTe in PbTe is significant and essentially depends on temperature [3]. A number of authors [4, 5] have revealed a ferroelectric phase transition in solid solutions based on PbTe. The temperature of the phase transition increases sharply with growing x, reaching $T = 100$ K at $x = 0.03$ [6].

The synthesized polycrystalline samples were subjected to homogenizing annealing at 820 K and slowly cooled. The limit of solubility of GeTe in PbTe, determined by microstructural and X-ray diffraction methods as well as from measurements of microhardness H, was found to be ≈ 3.5 mol%. For the prepared samples there was obtained temperature dependence of electrical conductivity σ, Hall coefficient R_H, coefficient of thermal electromotive force S and mobility μ_H in the range of 77–300 K. There were noticed anomalies in temperature dependence of σ and R_H. The temperature of the anomalies corresponds to ferroelectric transition temperature found previously by other authors [6]. On the basis of the obtained temperature dependence the isotherms of properties were plotted for $T = 80$ K and $T = 300$ K (Figs. 1 and 2). From the figures one can see that within homogeneity region the dependence of properties is non-monotonic. In the curves one can distinguish four subregions. In the first one ($x \approx 0 \div 0.008$) σ, S, R_H and μ_H

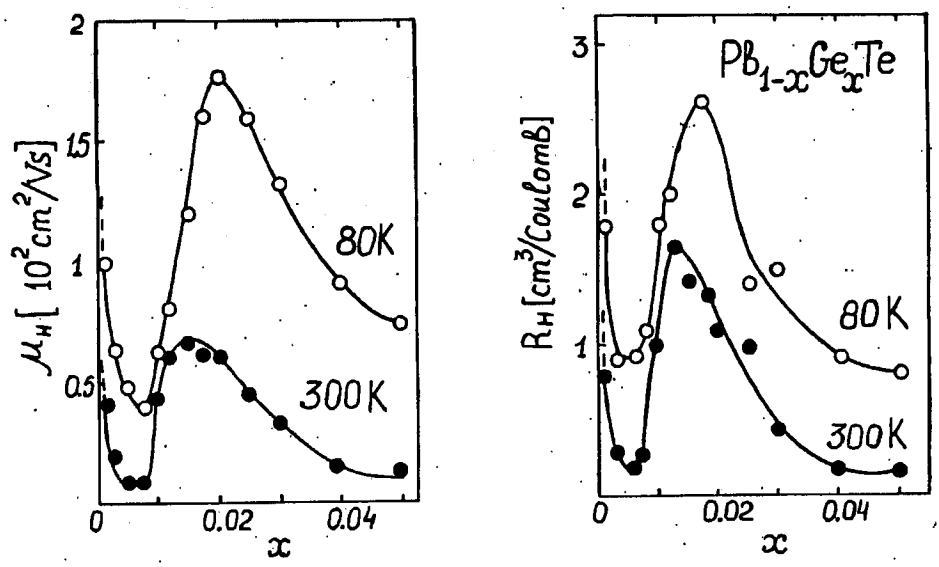

Fig. 1. Dependence of the Hall mobility μ_H and Hall coefficient R_H on the composition of $Pb_{1-x}Ge_xTe$ alloys at 80 K and 300 K.

