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ANISOTROPY OF THERMOELECTRIC PROPERTIES OF MULTI-VALLEY SEMICONDUCTORS OF CUBIC SYMMETRY UNDER THE INFLUENCE OF EXTERNAL DIRECTIONAL EFFECTS

Analysis of electronic processes developed in multi-valley semiconductors of cubic symmetry under the influence of uniaxial elastic strain and magnetic (nonquantizing) field of arbitrary intensity has been performed. The relationships between thermoEMF anisotropy $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ and the anisotropy parameters of electron-phonon drag thermoEMF $M = \alpha_{\parallel}^{ph}/\alpha_{\perp}^{ph}$ and mobility anisotropy $K = \mu_{\perp}/\mu_{\parallel}$ in a single isoenergetic ellipsoid, as well as changes in resistivity $\Delta\rho$ in a field of directional pressure or in an external magnetic field have been investigated.

Key words: multi-valley semiconductors, kinetic phenomena, scattering anisotropy, electric and magnetic fields, directional elastic strain.

Introduction

The use of thermoelectricity and increase of its role in metrology and power engineering is related to creation of thermoelectric materials with maximum values of thermoelectric figure of merit *ZT*. In particular, semiconductors used as thermocouple legs with thermoelectric figure of merit $ZT \geq 1$ have been already synthesized [1, 2]. Certain advances have been made in the theory of thermoelectric effects, though for the anisotropic semiconductors of noncubic symmetry it is not sufficiently developed. The boundary values of thermoelectric figure of merit for such semiconductors have not been found yet, the influence of structural features on their thermoelectric properties has not been determined.

The electrophysical properties of semiconductors are largely dependent not only on microlevel anisotropy (anisotropy of dispersion law and mechanisms of carrier scattering on phonons and impurity centres, phonon-phonon scattering, etc), but also on macrolevel anisotropy, that is, on the natural (or induced, for instance, by means of directional elastic strain) anisotropy of the entire crystal.

Prior to the development of anisotropic scattering theory there had been no substantiated and consecutive analysis of the results of microlevel anisotropy transformation into macrolevel under the influence of external effects on the crystal.

The purpose of this paper is to perform a consecutive analysis of the influence of both internal characteristics (structural and anisotropic features) of crystals, and the external effects on their thermoelectric and thermomagnetic properties. Attention is focused on the mechanisms of formation and methods of revealing the macroscopic anisotropy of thermoelectric properties of multi-valley semiconductors of cubic symmetry under the influence of external directional effects.

Thermoelectric effects in semiconductors

In semiconductors with the anisotropic energy spectrum of carriers the kinetic coefficients in the general case are of tensor nature. In particular, the Seebeck coefficient α in the anisotropic semiconductor is a second-rank tensor ($\hat{\alpha}$). Unlike the tensors $\hat{\sigma}$, $\hat{\rho}$ and $\hat{\chi}$, the thermoEMF tensor is nonsymmetrical. Let us consider in more detail the properties and features of tensor $\hat{\alpha}$ in semiconductors and the physical factors that determine it.

The tensor nature of $\hat{\alpha}$ is first of all responsible for thermoEMF anisotropy. The primary reason for all peculiarities of thermoelectric effects, including origination of thermoEMF anisotropy, is, no doubt, the kind of dependence of carrier energy $\mathscr{E}$ on quasi-pulse $\vec{p}$, that is the form of dispersion law $\mathscr{E}(\vec{p})$. The influence of dependence $\mathscr{E}(\vec{p})$ on the properties of tensor $\hat{\alpha}$ is defined by superposition of the internal and external (with regard to semiconductor) conditions which, in fact, assure transformation or joint exhibition of micro- and macrolevel anisotropies. Analyzing these factors, one can conclude that in each specific case the thermoEMF anisotropy arises only when a number of conditions are fulfilled.

