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Abstract: The chapter reviews the present status of our experimental studies aimed at confirming the existence of anomalies in the dependences of thermoelectric (TE) and other properties on composition in semiconductor IV-VI-based solid solutions in the region of small impurity concentration. For all studied solid solutions, we observed an anomalous behavior of the isotherms of electrical conductivity, phonon thermal conductivity, heat capacity, charge carrier mobility, microhardness, the Seebeck coefficient, and TE figure of merit in the vicinity of (0.5–1) at. % of impurity. We believe that the observed phenomenon is connected with the existence of percolation-type phase transitions corresponding to the transition from dilute solid solutions to the impurity continuum and is accompanied by self-organization processes. The non-monotonic behavior of the concentration dependences of the TE properties and the underlying percolation phenomena should be taken into consideration when developing efficient TE materials and optimizing their properties. To get additional confirmation of the assumption regarding the universal character of phase transitions connected with the formation of the impurity continuum, it is necessary to expand the range of objects to be studied as well as spectrum of properties to be measured.

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