Electronic properties of multi–phase systems with varying configuration of inclusions

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ABSTRACT

Multi-component systems (heterophases, layered, porous, misfit, composite) present the interest for different spheres of science and engineering. The paper covers both theoretical and experimental investigations of such systems with varying concentration and configuration of inclusions. Equations describing the dependence of electronic properties (thermomagnetic and galvanomagnetic as well as electrical and thermoelectric ones) of such systems on concentration and configuration of inclusions are presented. The equations derived may be used for analysis of electronic properties of advanced heterostructures. The above model describing the dependence of electronic properties of multi-component heterophase systems on concentration and configurations of inclusions allows to point out the ways for improving of electronic properties (thermoelectric effectiveness, thermoelectric and thermomagnetic figure of merit, etc.) and for extending of functional possibilities of such systems. So, the approach offered may be used for optimization of properties and for design of microdevices with improved characteristics.

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1. INTRODUCTION

The modern ultrahigh pressure technique with diamond anvils allows to test the samples with the sizes about electronic micro-devices ones ~ 10–100nm [1]. The non-electrical type of investigations (various optics, X-ray, etc) was developed more actively, than electrical ones – electrical resistance [2], thermoelectric power S [3,4] and magnetoresistance (MR) measurements at ultrahigh pressure [5]. The MR-technique at high pressures developed by using of sintered diamond anvils with pressed outputs to a sample [5] was able to test the value of mobility of charge carriers and the variation of scattering mechanism at high pressure phases of HgX (X-Te, Se, S, O) [5]. The similar two-terminal MR-technique have been offered for determination of concentration and mobility of electrons in semiconductor micro-devices (HgCdTe infrared detectors of 100*50*8 mkm sizes) [6]. In papers [7-9] the technique of thermomagnetic (TM) measurements have been developed at ultrahigh pressures up to 30 GPa allowing to estimate the mobility of charge carriers and directly to determine the scattering parameter of ones [10]. It seems, that TM measurements are more effective in compare with galvanomagnetic (GM) analogous (Hall effect and MR) [7-11], while the TM testing of microsamples was absent even at ambient pressure [9].

In the vicinity of phase transitions under pressure applied the materials are the mixture of phases. Varying the value of pressure one may change the concentration and configuration of phase inclusions. So, heterophase structures may serve as a model of real layered fabricated devices, the most properties of which being dependent on the concentration and
configuration of phases inclusions [12-14]. The interest to the investigations of these phenomena is connected with proposed application in engineering. Thus, semiconductor-metal phase transitions induced by nanosecond heating and cooling of small regions of the memory cell may be used for nonvolatile memory develop [15]. The approach to a real heterophases structures was developed by the orientated inclusions model with the variable phase configuration, and the calculations of the thermoelectric and galvanomagnetic properties were performed [12,16,17]. But TM properties of heterophase systems weren’t considered up to now. The automated setup for simultaneous measurements of electrical, thermal and volumetric properties of thin microsamples at high pressures up to 30 GPa was developed in [13,14,16], and a big amount of semiconductors undergoing the pressure-induced phase transitions were tested by using of one [18-31]. The crystal structure investigations by X-ray, synchrotron and neutron radiation allowed to attribute origin of unusual properties at high pressure to inclusions of phases [32].

The purpose of the present paper was to obtain the mathematical equations for TM and GM effects, including longitudinal and transverse Nernst-ETtingshausen ones, Maggi-Righi-Leduc, and Magnetoresistance for multi-component heterosystems. The equations for thermoelectric effectiveness and figure of merit will be also derived. Such equations will allow to analyze the electronic properties of multi-component systems under the variation of concentration and geometrical configuration of components. Using the equations one can establish the optimal internal parameters (concentration and configuration of components) corresponding to optimal electronic properties, including thermoelectric effectiveness and figure of merit. Thus, the equations may be used for design of multi-component heterosystems for different applications.

2. THE MODEL OF CALCULATIONS

Fig. 1. Peculiar cases of materials with various configuration of component’s inclusions (planes). The parameters \( A \) for different cases are given at the figures.
The calculations were performed by using of simple but pictorial model of heterophase system (Fig. 1) [12-14]. Usually characteristics of material determined from experiments are the effective one’s (averaged over total volume of substance measured ). These effective properties contain “geometrical” parameters of every phase: concentration, shape, and position of inclusions [33-35]. Effective properties (thermal, magnetic, mechanical [33]) usually are calculated by two main approaches: in the first local properties of system are supposed to be well-known functions of coordinates, in the second one they are considered statistically as random fields. The expressions for effective specific resistance \( \rho \) of multi-component heterosystem were got from the solving a problem of isotropic dielectric ellipsoid in electric field [36].