1. Suppose that we have a single-valley semiconductor, and carriers of one sort take place in charge transport. Charge carrier scattering will be assumed to be nearly isotropic. The expression for the Seebeck coefficient in this case is of the form [2]:

$$\alpha_i = \frac{k}{e} \frac{\int \tau(\mathscr{E}) \frac{\partial n}{\partial \mathscr{E}} \upsilon_i^2 \left(\frac{\mathscr{E} - \xi_0}{kT} \right) \mathrm{d}\mathscr{E}}{\int \tau(\mathscr{E}) \frac{\partial n}{\partial \mathscr{E}} \upsilon_i^2 \, \mathrm{d}\mathscr{E}}, \tag{1}$$

where $\tau(\mathscr{E})$ is relaxation time, ξ_0 / kT is a reduced chemical potential. From (1) it follows that in the case when, for instance, the degree of nonparabolicity of quasi-pulse dependence of energy at least for two different directions is different (hence, the energy dependence of components of velocity υ of charge carriers has a different form for these directions), the thermoEMF anisotropy can arise.

2. Let there be two sorts of carriers in a semiconductor and at least one of which (for instance, electrons) is characterized by the anisotropic effective mass. It can be shown [3] that under this condition the thermoEMF anisotropy is created

$$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} = \frac{\sigma_{\perp} - \sigma_{\parallel}}{\sigma} \frac{\alpha_p - \alpha_n}{\left(1 + \frac{\sigma_{\parallel}}{\sigma}\right)\left(1 + \frac{\sigma_{\perp}}{\sigma}\right)}, \tag{2}$$

where α_p and α_n are the Seebeck coefficients of holes and electrons, respectively, $\sigma_{\parallel}$ and $\sigma_{\perp}$ are components of the electric conductivity tensor of electrons, σ is the electric conductivity of holes.

3. Suppose that the energy spectrum of one sort of carriers in a single-valley semiconductor is anisotropic, and

$$\mathscr{E}(\vec{p}) = \frac{p_1^2 + p_2^2}{2m_1} + \frac{p_3^2}{2m_3}. \tag{3}$$

Here, m_1 and m_3 are the transverse and longitudinal effective masses of carriers in constant-energy ellipsoid, respectively; p_1 and p_2 ($p_1 = p_2$) are the components of the pulses in ellipsoid transverse section, and p_3 – in longitudinal section. Assuming that $m_3 > m_1$, the constant-energy surface in this case will have the form of an elongated ellipsoid of revolution. The effective mass anisotropy causes

in the general case the anisotropy of scattering [4], and the symmetry of differential mobility tensor corresponds to the symmetry of energy minimum. Let in the presence of one or several scattering mechanisms the dependence $\hat{\mu}(x)$ (of relaxation time tensor) on the reduced energy of charge carriers $x = \mathscr{E}/kT$ be written as

$$\left.\begin{aligned} \mu_\perp(x) &= \mu_\perp(T)\, x^{-q}\, f_\perp(x) \\ \mu_\parallel(x) &= \mu_\parallel(T)\, x^{-q}\, f_\parallel(x) \end{aligned}\right\}, \tag{4}$$

(where $f_\perp(x)$ and $f_\parallel(x)$ are certain functions of x, effective masses and other semiconductor parameters). Then for the nondegenerate semiconductor

$$\left.\begin{aligned} \alpha_\perp &= \frac{\langle \alpha(x)\,\mu_\perp(x)\rangle}{\langle \mu_\perp(x)\rangle} \\ \alpha_\parallel &= \frac{\langle \alpha(x)\,\mu_\parallel(x)\rangle}{\langle \mu_\parallel(x)\rangle} \end{aligned}\right\}, \tag{5}$$

where angular brackets in (5) denote the generally accepted averaging over energy, and

$$\alpha(x) = \frac{k}{e}\,\frac{\mathscr{E} - \xi_0}{kT} \tag{6}$$

has the meaning of the Seebeck coefficient of a group of electrons with the energy $\mathscr{E}$.

Note that with the power energy dependence $\hat{\mu}(x)$ and $f_\perp = f_\parallel = 1$ the thermoEMF anisotropy disappears. For a more complicated than that expressed by formula (3) energy spectrum of charge carriers (for instance, the Kane one) the symmetry of tensor $\hat{\alpha}$ is reduced.

