Charge carrier mobility in semiconductor solid solutions and percolation phenomena

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Abstract. The existence of a range of an anomalous growth in charge carrier mobility under the transition to heavy doping is established for Bi_2Te_3 -Sb_2Te_3 solid solutions. This confirms our suggestion about the universal character of critical phenomena accompanying the transition from impurity discontinuum to impurity continuum. The experimental results are analyzed in terms of percolation theory taking into account alloy scattering and spatial correlations of impurity centers.

1. Introduction

Materials based on heavily doped semiconductors are widely used in various semiconductor devices [1]. That is why studying the transition from weak to heavy doping when the interaction between impurity atoms starts to make a substantial contribution to the formation of crystal properties, is of special interest. In the available literature on heavy doping, the behavior of the electron subsystem under changing impurity concentration is usually considered (e.g. the Mott transition). At the same time, it is the lattice subsystem that determines such important parameters as charge carrier mobility, phonon thermal conductivity, lattice specific heat, and so on. This stimulates detailed studies of the dependences of properties on the composition in the range of small impurity concentrations.

Earlier, we revealed anomalies in the behavior of different physical properties in IV-VI – based semiconductor solid solutions in the range of small impurity concentrations (0.5-1.0 at.%) and suggested that those anomalies have a universal character and are connected with the transition to heavy doping (see, for example [2-7]). Such transition is expected to be accompanied by critical phenomena, which, in turn, manifest themselves through anomalies in the concentration dependences of different properties. To confirm the suggestion about the universal character of the concentration-dependent anomalies of properties in solid solutions, it is necessary to expand the scope of objects and properties to be studied.

The objects studied in this work are Bi_2Te_3- and Sb_2Te_3-based semiconducting solid solutions in the Bi_2Te_3 -Sb_2Te_3 system. Bi_2Te_3 and Sb_2Te_3 have a rhombohedral crystal lattice of a tetradymite type and form between themselves a continuous series of solid solutions [8]. The stoichiometric Bi_2Te_3 and Sb_2Te_3 exhibit *p*-type conductivity due to the presence of antisite defects. Bi_2Te_3-Sb_2Te_3 solid solutions belong to the best low temperature thermoelectric materials, broadly applied for manufacturing various types of refrigerating devices, and the most efficient materials for use near room temperature [8-10]. One of the most important tasks of the development of efficient thermoelectric materials is increasing the ratio of charge carrier mobility μ to lattice thermal conductivity, which is usually attained by forming solid solutions. That is why understanding the behavior of properties of those materials under the introduction of new components is very important from not only the scientific but also the practical point of view.

Recently, interest in investigating the V_2VI_3 semiconducting compounds has grown sharply due to the prediction and subsequent experimental evidence of their special properties characteristic of 3D-topological insulators. It is pointed out that one of the ways of using these unique surface properties in practice, in particular for thermoelectric applications, is the introduction of impurities with a view to reducing charge carrier concentration in the volume of a crystal [11-13].

The goal of the present work is to study the behavior of the Hall charge carrier mobility in the range of compositions corresponding to the transition from weak to heavy doping in Bi_2Te_3 -Sb_2Te_3 solid solutions.

2. Experimental

Two series of solid solutions in the Bi_2Te_3 -Sb_2Te_3 system were synthesized: Bi_2Te_3-based (0 – 7 mol.% Sb_2Te_3) solid solutions and Sb_2Te_3-based (0 – 7 mol.% Bi_2Te_3) solid solutions. Polycrystalline samples were prepared by direct melting of high-purity elements in evacuated quartz ampoules at 1070 K with subsequent annealing at ∼ 650 K for 300 h. X-ray spectroscopy and selective chemical analysis confirmed the homogeneity of the samples and showed that deviation of the actual chemical composition of the prepared samples from the intended one did not exceed ± 0.02 at. %. The electrical conductivity σ and the Hall coefficient R_H were measured at room temperature using the van der Pauw method with an error not exceeding 5 %. The Hall carrier mobility μ_H was calculated as $\mu_H = \sigma \cdot R_H$. All the alloys exhibited p-type conductivity.

3. Results and discussions

In figure 1, the room-temperature dependences of Hall charge carrier mobility on the Sb_2Te_3 (for the Bi_2Te_3-based solid solutions) or Bi_2Te_3 (for the Sb_2Te_3-based solid solutions) content are presented. It is seen that for both the Bi_2Te_3-based and Sb_2Te_3-based solid solutions, after the initial drop in μ_H which occurs under increasing concentration of Sb_2Te_3 (or Bi_2Te_3) up to ∼ 0.5 mol.%, μ_H grows in the interval between ∼ 0.5 and ∼ 1 mol.% and then decreases.

