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Investigations of multiphase states in vicinity of pressure-induced phase transitions

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In the present work equations have been derived for thermomagnetic and galvanomagnetic effects of multiphase systems. The equations allow us to analyse complex thermal–electrical–magnetic properties of semiconductors under variation of concentration and configuration of inclusions. The results obtained make it possible, for example, to explain discrepancies between values of phase-transition pressure determined from thermal, electrical, volumetric and other effects. A model developed has been applied for analysis of semiconductor–metal phase transitions. The approach offered allows us also to search for ways for improvement of thermoelectric and thermomagnetic effectiveness and figure of merit of complex semiconductor systems.

1 Introduction

The modern ultra-high-pressure technique with diamond anvils allows us to test samples with sizes about that of electronic microdevices ~10–100 μm [1]. Non-electrical types of investigations at ultra-high pressure (optical, X-ray, synchrotron, etc.) are developed more actively than electrical ones – electrical resistance [2], thermoelectric power S [3, 4] and magnetoresistance (MR) measurements [5]. The MR technique at high pressure developed by using sintered diamond anvils with pressed outputs to a sample [5] was able to test a value of mobility of charge carriers and changing of scattering mechanism in high-pressure phases of HgX (X – Te, Se, S, O) [5]. Similar two-terminal MR techniques have been applied for determination of concentration and mobility of electrons in semiconductor microdevices (HgCdTe infrared detectors of $100 \times 50 \times 8$ μm size) [6]. In Refs. [7–9] a technique of thermomagnetic (TM) measurements has been developed at ultra-high pressures up to 30 GPa allowing us to estimate mobility and scattering parameters of charge carriers [10]. It seems that TM measurements are more effective in comparison with analogous galvanomagnetic (GM) ones (Hall effect and MR) [7–11].

In the vicinity of phase transitions under pressure the materials become a mixture of phases. By varying pressure one can change both concentration and configuration of phase inclusions. Interest in investigating these phenomena is due to proposed applications in engineering [12–15]. For a description of the properties of real heterophase structures an approach was developed using a model of oriented phase inclusions with variable geometrical configuration; the calculations of thermoelectric properties were performed in Refs. [12, 16, 17]. But TM properties of heterophase systems were not considered up to now. By using an automated setup [13, 14, 16] the simultaneous measurements of electrical, thermal,

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thermomagnetic, volumetric, etc., properties of a large amount of semiconductors undergoing pressure-induced phase transitions have been performed up to 30 GPa and some peculiarities have been found near the phase-transition points [18–31]. Crystal structure investigations by X-ray, synchrotron and neutron radiation allowed us to attribute an origin of unusual properties of samples in the vicinity of pressure-induced phase transitions to phase inclusions [32–34]. Now the effect of phase mixing on TM properties is also of interest.

So, the purpose of the present paper was to obtain mathematical equations for TM and GM effects, including longitudinal and transverse Nernst–Ettingshausen (N–E) ones, and the Hall effect for multicomponent heterosystems.

2 Model of calculations

The calculations have been performed with the assistance of a simple but pictorial model of a heterophase system (Fig. 1) [12–14]. Usually, in experiments one can determine only effective characteristics of material (averaged over the total volume of the substance measured). These effective properties contain "geometrical" parameters of every phase: concentration, shape and position of inclusions [35–37]. Effective properties (thermal, magnetic, mechanical [35]) are calculated by two main approaches: in the first, the local properties of the system are supposed to be well-known functions of coordinates; in the second, they are considered statistically as random fields [35–37].

The equations for effective electrical resistivity (ρ) of a multiphase heterosystem have been obtained by solving the problem of an isotropic dielectric ellipsoid in an electric field [38]. In Ref. [35] the expressions were considered for upper and lower bounds of the effective conductivity of the system in the cellular model of the statistical approach. In the cellular model, the total volume is covered by a system of non-overlapping cells in the form of ellipsoids. Under chaotic packing of ellipsoids a dependence of bounds on the form of the inclusions is determined by parameters G_i ($\frac{1}{9} \le G_i \le \frac{1}{3}$), which are equal to $\frac{1}{9}$, $\frac{1}{6}$ and $\frac{1}{3}$ for spherical, needle and disc inclusions, respectively. To take into account the different ways of packing ellipsoids, in this approach two additional parameters have been inputted; in some cases similar values for upper and lower bounds of ρ may be obtained [35]. However, the approach described is very laborious because of enormously awkward calculations.