4. Suppose that the conditions of the previous item are fulfilled, but crystal temperature is considerably lower than the Debye temperature. In this case (in the presence of temperature gradient ∇T) of considerable importance will be the effect of charge carrier drag by the long-wave phonons. From the kinetic theory it follows that under these conditions even in the case of power dependence of $\hat{\mu}$ on x, components of the tensor of electron-phonon drag thermoEMF are not identical and are described by the expressions [5]

$$\alpha_\perp^{ph} = \frac{\langle \mu_\perp(x)\,\alpha_\perp^{ph}(x)\rangle}{\langle \mu_\perp(x)\rangle}, \tag{7}$$

$$\alpha_\parallel^{ph} = \frac{\langle \mu_\parallel(x)\,\alpha_\parallel^{ph}(x)\rangle}{\langle \mu_\parallel(x)\rangle}. \tag{8}$$

As long as with the drag of electrons by long-wave phonons the anisotropy parameter of the drag thermoEMF is $M = \alpha_\parallel^{ph}(x)/\alpha_\perp^{ph}(x) \sim m_3/m_1$ (m_3/m_1 is the ratio of the effective masses of charge carriers along the principal axes of isoenergetic ellipsoid), its numerical value can become considerable (for instance, in *n-Ge* $M = 9.7$).

5. Let us consider a multi-valley semiconductor with S valleys in the Brillouin zone, in each of which the law of dispersion is defined by expression (3). In this case the energy minima in crystal of cubic symmetry will be located on triad or tetrad axes, all the valleys under given conditions being energetically equivalent. Adding currents in each valley that are described by the generalized electric conductivity law

$$\vec{j} = \hat{\sigma}^{(k)} \left(\frac{\nabla \xi}{e} + \hat{\alpha}^{(k)} \nabla T \right), \tag{9}$$

where $\hat{\sigma}^{(k)}$ and $\hat{\alpha}^{(k)}$ are the tensors of the electric conductivity and thermoEMF in k-th valley, respectively, and ξ is electrochemical potential, it is easy to verify that due to cubic symmetry all kinetic tensors degenerate into scalars. So, not only thermoEMF, but even electric conductivity in a cubic semiconductor is isotropic.

The situation will be quite different if in the case of a cubic multi-valley semiconductor we remove, for instance, via uniaxial elastic strain the degeneration of isoenergetic ellipsoids in energy. Assuming that the only result of the influence of uniaxial elastic strain will be redistribution of electrons among the valleys, the nonequivalence of the latter can be conveniently characterized by the relative number of electrons $n_k = N_k/N$ in k-th valley of a strained semiconductor, where N_k is the absolute number of electrons in k-th valley of a strained semiconductor, and $N = SN_0$ is the total number of electrons in S valleys (N_0 is the number of electrons in one valley of an unstrained crystal). As a result of adding currents in the valleys, the tensors

$$\hat{\sigma} = \sum_{k=1}^{S} \hat{\sigma}^{(k)}, \ \hat{b} = -\sum_{k=1}^{S} \hat{\sigma}^{(k)} \hat{\alpha}^{(k)}, \tag{10}$$

characterizing an uniaxially strained crystal, do not generate into scalars, but become proportional either to tensor

$$\hat{C} = \sum_{k=1}^{S} n_k \hat{Q}^{(k)} \tag{11}$$

(tensor $\hat{C}$ is the phonon part of tensor $\hat{b}$), or to tensor $\hat{C}$ and tensor

$$\hat{\hat{C}} = \sum_{k=1}^{S} n_k \ln \frac{n_0}{n_k} \hat{Q}^{(k)} \tag{12}$$

(tensor $\hat{\hat{C}}$ is the electron part of tensor $\hat{b}$).

Tensor $\hat{Q}^{(k)}$ in (11) and (12) is of geometric origin, since its components are assigned by the equality

$$Q_{ij}^{(k)} = g_{i3}^{(k)} g_{j3}^{(k)}, \tag{13}$$

where $g_{i3}^{(k)}$ is an element of transition matrix from a coordinate system related to the principal axes of k-th mass ellipsoid to a design coordinate system. As long as in a strained system $\hat{\sigma}$ (or $\hat{\rho}$) and $\hat{b}$ are tensors, the Seebeck coefficient should also exhibit tensor properties, namely:

$$\hat{\alpha} = -\hat{\rho} \hat{b}. \tag{14}$$

Let us dwell in more detail on the analysis of thermoEMF anisotropy in uniaxially strained germanium and silicon of n-type. We will arrange strain axis in $(1\bar{1}0)$ plane, and its orientation will be assigned by angle γ which can be conveniently counted off (in the same plane $(1\bar{1}0)$ from direction $[00\bar{1}]$ toward the strain.