It is natural to attribute the drop in μ_H under the introduction of the first portions of the impurity to an increase in scattering of holes by impurity defects, but the subsequent sharp growth in hole mobility cannot be interpreted in terms of the traditional model of alloy scattering which is usually applied to explain a decrease in μ_H in solid solutions when an impurity is introduced.

The anomalous increase in charge carrier mobility that we observed in the two studied systems within a narrow concentration interval in the range of small impurity concentrations indicates the existence of a phase transition. Within the framework of ideas we have developed earlier [14,15], this is a percolation-type transition from an impurity discontinuum to an impurity continuum.

According to modern notions [16-18], there is a direct analogy between percolation theory and fluctuation theory of second-order phase transitions. In both cases, in the vicinity of a transition, properties of the system are determined by strongly developed interacting fluctuations, peculiarities of thermodynamic quantities obey a power law, and their exponents are called critical exponents.

The effects observed in this work provide additional support for our proposition about the universal character of critical phenomena accompanying the transition from weak to heavy doping. For comparison, we also show previously obtained data for the PbTe - PbSe system [2]. It is seen that in that system, in a relatively narrow concentration range of a second component (~0.5-2.0 mol.%), the anomalous increase in μ_H is also observed.

Applying the short-range interaction approximation, assuming a random distribution of impurity atoms and using the ideas of percolation theory, one can estimate the radius of the impurity atom's "action sphere" R_o, knowing the concentration of impurity atoms corresponding to the percolation threshold x_C at which a continuous chain of overlapping deformation fields passing through the entire crystal (infinite cluster) is formed. In accordance with one of the problems of percolation theory – the problem of spheres – one can write:

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

where N_c is the average number of sphere centers per volume unit, corresponding to the percolation threshold. Determining the percolation threshold as the concentration of the impurity component (Bi_2Te_3 or Sb_2Te_3) corresponding to the beginning of the anomalous section of the curve (0.5 mol. %), we obtain that for the Bi_2Te_3–based (Sb_2Te_3-based) solid solutions $R_0 \approx 1.5$ a_0 (a_0 is the Bi_2Te_3 (Sb_2Te_3) pseudocubic unit cell parameter calculated as $a_0 = V^{1/3}$, where V is the unit cell volume of the Bi_2Te_3 (Sb_2Te_3) crystal).
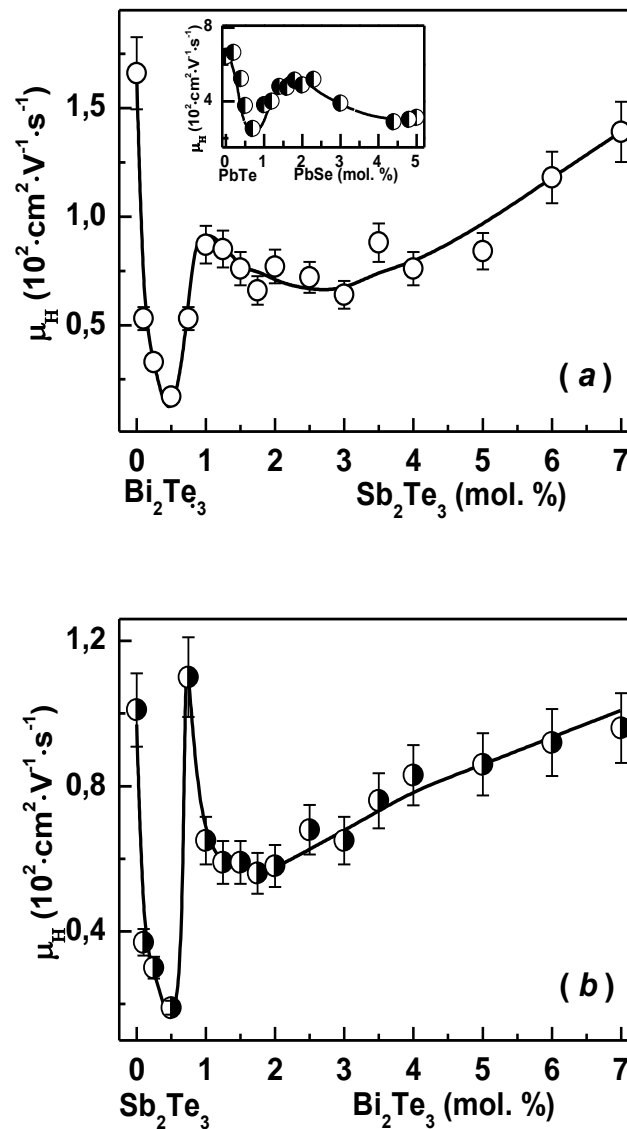