In Refs. [12–14] an approach has been developed for multicomponent composite materials. Unlike most previous models [37–39], where the shape of the inclusions was fixed, in the model a configuration parameter of phase inclusions is variable between extreme limiting cases of parallel and consequent (electrical, thermal) connections. The second novel feature of the model is simultaneous consideration

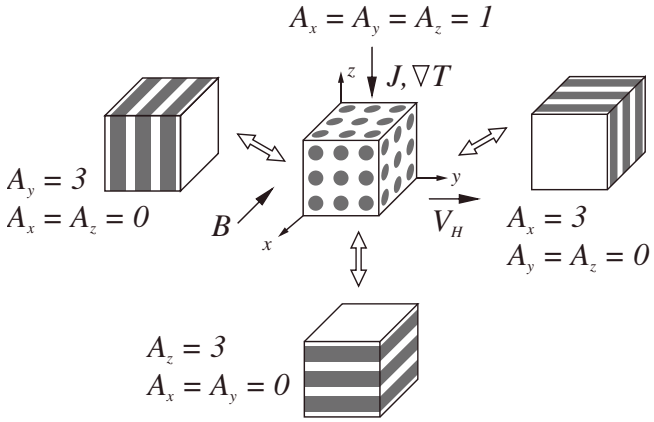

Fig. 1 Peculiar cases of materials with various configurations of phases' inclusions (planes). Parameters A for different cases are given in the figures. The black arrows show directions of electrical current J (thermal gradient ∇T), magnetic field B and resulting voltage V_H of transverse Nernst–Ettingshausen and Hall effects.

and comparison of several properties of the material for the same geometrical configuration. In this approach an effective electrical resistivity ρ and conductivity $\sigma = 1/\rho$ (and thermal conductivity λ) are viewed as normalized sums of phase contributions in two equivalent considerations of "consequent" and "parallel" electrical (thermal) connections of phases [12–14]:

$$\rho = \sum c_i \rho_i f_i(\rho) \left(\sum c_i f_i(\rho) \right)^{-1}, \tag{1}$$

$$\sigma = \sum c_i \sigma_i f_i(\sigma) \left(\sum c_i f_i(\sigma) \right)^{-1}, \tag{2}$$

where the sum of the phase concentrations c_i is equal to 1 and the configuration parameters along the electrical (thermal) current are

$$f_i(\rho) = 3\rho / [A\rho + (3-A)\rho_i], \qquad f_i(\sigma) = 3\sigma_i / [A\sigma_i + (3-A)\sigma]. \tag{3}$$

When the constant A equals 0, 3 or 1, Eqs. (1) and (2) coincide with the cases of parallel, and consequent electrical connections, and with the spherical shape of the phase's inclusions, respectively (Fig. 1) [37, 38]. Intermediate values of A ($0 < A < 3$) correspond to an interpolated configuration of inclusions in a certain direction (like elongated or contracted ellipsoids) (Fig. 1).

For two-phase heterosystems, we obtain a second-order polynomial:

$$A\rho^2 + \rho[\rho_2(3c_1 - A) + \rho_1(3c_2 - A)] - \rho_1\rho_2(3-A) = 0, \tag{4}$$

and the dependences of ρ and λ^{-1} on c_i (Fig. 2) are similar to ones of certain models of spherical and ellipsoidal inclusions [35–40]. By using the analogy between electrical, elastic, etc., phenomena [35] similar equations may also be obtained for elastic properties. An appropriate equation for S of heterophase materials taking into account both thermal flux and electrical current distribution within the sample's volume is as follows:

$$S = \left(\sum_i S_i c_i f_i(\rho)\, \lambda_i^{-1} f_i(\lambda) \right) \Big/ \left(\sum_i c_i f_i(\rho) \sum_i c_i \lambda_i^{-1} f_i(\lambda) \right). \tag{5}$$

Equations (1)–(4) give a similar coincidence with results of the model used for heterophase systems with a certain configuration (ellipsoidal, spherical, etc.) of inclusions [39–45], and Eq. (5) accords well with exact results obtained for spherical inclusions [41, 44] and for randomly distributed inclusions [42].