In the temperature range where electron-phonon drag is negligible, it gives rise to electron thermoEMF anisotropy that essentially depends on mechanical strain X and strain angle γ. Fig. 1 (*n-Ge*) and Fig. 2 (*n-Si*) show the dependences of electron (diffusion) thermoEMF anisotropy on strain angle.

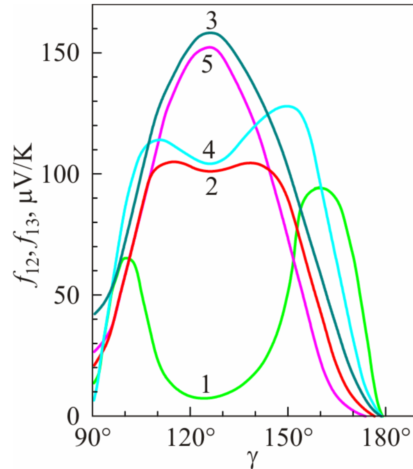

Fig. 1. Dependences of the difference in diagonal components of tensor $\hat{\alpha}$ on strain angle in n-Ge ($\alpha_{11} - \alpha_{22} = f_{12}$ and $\alpha_{11} - \alpha_{33} = f_{13}$) at T = 300 K. f_{13}, X (GPa): 1 – 2; 3 – 0.7; 4 – 1.2. f_{12}, X (GPa): 2 – 1.2; 5 – 0.7.

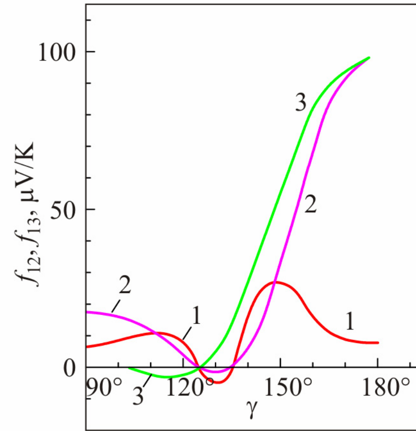

Fig. 2. Angular dependences of the difference in diagonal components $\alpha_{11} - \alpha_{22} = f_{12}$ and $\alpha_{11} - \alpha_{33} = f_{13}$ of tensor $\hat{\alpha}(X)$ in n-Si at T = 300 K. f_{12}, X (GPa): 1 – 2; 2 – 0.7. f_{13}, X (GPa): 3 – 0.7.

The electron thermoEMF anisotropy in *n-Ge* reaches its maximum under crystals strain along the volumetric diagonal <111>, and in *n-Si* – under strain along cube edge <100> due to intermediate values of X. It can be shown that for the above orientations of strain axis in *n-Ge*

$$\Delta\alpha^{e} = \frac{4k}{e}\,\frac{K-1}{K}\,\frac{2K+1}{3K}\,\frac{n_1 n_2 \ln\dfrac{n_1}{n_2}}{\left(1-\dfrac{4}{3}n_2\dfrac{K-1}{K}\right)\left(\dfrac{1}{K}+\dfrac{8}{3}n_2\dfrac{K-1}{K}\right)}, \tag{15}$$

and in *n-Si*

$$\Delta\alpha^{e} = \frac{4k}{e}\,\frac{K-1}{K}\,\frac{2K+1}{3K}\,\frac{n_1 n_2 \ln\dfrac{n_1}{n_2}}{\left(1-2\,n_1\dfrac{K-1}{K}\right)\left(1-2\,n_2\dfrac{K-1}{K}\right)}, \tag{16}$$

where n_1 is a relative number of electrons in a valley located along strain axis, n_2 – in each of the valleys located at an angle to strain axis, $K = \mu_{\perp}/\mu_{\parallel}$ is mobility anisotropy parameter.

Formulae (15) and (16) show that *a*) electronic thermoEMF anisotropy in uniaxially strained

multi-valley semiconductors (the microlevel electronic thermoEMF anisotropy) is exceptionally due to mobility anisotropy on a microlevel (that is, in isoenergetic ellipsoid taken individually); *b*) the thermoEMF anisotropy $\Delta\alpha^e$ value vanishes in *n-Ge* and in *n-Si* both in the absence of strain ($n_1 = n_2$), and in the presence of heavy strain providing full migration of electrons into one ellipsoid ($n_1 = 0$ or $n_2 = 0$).

