

## Critical Phenomena in Heavily-Doped Semiconducting Compounds

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One of the main ways of controlling properties of semiconducting materials is introduction of new components—doping—which is accompanied by solution of impurities in the matrix crystal lattice. Solid solutions, the most widespread materials, have wide practical applications.

It is usually considered<sup>1)</sup> that the properties change in a monotonous way in the solid solution region and appearance of inflection points in the composition dependences of properties indicates the intersection of phase region boundaries. However the analysis of literature data on investigation of solid and liquid solutions of different types shows that in a number of cases in the range of small impurity concentrations (up to ~ 1 at.%) anomalies are observed. Different authors explain them in different ways, *e.g.* by deviation from stoichiometry, valency change, interactions between intrinsic and impurity defects, ordering etc.<sup>2-5)</sup>

From our standpoint, the existence of the anomalies is the universal property of solid and liquid solutions.

Let us consider what occurs in solid solutions upon increasing impurity concentration. Assuming that the properties are isotropic and interactions are shortrange, let us designate the radius of impurity atom “action sphere” within which the crystal properties differ considerably from matrix properties as  $R_0$ . At small impurity concentrations when  $d \gg R_0$  ( $d$  is the average distance between impurity defects) impurity atoms being the centers of local distortions of electron and phonon spectra are distributed in a crystal statistically and interactions between them can be neglected. Upon increasing the impurity concentration the condition  $d \gg R_0$  is infringed and regions of perturbation begin to overlap.

From general considerations it is evident that regardless of character of interaction between impurities (Coulomb, deformational, magnetic etc.) the properties of liquid or crystal will change qualitatively when uninterrupted chain of overlapping impurity spheres is formed since formation of the channels penetrating the whole crystal is connected with change of elementary excitation propagation speed. This is confirmed in particular by existence of Mott transition (metal-insulator) occurring on introducing shallow impurities into semiconductor, appearance of magnetization at definite concentration of ferromagnetic atoms in paramagnetic matrix.

Let us designate the uninterrupted chains of overlapping spheres of radius  $R_0$  without taking into account the type of interactions as “impurity condensate” and the process of their formation as “condensation of impurity vapour”.

There arises the question: is there definite critical concentration of impurity atoms at which the uninterrupted chain of impurity spheres is formed or transition to the indicated state occurs permanently? This problem should be considered in the framework of percolation theory<sup>6,7)</sup> which deals with coherency of great amount of elements under condition that the bond of each element although being defined in some particular way has casual character. In accordance with one of the problems of percolation theory, viz. “problem of spheres”, for the model described above there is a critical concentration-percolation threshold at which in some infinite system the channels penetrating the whole system appear and infinite cluster consisting of overlapping spheres of radius  $R_0$  is formed. This concentration is determined by the condition;

$$\frac{4}{3} \pi \cdot N_c (2R_0)^3 \approx 2.7, \quad (1)$$

where  $N_c$  is average number of sphere centers per volume unit. From the abovestated one can predict the critical phenomena in any liquid or solid solution associated with existence of “percolation threshold”.

The formation of the “impurity condensate” is expected to result in appearing anomalies of properties in vicinity of critical composition. The character of change of properties is probably similar to one which occurs at critical phenomena when abrupt fluctuation growth leads to anomalous scattering of electromagnetic waves, drop of charge carrier mobility, thermal conductivity and etc. In some cases percolation transition is accompanied by appearance of qualitatively new property absent in matrix (Mott transition, appearance of magnetic, ferroelectric and other properties). Reaching the critical concentration stimulates process of impurity atom redistribution over the crystal so as to realize the configuration corresponding to minimum thermodynamical potential-ordering of impurity atoms, complex formation and so on.

Far ordering of impurity atoms (“crystallization of impurity liquid”) requires the following conditions: 1)  $N \geq N_c$ ; 2) energy of ordering is high enough in comparison with  $kT$ ; 3) the average distance between impurity atoms corresponds to their regular distribution in the sites of appropriate sublattice ( $d = na_0$  and  $d = 2na_0/\sqrt{3}$ , respectively for cubic simple and fcc lattices formed by impurity atoms,  $n$  is integer,  $a_0$  denotes unit-cell parameter of matrix). The formation of superstructure is expected to cause appearance of extremum points in dependences of properties. In the absence of ordering the anomalies in the curves of properties connected with the beginning of percolation will not be so pronounced.