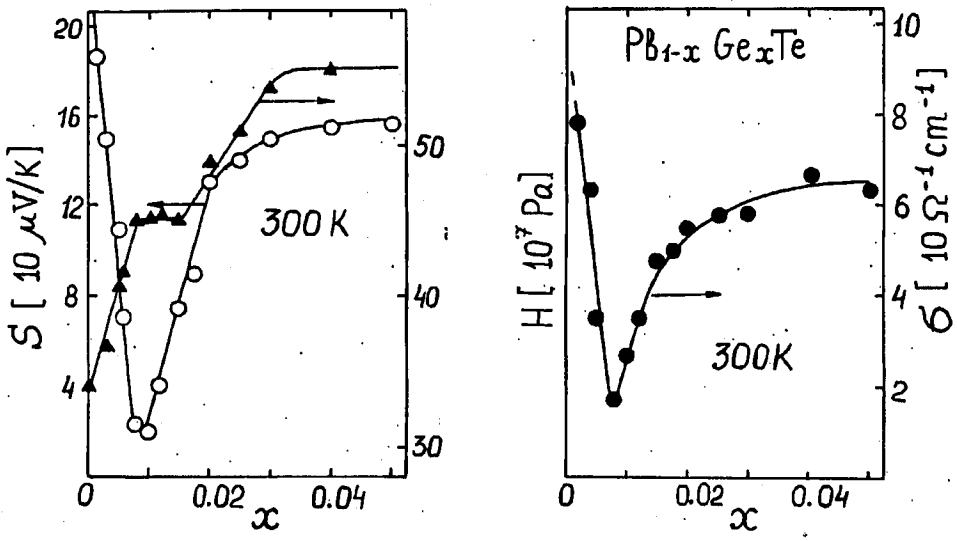

Fig. 2. Microhardness H, coefficient of thermal electromotive force S and electrical conductivity σ as functions of $Pb_{1-x}Ge_xTe$ alloy composition x at 300 K.

decrease, H grows; in the second one up to $x = 0.012 \div 0.02$ (it depends upon temperature) S, σ, R_H and μ_H grow, H remains practically constant. The third interval, which spreads to the boundary of homogeneity region ($x \approx 0.035$), is

characterized by a growth of S, σ, H, and a drop of R_H and μ_H. In the last subregion corresponding to the transfer into the two-phase region all the parameters remain virtually constant.

The abrupt decrease of μ_H and the sharp growth of H in the range of $x = 0 \div 0.008$ show that the introduction of the first portions of impurity ions of Ge, which are non-central into PbTe [6], leads to the strong distortion of periodical crystal field reaching its maximum degree at $x = 0.008$. The appearance of concentration anomalies of properties at subsequent increase in x can be interpreted in terms of our supposition about universal character of the anomalies reported earlier [1]. We believe that in any solid solution irrespective of microscopic nature of interactions between impurity atoms, there is a concentration phase transition into a qualitatively new state when perturbation in matrix caused by presence of impurity atoms becomes delocalized. This idea is based on the basic principles of the percolation theory [7].

Assuming the properties to be isotropic let us denote the radius of "action sphere" of impurity atom as R_0. In diluted solid solution impurity atoms are located at so large distances from each other that these spheres virtually are not contiguous. One can expect a qualitative change of properties when "action spheres" begin to overlap all over the crystal. According to one of the problems of percolation theory, the problem of spheres, if in a three-dimensional space there are spheres of radius R_0, whose centers are distributed randomly and at average evenly with concentration N_c, there is a critical concentration (percolation threshold) at which percolation through the overlapping spheres arises, in other words there arise the ways (infinite clusters) penetrating the whole crystal. This concentration is determined from the condition [8]

$$\frac{4}{3}\pi N_c (2R_0)^3 \approx 2.7. \tag{1}$$

Taking into account all the above mentioned, one can predict critical phenomena in any solid or liquid solution connected with existence of the percolation threshold.

From the stand point of this concept there are two qualitatively different states of solid solution within homogeneity region. The transition from one to the other should be accompanied by the critical phenomena and appearance of anomalies in dependence of property on composition. The value of the critical concentration x_c depends on R_0.

In accordance with the data obtained (Figs. 1, 2) the critical point is close to $x \approx 0.008$. The subsequent growth of σ, R_H, S, μ_H and the drop of H are supposed to be connected with formation of the percolation channels because the appearance of the latter causes the change of elementary excitation propagation speed. As it is seen from Figs. 1 and 2 the extention of anomalous region is determined by temperature: at 300 K $x \approx 0.008 \div 0.012$, at 80 K $x \approx 0.008 \div 0.02$. The possible interpretation of this fact is as follows. At 80 K ferroelectric phase transition can be observed at $x \approx 0.02$ and above, whereas at 300 K this concentration is essentially higher [6]. Therefore, at 80 K concentrations corresponding to the percolation transition ($x \approx 0.008$) and ferroelectric transition ($x \approx 0.02$) are rather close which

makes it practically impossible to distinguish them in isotherms of properties. The idea of existence of two concentration phase transitions is supported by observed broadening of curves and shift of maxima of R_H and μ_H to the region of higher x at 80 K in comparison with 300 K. At 300 K we can notice only the percolation transition. The calculation performed using formula (1) ($N_c \approx 1.2 \times 10^{20}$ cm^{-3}) shows that R_0 is roughly equal to $1.36a_0$, where a_0 is the unit-cell parameter. This value is close to $R_0 = 1.4a_0$, which corresponds to close packing of impurity spheres with formation of fcc lattice with the unit-cell parameter $a = 4a_0$. Thus, the formation of superstructure in impurity subsystem of crystal at the critical concentration is quite possible.

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