Maximum value of drag thermoEMF anisotropy is observed under strain of *n-Ge* along <111> and *n-Si* along <001> (as in the case of electronic component), and change in $\Delta\alpha^{ph}$ under strain is basically different from the similar dependences for $\Delta\alpha^e$ which immediately follows from comparison of formulae (15) and (16) to relations (17) and (18) (where $\Delta\alpha^{ph}$ is the phonon component of thermoEMF in unstrained crystal).

For *n-Ge*

$$\Delta\alpha^{ph} = \alpha_0^{ph}\ \frac{M-1}{K}\ \frac{2K+1}{2K+M}\ \frac{n_1 - n_2}{\left(1-\frac{4}{3}n_2\ \frac{K-1}{K}\right)\left(\frac{1}{K}+\frac{8}{3}n_2\ \frac{K-1}{K}\right)}. \tag{17}$$

For *n-Si*

$$\Delta\alpha^{ph} = 2\ \alpha_0^{ph}\ \frac{M-1}{K}\ \frac{2K+1}{2K+M}\ \frac{n_1 - n_2}{\left(1-2\,n_1\ \frac{K-1}{K}\right)\left(1-2\,n_2\ \frac{K-1}{K}\right)}. \tag{18}$$

The reason for drag thermoEMF anisotropy in this case (see (17) and (18)) is not only drag thermoEMF in each of the valleys, but also strain-caused nonequivalence of the latter.

The specific feature of the anisotropy of the phonon part of thermoEMF $\Delta\alpha^{ph}$ is that unlike $\Delta\alpha^e$, with increase in crystal mechanical compression strain X, it continues to increase and with rather high values of X reaches the saturation, whereas $\Delta\alpha^e(X)$, on passing the maximum, with further increase in X tends to zero.

Under conditions whereby its contribution to thermoEMF anisotropy of a semiconductor with a damaged cubic symmetry (due to uniaxial elastic strain) is made by the nonequivalence of valleys (where the energy spectrum is anisotropic even in the absence of strain), the same nonequivalence of valleys leads to the anisotropy of $\hat{\rho}$, and the relation between tensors $\hat{\alpha}^{ph}$ and $\hat{\rho}$, according to reliable calculations, can be given as

$$\hat{\alpha}^{ph} = \alpha_0^{ph}\left[\frac{K-M}{K-1}\ \frac{2K+1}{2K+M}\ \hat{I} + \frac{M-1}{K-1}\ \frac{3K}{2K+M}\ \frac{\hat{\rho}}{\rho_0}\right]. \tag{19}$$

From this formula follows a linear dependence of the nondiagonal components of tensors $\hat{\alpha}$ and $\hat{\rho}$, and at sufficiently high X ($X \geq 0.6$ GPa) the electronic part of nondiagonal components vanishes. Hence, relation (19) allows experimental determination of parameter M.

Formula (19) yields two nontrivial and practically useful results. First, it implies that relative changes in $\Delta\alpha^{ph}/\Delta\alpha_0^{ph}$ and $\Delta\rho/\Delta\rho_0$ induced by uniaxial elastic strain are interrelated by boundary simple relation

$$\frac{\Delta\alpha^{ph}}{\alpha_0^{ph}} = \frac{M-1}{K-1}\cdot\frac{3K}{2K+M}\cdot\frac{\Delta\rho}{\rho_0}, \tag{20}$$

which makes it possible to measure the value of M (with known K) according to measured values $\Delta\alpha^{ph}/\Delta\alpha_0^{ph}$ and $\Delta\rho/\Delta\rho_0$. Second, formula (19) assures (with known K and M) producing the drag thermoEMF anisotropy $\Delta\alpha^{ph}/\Delta\alpha_0^{ph}$ according to the values of resistivity anisotropy $\Delta\rho/\Delta\rho_0$ for the same crystal.