In book [33] expressions were received for upper and lower bound of effective conductivity of system in cellular model of statistic approach. In cellular model total volume is covered by system of non-overlapping cells in form of ellipsoids. Under the chaos packing of ellipsoids the dependence of bounds on form of inclusions are determined by parameters \( G_i \) \( (1/9 \leq G_i \leq 1/3) \), which are equal \( 1/9, 1/6, 1/3 \) for spherical, needle and disk inclusions respectively. To take into account the manner of ellipsoids packing in this approach two additional parameters ought to be inputted, and in some cases the close values for upper and lower bounds of \( \rho \) may be received [33]. But this approach is very difficult because of enormous awkward calculations, so it’s using quite seldom. In recent papers [12-14] the approach was developed for multi-component composite materials. Unlike the most previous models [37-39] where the shape of inclusions is fixed, the configuration parameter of phase inclusions in a mentioned one is variable between the extreme limiting cases of parallel and consequent (electrical, thermal) connection. The second novel feature is the considering and comparing of several properties of material simultaneously for the same configuration. The validity of the “geometry” parameters choice obtained for any one feature may be proved or rejected by such combined testing. Effective electrical resistivity \( \rho \) or conductivity \( \sigma \) (and thermal conductivity \( \lambda \)) in this approach are viewed as a normalized sum of phase contributions in two equivalent considerations of “consequent” and “parallel” electrical (thermal) connection of phases [12-14].

\[
\rho = \sum c_i \cdot \rho_i \cdot f_i \cdot (\sum c_i \cdot f_i)^{-1}
\]

\[
\sigma = \sum c_i \cdot \sigma_i \cdot f_i (\sigma) \cdot (\sum c_i \cdot f_i (\sigma))^{-1}
\]

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

\[
f_i = 3 \rho / [A \rho + (3 - A) \rho], \quad f_i (\sigma) = 3 \sigma / [A \sigma + (3 - A) \sigma].
\]

For constant \( A \) equal to 0, 3 and 1 Eqs. 4, 5- coincide respectively with the cases of parallel and consequent electrical connections, and the spherical shape of component inclusions (Fig. 1) [37,38]. Intermediate values of \( 0 < A < 3 \) correspond to interpolated configuration of inclusions in the certain direction (like elongated or contracted ellipsoids) (Fig.1).

For two-phase composite Eq. 4 goes to:

\[
A \cdot \rho^2 + \rho \cdot [\rho_2 \cdot (3c_1 - A) + \rho_1 \cdot (3c_2 - A)] - \rho_1 \cdot \rho_2 \cdot (3 - A) = 0
\]

and the dependencies of \( \rho \) and \( \lambda \) on \( c_i \) are similar to ones of the certain models of ellipsoidal inclusions [35-40]. The dependencies for \( \rho(c), \lambda(c) \) obtained for typical cases are shown at Figs. 2,3. By using of the analogy between the electrical, elastic etc. phenomena [41] the similar equations may be obtained for elastic properties. The appropriate equation for \( S \) of heterophase materials is:

\[
S = \left( \sum S_i \cdot c_i \cdot f_i \cdot \rho_i \cdot \lambda_i \cdot f_i (\lambda) \right) / \left( \sum c_i \cdot f_i \cdot \rho_i \cdot \lambda_i \cdot f_i (\lambda) \right).
\]

In [12,14] the altering equation for \( S \) instead of Eq. 5 was obtained by interpolation procedure from limiting cases \( \lambda = 0, 3 \) and spherical shape of inclusions \( \lambda = 1 \) [42-44].

\[
S = \left( \sum S_i \cdot c_i \cdot \varepsilon_i \cdot \rho_i \cdot \lambda_i \cdot \varepsilon_i (\lambda) \right) / \left( \sum c_i \cdot \varepsilon_i \cdot \rho_i \cdot \lambda_i \cdot \varepsilon_i (\lambda) \right).
\]
Fig. 2. Calculated dependencies of resistivity $r=\rho(c_1)$ of two-component heterosystem ($\rho_1=10^3$, $\rho_2=1$ a.u.) on concentration of $c_1$ component I. The component I has been taken as low conducting. 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.

Fig. 3. Calculated dependencies of thermal conductivity $L=\lambda(c_1)$ of two-component heterosystem ($\lambda_1=1$, $\lambda_2=100$ a.u.) on concentration $c_1$ of component I. 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.
The divergence of Eq. 8 and Eq. 9 may be revealed only in case $\lambda_1 <\ll \lambda_2$ near the threshold of “insulator” - “metal” transition (Fig. 4), and in particular for $\lambda_1 \rightarrow 0$ (porous material). It's interesting to choose ultimately correct version for equation for $S$, but now there are a few experimental data. Corresponding equations for magnetoresistance (MR) and Hall effect ($R$) were considered in [31]. By using the approach above the similar equations were obtained for thermomagnetic Nernst-Ettinsghausen effects (in next Section). Based on the above equations, the dependencies of figure of merit as well as thermoelectric effectiveness as functions of variable geometrical configuration and concentration of inclusions (components) were obtained in the present work.