As an example let us consider the influence of interactions of static deformation fields formed by impurity atoms on mechanical properties, in particular on microhardness  $H$ . From the stand-point of contemporary concepts the main mechanism of strain hardening due to point defects consists in blocking dislocation movement by impurity atoms. The interaction of elastic deformation local fields of impurity atoms with elastic deformation field of dislocation results in impeding dislocation movement. As it is known from experiment the hardening in diluted solid solutions is usually proportional to concentration. It is associated with the big distance between impurity atoms ( $d \gg R_0$ ). As a result elastic deformation fields are localized and isolated from each other and give an additional contribution into  $H$  magnitude.

Let us model elastic interactions between impurity atoms by the interaction between deformation spheres with radius  $R_0$ . At  $d = 2R_0$  spheres are contiguous to each other. Subsequent decrease of  $d$  leads to their overlapping which means the beginning of elastic interaction. This interaction causes redistribution of elastic deformation field energy and, consequently, change in energy of interaction between dislocation and impurity atom. In the region of overlapping of the spheres strains are partially relaxed due to compensation of the strains of opposite signs, relaxing of strains being maximum at  $d = R_0$ . For  $d < R_0$  the character of strain redistribution changes. When impurity atoms are distributed regularly the interactions between the spheres begin simultaneously over the whole crystal, diminution of strains has a cooperative character and at definite impurity atom concentration one can expect the sharp drop of  $H$ . Extremum or inflection point in  $H$  vs concentration curve indicates beginning of cooperative deformation interaction between impurity atoms corresponding to the formation of infinite cluster. From the location of this point one can estimate  $R_0$  using eq. (1).

We have performed the systematical investigations of properties vs composition curves of solid solutions based on  $A^{IV}B^{VI}$  binary compounds as well as  $A^I B^{III} C_2^{VI}$  ternary ones. The investigation of a great number of solid solutions shows that in the region of small impurity concentrations (up to 1 at.%) in the concentration dependences of properties there are observed the anomalies. In Fig. 1 the graphs of microhardness, Hall mobility and charge carrier concentration  $n$  as functions of concentration in PbTe-CdTe system are given. In the vicinity of some concentration close to  $\sim 0.5$  mol.% the anomalous behaviour of dependences is noticed. In PbTe-CdTe system within homogeneity region one can mark out at least three subregions with different character of concentration dependences of properties: 1) 0–0.4; 2) 0.4–0.6 and 3) above 0.6 mol.% CdTe. From our point of view the first interval is a region of diluted solid solutions; the second one is a critical region corresponding to percolation and formation of infinite cluster and the third is an interval of concentrated solid solutions. The abrupt growth of  $n$ ,  $H$  and decrease of  $\mu_H$  in the range from 0 up to  $\sim 0.4$  mol.% CdTe shows that upon introducing the first portions of impurity the strong crystal distortion occurs, the latter reaching its maximum at approximately 0.4 mol.%

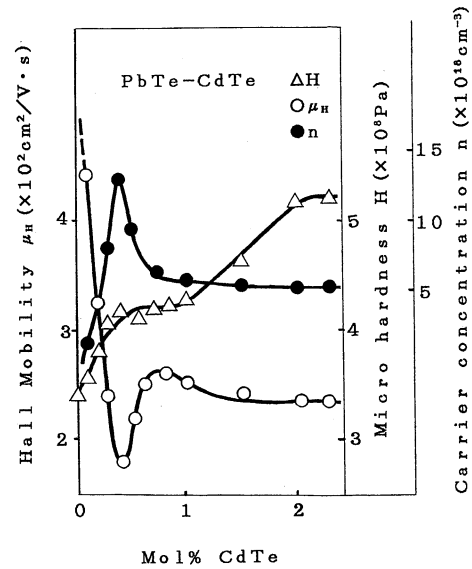


Fig. 1. Dependence of microhardness  $H$  ( $\Delta$ ), Hall mobility of charge carriers  $\mu_H$  ( $\circ$ ) and concentration of charge carriers  $n$  ( $\bullet$ ) on CdTe content of solid solutions based on PbTe in PbTe-CdTe system.