Note that $\Delta\alpha^{ph}$ and $\Delta\rho$ in (20) correspond to the difference in diagonal components, since during

the experimental investigations of tensors $\hat{\alpha}^{ph}(X;\gamma)$ and $\hat{\rho}(X;\gamma)$ one usually restricts oneself to the most characteristic orientations of strain axis that assure at high X a realization of single- or double-valley model. In *n-Ge* such orientations are matched by $\gamma = \delta$ (single-valley model) and $\gamma = 90°$ (two-valley model), and in *n-Si* – $\gamma = 0$ and $\gamma = 90°$, respectively. In so doing, δ is the angle that determines a direction of strain axis along the volumetric diagonal of the cube, when $\mathrm{tg}\,\delta = \sqrt{2}$. At $\gamma < \delta$ the angle δ is between the directions $[00\bar{1}]$ and $[\bar{1}\bar{1}1]$.

Fig. 3 shows angular dependences of the components of tensor $\hat{\alpha}$ calculated and experimentally measured for *n-Ge* crystals at $X = 1$ GPa and $T = 85$ K, and Fig. 4 shows the angular dependence of the drag piezothermoEMF $\alpha_{11} = f(\gamma)$, found for *n-Si* crystals at $X = 0.8$ GPa and $T = 85$ K. The results presented in these figures testify to a good agreement between theory and experiment. Emphasis should be placed on the value of thermoEMF and its anisotropy in strained silicon that increases the respective values for other materials by two-three orders.

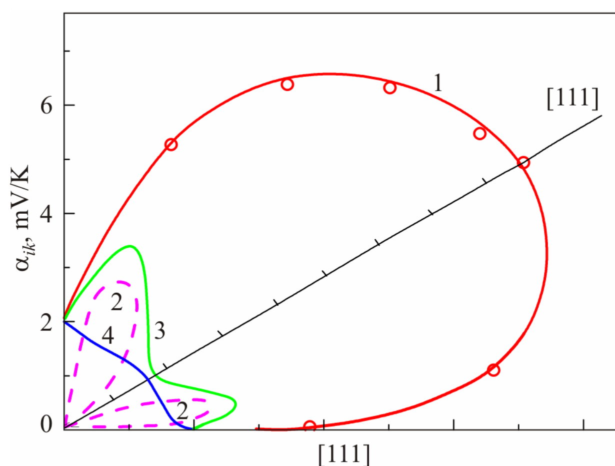

Fig. 3. Angular dependences of the components of tensor $\hat{\alpha}$ in plane $(1\bar{1}0)$ for n-Ge with $n_e = 1.6\cdot10^{13}$ cm^{-3} at $X = 1$ GPa and $T = 85$ K. 1 – α_{11}, 2 – α_{21}, 3 – α_{22}, 4 – α_{33}.
○ are for experimental data, the solid and dashed lines – for calculated data.

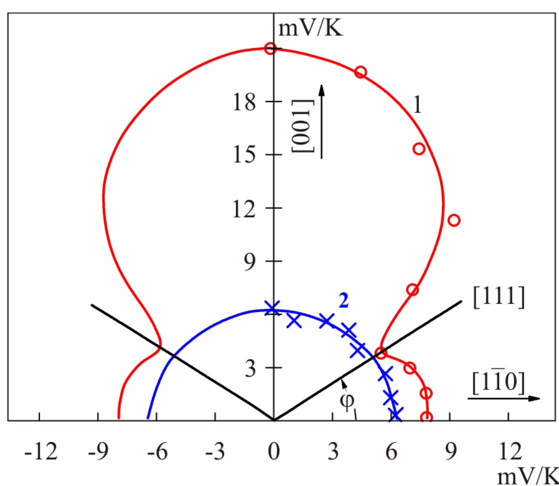

Fig. 4. Angular dependences of the drag piezothermoEMF $\alpha_{11} = f(\gamma)$ measured on strained (at $X = 0.8$ GPa – dependence 1) and unstrained ($X = 0$ – dependence 2) n-Si crystals with $n_e = 6.55\cdot10^{14}$ cm^{-3} at $T = 85$ K. ○, × – experimental results.

Using of microlevel anisotropic characteristics of multi-valley semiconductors for describing the macrolevel anisotropy of decisive importance are not only detail studies on the mechanisms of

origination of thermoEMF anisotropy within the microtheory, but also revealing the properties of transformation and total manifestation of anisotropies appeared on different levels, depending on crystal symmetry and its change due to the influence of external effects that have the assigned axial orientation (X, H, etc.).

Fig. 5 presents the results of measuring $\alpha_{ik}^{ph} / \alpha_0^{ph}$ and ρ_{ik} / ρ_0 versus X that fully confirm formula (19).