3. RESULTS AND DISCUSSION

All entities in Eq. (8) at $B \neq 0$ - $\rho$, $\rho_1$ and $\rho_2$, $\lambda_1$, $\lambda_2$ and $S_1$ and $S_2$ are functions of magnetic field $B$. In thermal conductivities $\lambda_1$ and $\lambda_2$ only electronic part $\lambda_{ie}$ are dependent on $B$, while the lattice contributions $\lambda_{ip}$ are constants:

$$\lambda_i(B) = \lambda_{ie}(B) + \lambda_{ip}$$

(11).

Fig. 4. Calculated dependencies of thermoelectric power $S(c;/g^{20})$ of two-component heterosystem ($\lambda_1=1$, $\lambda_2=100$, $\rho_1=10^5$, $\rho_2=1$, $S_1=10$, $S_2=1$ a.u.) on concentration $c_i$ of component I. The component I has been taken as low conducting. The parameters $A$ are equal to:

(a): $I=0.1$; $2=0.5$; $3=1.0$; $4=1.5$; $5=2.0$; $6=2.5$; $7=2.9$; (b): $I=0.1$; $2=0.5$; $3=1.0$; $4=1.5$; $5=2.0$; $6=2.5$; $7=2.9$;

By exploring the above approach the coefficient of transverse Nernst-Ettinsghausen effect $Q$ for heterophase system was obtained:

$$Q = \frac{\sum c_i \cdot Q_i \cdot f_i^T(\lambda) \cdot \lambda_{ie}^{-1} \cdot f_i(\rho)}{\left( \sum c_i \cdot f_i(\lambda) \right) \cdot \left( \sum c_i \cdot f_i^H \right)}$$

(12),

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where \( f_i^T \) and \( f_i^H \) are configuration parameters along the thermal gradient \( \Delta T \) and along the Hall direction \( V_H \) (Fig.2).

In work [12] the approximate Equation for \( S \) was obtained (corresponding to Eq. 9):

\[
S = S_2 + (S_1 - S_2) \left( \frac{\rho \lambda - \rho_2 \lambda_2}{\rho_1 \lambda_1 - \rho_2 \lambda_2} \right)
\]  

Eq.(13) tends to

\[
S(B) = \frac{S_1(B)\left( \rho(B)\lambda(B) - \rho_2(B)\lambda_2(B) \right) - S_2(B)\left( \rho(B)\lambda_2(B) - \rho_1(B)\lambda_1(B) \right)}{\rho_1(B)\lambda_1(B) - \rho_2(B)\lambda_2(B)}
\]  

For intrinsic non-degenerate electron gas at low magnetic fields \( \mu B < 1 \) the dependence of electron part of conductivity is described as follows:

\[
\lambda_{ie}(B) = n_i \mu_i \left( r + \frac{5}{2} \right) \frac{k^2}{e} \left[ 1 - a_i (\mu_i^2 B) \right]
\]  

Where \( n_i \) the electronics (holes) concentration and \( a_i \) the multiplier depending on \( r \). For acoustic phonons \( r = -1/2 \), \( a_r = 1.6 \), for charged centers scattering \( r = 3/2 \), \( a_r = 2.8 \) [34]. The thermal conductivity of lattice is usually much more than electronic one, so the variation of \( \lambda \) on \( B \) may be neglected [10]. By submitting the phase entities as well as “effective entities” \( \rho, \lambda \) determined by Eq. (4-7) it’s possible to calculate the transverse and longitudinal N-E effects for heterophase systems (Eq. 12-14)

It’s interesting to compare the behavior of transverse galvanomagnetic Hall effect and the thermomagnetic Nernst-Ettingshausen effects at the simplest limiting cases. The first interesting case is the stock of layers perpendicular to the thermal gradient the magnetic field is in place of layers (Fig. 1a). The expression for Hall effect and transverse Nernst-Ettingshausen one are:

\[
R = \sum C_i R_i \rho_i^{-1} \left( \sum C_i \rho_i^{-1} \right)^{-1}
\]

\[
Q = \left( \sum C_i Q_i \lambda_i^{-1} \right) \left( \sum C_i \rho_i^{-1} \right)^{-1} \left( \sum C_i \lambda_i^{-1} \right)^{-1}
\]  

The second and third limiting cases are the layers along the thermal flow, the magnetic field being perpendicular to layers planes or along (Fig. 1b,c).