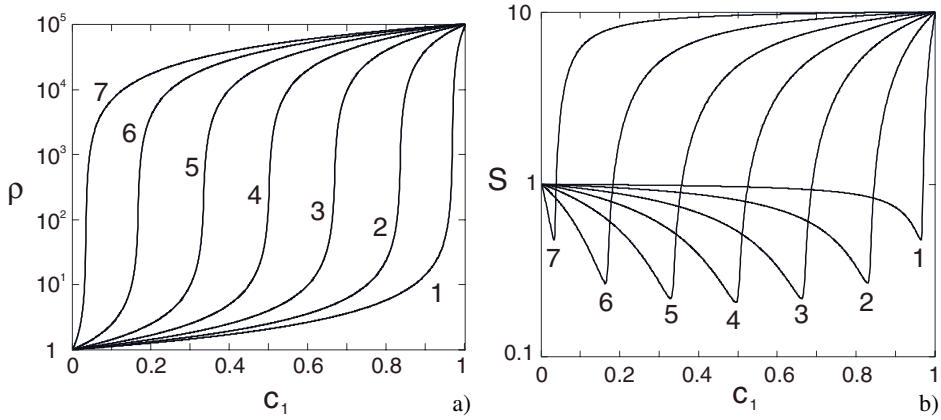

Fig. 2 Calculated dependences of resistivity $r = \rho(c_1)$ (a) and thermopower $S(c_1)$ (b) of two-phase system ($\lambda_1 = 1$, $\lambda_2 = 100$, $\rho_1 = 10^5$, $\rho_2 = 1$, $S_1 = 10$, $S_2 = 1$ a.u.) on concentration c_1 of phase 1. The parameters A are equal to: 1 – 0.1; 2 – 0.5; 3 – 1.0 (spheres); 4 – 1.5; 5 – 2.0; 6 – 2.5; 7 – 2.9.

3 Results and discussion

By exploring the above approach a coefficient of the transverse Nernst–Ettinsghausen effect Q for a heterophase system may be derived as follows:

$$Q = \frac{\sum_i c_i Q_i f_i^T(\lambda)\, \lambda_i^{-1} f_i^H(\rho)}{\left(\sum_i c_i \lambda_i^{-1} f_i^T(\lambda)\right)\left(\sum_i c_i f_i^H(\rho)\right)}, \tag{6}$$

where f_i^T and f_i^H are configuration parameters of inclusions along the thermal gradient ΔT and along the Hall direction V_H (perpendicular to magnetic field B), respectively (Fig. 1).

Equation (5) describes a longitudinal Nernst–Ettingshausen effect if one takes into account a dependence of all entities involved on magnetic field B. The equation for the Hall constant R has the form

$$R = \frac{\sum c_i R_i f_i\,(\rho)\, f_i^H(\rho)}{\sum c_i f_i\,(\rho) \sum c_i f_i^H(\rho)}. \tag{7}$$

For limiting cases of inclusions (see Fig. 1), Eq. (7) coincides with the formulas in Ref. [36]. In Fig. 3 the dependence of the transverse N–E effect (Q) on composition is shown for various thermal conductivities of phases for a case when A = 1. The behaviour of $Q(c)$ looks like the one of thermoelectric power S (see Fig. 2b). Using the equations obtained, it is possible to compare the behaviour of R and S for real substances (HgX, PbX, Te, Se, Si) near phase-transition points, as well as for layered semiconductor microdevices [45–51].

Thermoelectric effectiveness (κ) and thermoelectric figure of merit (Z) of heterophase systems:

$$\kappa = \frac{S^2}{\rho}, \qquad Z = \frac{S^2}{\rho \cdot \lambda}, \tag{8}$$

have also to be functions of phase parameters, as ρ, λ, S depend on concentration and geometrical configuration. One can try to analyse peculiarities of κ and Z in a two-phase heterosystem. The examples given in Fig. 4 have shown that thermoelectric effectiveness of a composite is able to exceed significantly values of κ of each phase. Losing a little in the thermoelectric figure of merit can increase greatly the thermoelectric effectiveness (Fig. 4). A magnetic field can improve additionally the thermoelectric

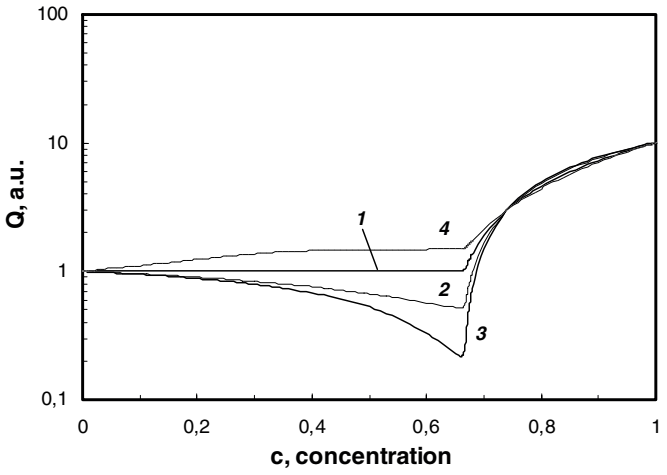

Fig. 3 Dependences of transverse Nernst–Ettingshausen effect $Q(c)$ of two-phase heterosystem ($\rho_1 = 10^5$, $\rho_2 = 1$, $S_1 = 10$, $S_2 = 1$, $Q_1 = 10$, $Q_2 = 1$ a.u.) on concentration of phase 1 in a case when $A = 1$ (spheres). 1 – $\lambda_1 = 1$, $\lambda_2 = 1$ a.u.; 2 – $\lambda_1 = 1$, $\lambda_2 = 10$ a.u.; 3 – $\lambda_1 = 1$, $\lambda_2 = 100$ a.u.; 4 – $\lambda_1 = 1$, $\lambda_2 = 0.01$ a.u.