Figure 1. Room-temperature dependences of Hall charge carrier mobility μ_H on Sb_2Te_3 (a) or Bi_2Te_3 (b) concentration in Bi_2Te_3-Sb_2Te_3 solid solutions. Inset: the analogous dependences for the PbTe - PbSe system [2]

The formation of continuous chains of interacting impurity atoms can stimulate a redistribution of impurity atoms leading to the realization of their configuration corresponding to a minimum of the thermodynamic potential. Possible self-organization processes may include a long-range ordering of

impurity atoms. The sharp change in the properties in the vicinity of the percolation threshold suggests that the formation of an infinite cluster may be a trigger mechanism for the ordering of atoms, for example as a result of deformational interactions.

On the other hand, the Coulomb attraction between charged defects of opposite signs stimulates processes of chemical interaction leading to the formation of neutral molecular complexes. In this case new structural elements appear, and the formation of percolation channels through these elements becomes possible. Such processes are more probable in heterovalent solid solutions than in isovalent ones, and we observed them, for example in PbTe-Bi_2Te_3 solid solutions [19]. We introduced the concept of "the complex formation threshold" [20], which is somewhat similar to the percolation threshold but in this case percolation occurs not via separate atoms but via complexes. In the isovalent Bi_2Te_3-Sb_2Te_3 solid solution such processes are less probable, than in heterovalent ones, and, judging from figure 1, no additional anomalies in the μ_H dependence on composition are observed.

4. Conclusions

It is shown that in the Bi_2Te_3-Sb_2Te_3 solid solutions, at impurity concentrations in the range 0.5-1.0 mol % in the dependences of Hall charge carrier mobility on composition, an anomalous growth in μ_H is observed. We attribute these peculiarities to the transition, occurring under increasing impurity content, to the impurity continuum when the interaction of impurity atoms becomes cooperative. The results obtained in this work for the isovalent solid solutions formed by cation substitution represent another evidence for the proposition about the universal character of critical phenomena accompanying the transition from weak doping to the formation of impurity continuum.

Acknowledgement

References

[1] Bonch-Bruevich V L and Kalashnikov S G 1978 *Semiconductor Physics* (Moscow: Nauka)
[2] Rogacheva E I and Vodorez O S 2013 *J. Thermoelectricity* **2** 61
[3] Rogacheva E I, Sinelnik N A and Nashchekina O N 1993 *Acta Phys. Pol.* **84** 729
[4] Rogacheva E and Krivulkin I 2002 *Semiconductors* **36** 966
[5] Rogacheva E 2003 *J. Phys. Chem. Solids* **64** 1579
[6] Rogacheva E, Vodorez O and Nashchekina O 2013 *J. Phys. Chem. Solids* **74** 35
[7] Rogacheva E *et al* 2014 *Phys. St. Sol.* B. **251** 1231
[8] Rowe D M 2012 CRC *Handbook of Thermoelectrics* (Boca Raton, FL: CRC Press, Taylor & Francis Group)
[9] Goldsmid H J 2014 *Materials* **7** 2577
[10] Bell L E 2008 *Science* **321** 1457
[11] Zhang H *et al* 2009 *Nat. Phys.* **5** 438
[12] Chen Y L *et al* 2009 *Science* **325** 178
[13] Xia Y *et al* 2009 *Nat. Phys.* **5** 398
[14] Rogacheva E I 1993 *Jpn. J. Appl. Phys.* **32** 775
[15] Rogacheva E I, Nashchekina O N and Dresselhaus M S 2005 *J. Thermoelectricity* **4** 82
[16] Stauffer D and Aharony A 1992 *Introduction to percolation theory* (London; Washington, DC: Taylor & Francis Group)
[17] Shklovskii B I and Efros A L 1984 *Electronic Properties of Doped Semiconductors* (New York: Springer-Verlag).
[18] Patashinskiy A Z, Pokrovskiy V L 1982 *The fluctuation theory of phase transitions* (Moscow Nauka).
[19] Rogacheva E I, Vodorez O S, and Nashchekina O N 2013 *J. Phys. Chem. Solids* **74** 35
[20] Rogacheva E I, 2009 *Phys Status Sol C*. **6** 1307