\[
R = \left( \sum C_i R_i \rho_i^{-1} \right) \left( \sum C_i \rho_i^{-1} \right)^{-1}
\]

\[
Q = \sum C_i Q_i
\]  

and

\[
R = \left( \sum C_i R_i \rho_i^{-2} \right) \left( \sum C_i \rho_i^{-1} \right)^{-2}
\]

\[
Q = \left( \sum C_i Q_i \rho_i^{-1} \right) \left( \sum C_i \rho_i^{-1} \right)^{-1}
\]  

At intermediate case of spherical inclusions \( (A^T=1) \) the equation for \( R \) and \( Q \) are the follows:

\[
R = \left( \sum C_i R_i \left( \frac{1}{\rho + 2 \rho_i} \right) \right) \left( \sum C_i \frac{1}{\rho + 2 \rho_i} \right)^{-2}
\]

\[
Q = \left( \sum C_i Q_i \left( \frac{\rho}{\rho + 2 \rho_i} \right) \frac{1}{\lambda_i + 2 \lambda} \right) \left( \sum C_i \frac{1}{\lambda_i + 2 \lambda} \right) \left( \sum C_i \frac{\rho}{\rho + 2 \rho_i} \right)^{-1}
\]
From the Eq. 16 the behavior of thermomagnetic and galvanomagnetic effects, namely Hall and N-E under mixing seems rather different. The most difference was seen from Eq. (16.b). By using the equations obtained it’s possible to compare the behavior of \( R \) and \( S \) for the certain substance (HgX, PbX, Te, Se, Si) near the phase transition points, as well as for a certain layered semiconductor micro-devices [45-51]. At Fig. 5 the dependence of \( Q \) on composition is shown for various thermal conductivities of components for a certain case \( (A=1) \). The behavior of \( Q(c) \) looks like one of thermoelectric power \( S \) (see Fig. 4a).

Thermoelectric effectiveness \( (\alpha) \) and thermoelectric figure of merit \( (z) \) are important thermoelectric parameters of materials depending on resistivity \( \rho \), thermal conductivity \( \lambda \), and thermoelectric power \( S \):

\[
\alpha = \frac{S^2}{\rho} \quad z = \frac{S^2}{\rho \cdot \lambda}
\]  

As all entities \( \rho, \lambda, S \) depend on concentration and geometrical configuration of each component of heterosystem, so the thermoelectric effectiveness \( (\alpha) \) and thermoelectric figure of merit \( (z) \) are also functions of components’ parameters. We will try to analyze the peculiarities of \( \alpha \) and \( z \) in example of two-component heterosystem.

The examples given at Figs. 6,7 have shown that thermoelectric effectiveness may have an extremum a certain value of \( c \), so the thermoelectric effectiveness of composite can significantly exceed \( \alpha \) of each component. In a certain region of concentrations the composite can possess the high values of thermoelectric effectiveness and thermoelectric figure of merit. That is loosing a little in thermoelectric figure of merit on can win greatly in thermoelectric effectiveness. Optimal values of concentration in this case correspond to \( A/3 \). As we see at Figs. 6, 7 the highest thermoelectric effectiveness will be in case of layered system.
Fig. 6. Dependencies of normalized thermoelectric figure of merit (a) and thermoelectric effectiveness (b) of two-component heterosystem calculated from Eq. 8 \((\lambda_1=1, \lambda_2=100, \rho_1=10^4, \rho_2=1, S_1=100, S_2=1\) a.u.) on concentration \(c_1\) of component 1. The component 1 has been taken as low conducting. 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;

Fig. 7 Dependencies of normalized thermoelectric figure of merit (a) and thermoelectric effectiveness (b) \(\alpha / \alpha_t\) of two-component heterosystem calculated from Eq. 9 \((\lambda_1=1, \lambda_2=100, \rho_1=10^4, \rho_2=1, S_1=100, S_2=1\) a.u.) on concentration of component 1. Parameter \(A\): (a): 1 – 0.1; 2 – 0.5; 3 – 1.0; 4 – 1.5; 5 – 2.0; 6 – 2.5; 7 – 2.9; (b): 1 – 0.1; 2 – 0.5; 3 – 1.0; 4 – 1.5; 5 – 2.0; 6 – 2.5; 7 – 2.9;
4. CONCLUSION

Mathematical approach developed for estimation of effective thermomagnetic properties as well as other electronic ones of composite materials with different orientations of inclusions has shown that complex behavior on concentration and geometrical configuration of components (Figs. 2-7). The equations derived may be used for analysis of heterostructures and micro-devices [6, 11]. Presence of components with peculiar shape in microdevices and microstructures can lead to both positive and negative effects. For example one can improve the heatsink from Integrated Circuits (IC), or improve the thermoelectric effectiveness and thermoelectric and thermomagnetic figures of merit of thermo-transducers. Negative effects may reveal themselves, for example, in appearance of parasitic thermoelectric or thermomagnetic signals in working microdevices. The model developed in the present work is able to account all effects arising due to configuration of components in real microdevices.

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