CdTe. Then interaction between particles stimulates structure ordering. The location of peculiarities (0.4 mol.% CdTe) corresponds to  $d \approx 4a_0$ . The calculations performed on the basis of eq. (1) show that radius  $R_0$  of sphere of deformation created by Cd atom is equal to  $1.9a_0$ . This value is close to one corresponding to close packing of spheres with radius  $R_0$ .

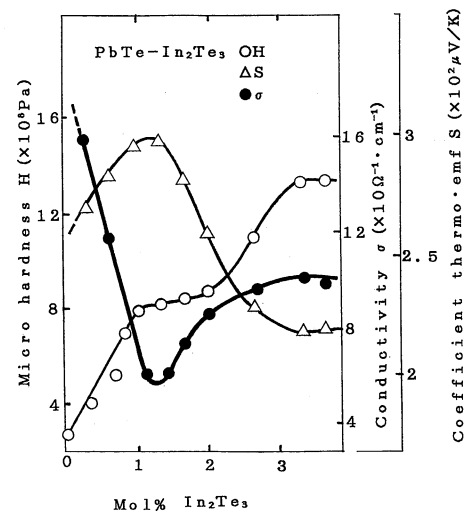


Fig. 2. Microhardness  $H$  ( $\circ$ ), coefficients of thermo-emf  $S$  ( $\Delta$ ) and electrical conductivity  $\sigma$  ( $\bullet$ ) as functions of  $In_2Te_3$  content in solid solutions based on PbTe in PbTe- $In_2Te_3$  system.

Figure 2 represents the concentration dependences of microhardness, electrical conductivity  $\sigma$  and thermo-emf coefficient  $S$  in PbTe- $In_2Te_3$  system which are also characterized by presence of anomalies near 1 mol.%  $In_2Te_3$ . From the curves in Fig. 3 one can see that at certain concentrations the monotonic behaviour of dependence of  $H$  vs composition is broken. It is observed not only at isova-

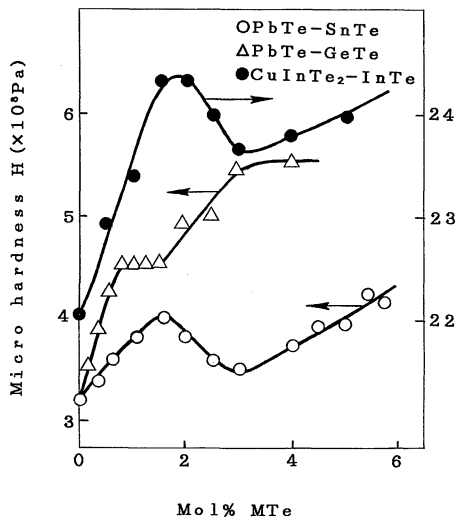


Fig. 3. Microhardness vs impurity content in solid solutions based on PbTe and CuInTe<sub>2</sub>: ○—PbTe-SnTe; △—PbTe-GeTe; ●—CuInTe<sub>2</sub>-InTe.

lent but also at heterovalent substitution. The location of inflection point in different systems differs. For instance, in PbTe-GeTe system  $N_c$  is approximately equal to

$1.1 \times 10^{26} \text{ m}^{-3}$  which corresponds to  $R_0 \approx 1.4a_0$ . In PbTe-SnTe and CuInTe<sub>2</sub>-InTe systems sharp drop of  $H$  begins at  $N_c \sim 2.2 \times 10^{26} \text{ m}^{-3}$  which is close to  $R_0 \approx 1.2a_0$ .

Thus, the present data point out to existence of threshold impurity concentration at which the qualitative change of solid solution state associated with formation of percolation channels in crystal and with transition from impurity discontinuum to impurity continuum occurs. Introduction of a doping component into the ordered crystal leads first to disordering crystal by uninteracting impurity atoms, but then condensation of "impurity vapour" induces ordering processes.

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