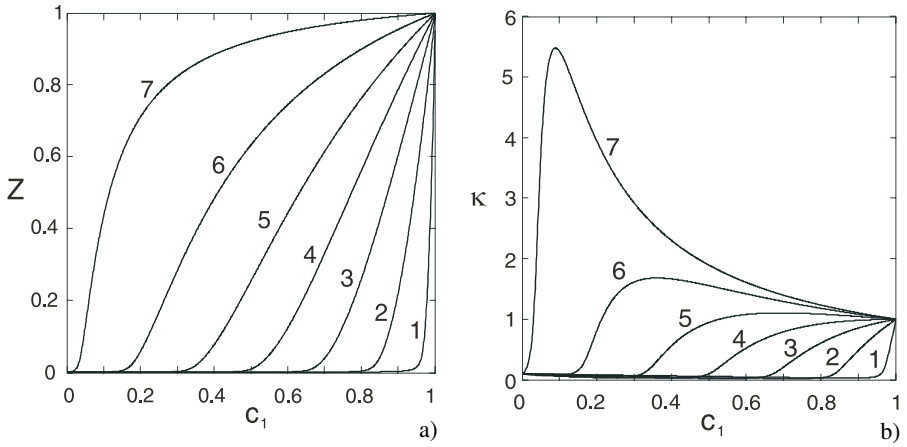

Fig. 4 Dependences of normalized thermoelectric figure of merit (a) and thermoelectric effectiveness (b) of two-phase heterosystem calculated from Eq. (5) (λ_1 = 1, λ_2 = 100, $\rho_1 = 10^4$, ρ_2 = 1, S_1 = 100, S_2 = 1 a.u.) on concentration c_1 of phase 1. The parameters A are equal to: (a) 1 – 0.1; 2 – 0.5; 3 – 1.0 (spheres); 4 – 1.5; 5 – 2.0; 6 – 2.5; 7 – 2.9; (b) 1 – 0.1; 2 – 0.5; 3 – 1.0 (spheres); 4 – 1.5; 5 – 2.0; 6 – 2.5; 7 – 2.9.

parameters κ and Z characterizing the work of thermoelectric cooling devices, as thermomagnetic cooling by the N–E effect is known to be preferable in comparison with a Peltier one [47–49]. Thus, the approach developed allows us to improve working parameters of thermoelectric generators.

The results of the calculations have shown an abrupt variation of effects near the threshold of semiconductor–metal phase transitions. But for different properties the behaviour is rather distinct, which can lead to a discrepancy between transition pressures found from these dependences in accordance with experiments described in Refs. [46–51].

Firstly, P. W. Bridgman had pointed out that values of the phase-transition pressure determined by volumetric effects are rather different from ones obtained in electrical resistance measurements [52]. Heterogeneity (inclusions) inside a material was found to be able to change significantly the results of testing of some physical properties while an effect on the remaining ones may be negligible. A clear example is a trigonal selenium crystal where due to intrinsic heterogeneity the mobility of holes estimated from the Hall effect is by hundreds of times less than the real one obtained from magnetoresistance measurements [53]. This result is clearly confirmed by Eq. (7).

The crucial role of heterophase states is seen near the phase transition, where inclusions of both initial and high-pressure phases exist. For HgSeS and HgSe single crystals undergoing a semimetal–semiconductor structural phase transition with an increase of electrical resistivity by 10^4–10^6 times [49], the Hall coefficient as well as the thermoelectric power in the vicinity of the phase transition did not change and were the same as for the initial semimetal phases [27, 54], which accords well with Eqs. (1)–(7). It is seen from Fig. 2 that at a "semiconductor–metal phase transition" an abrupt drop of S occurs, while the value of the effective resistance at the same concentration is still ~1–3 orders of magnitude higher than ρ of the metal phase and vice versa during the reversal "metal–semiconductor" phase transition. A similar relation corresponds to Hall-constant variation. These results of the calculation agree quantitatively both with the above experimental data for the behaviour of S at a phase transition in HgSe [54] and also with the low values of Hall mobility obtained in trigonal Se [53].

So, different methods of phase-transition investigations may give various values of phase-transformation pressure as in the examples above that have to be taken into account in the analysis of experimental data. According to Eqs. (1)–(7), a semiconductor–metal phase transition has to be seen from $S(P)$ and $R(P)$ dependences at less pressures than from resistivity measurements, and vice versa at a reversal metal–semiconductor transition. The last effects are usually observed also at a temperature-induced semiconductor–metal phase transition.

4 Conclusion

The mathematical equations for the thermoelectric power, resistivity, Hall coefficient and thermomagnetic effects obtained in the framework of the model developed explain visible discrepancies of experimental data of high-pressure investigations of materials. In particular, shifts of phase-transition pressure obtained by using various structural, electrical, thermal, magnetic and combined effects are clearly described.

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