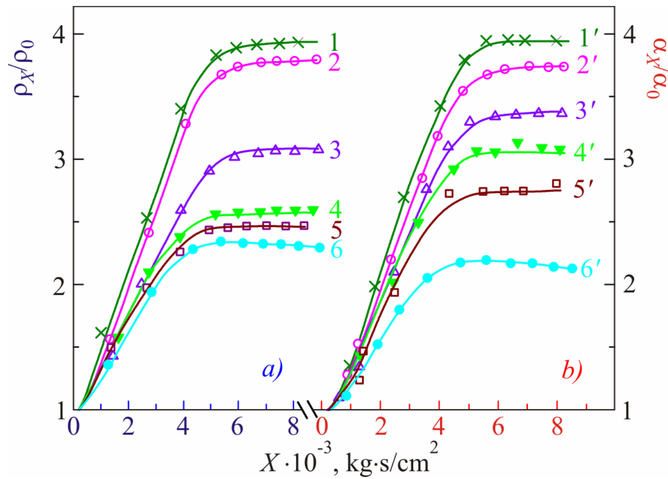

Fig. 5. Dependences of ρ_{11}/ρ_0 *(dependence 1 – 6) and* α_{11}/α_0 *(dependence 1′ – 6′) at T = 85 K on the value of* $\vec{X} // \vec{J}$, ∇T *// [001] for n-Si crystals with different concentration of electrons* n_e, *cm*$^{-3}$*:*
1 – $1.9\cdot10^{13}$*, 2 –* $1.29\cdot10^{14}$*, 3 –* $6.55\cdot10^{14}$*, 4 –* $2\cdot10^{15}$*, 5 –* $6.21\cdot10^{15}$*, 6 –* $2.6\cdot10^{16}$*.*

Thermomagnetic effects in semiconductors

Let us consider the thermoelectric properties of multi-valley semiconductors that are in a magnetic field. First of all we will study the symmetry properties of thermomagnetic sensor $\hat{\alpha}(\vec{H})$ in one valley. In semiconductors with a standard *c*-band (one valley, isotropic effective mass) components of the thermoelectric tensor in magnetic field $\hat{\alpha}(\vec{H})$ are interrelated by symmetry relations

$$\alpha_{i\kappa}(\vec{H}) = \alpha_{\kappa i}(-\vec{H}), \tag{21}$$

established by Onsager. We will show that due to the anisotropy of the energy spectrum of carriers the relation (21) in the presence of $\vec{H}$ is not fulfilled. This gives rise to two points that are of basic importance, namely on the form of commutation relations that would replace (21), as well as on possible creation of conditions that assure realization of these relations. For further consideration it is convenient to present tensor $\hat{\alpha}(\vec{H})$ as a sum of paired $\left(\hat{\alpha}^{+}(\vec{H})\right)$ and unpaired $\left(\hat{\alpha}^{-}(\vec{H})\right)$ in magnetic field parts and to dwell on each of them separately.

Let us introduce a variable

$$\hat{\Delta}(\vec{H}) = \hat{b}(\vec{H})\hat{\rho}(\vec{H}) - \hat{\rho}(-\vec{H})\,\hat{b}(-\vec{H}) \tag{22}$$

or

$$\Delta_{ik}(\vec{H}) = \alpha_{ik}(\vec{H}) - \alpha_{ki}(-\vec{H}), \tag{23}$$

that will be called the measure of commutation effect.

It turns out that

$$\hat{\Delta}^{+}\left(\vec{H}\right)=\frac{k}{e}\left(\mathcal{H}\hat{I}_3-\hat{I}_3\mathcal{H}\right)F_{+}\left(\vec{H}\right), \tag{24}$$

where

$$\mathcal{H}_{ik}=h_i\,h_k,\;\; \vec{h}=\frac{\hat{H}}{H},\;\; \left(\hat{I}_3\right)_{ik}=\delta_{i3}\,\delta_{k3},$$

and function $F_{+}\left(\vec{H}\right)$ depends on scattering mechanisms. In the case of power dependence $\hat{\mu}\left(\mathcal{E}\right)$ the function $F_{+}\left(\vec{H}\right)\sim\frac{K-1}{K}$. For the unpaired in $\vec{H}$ part of tensor $\hat{\Delta}\left(\vec{H}\right)$ the following relation will be valid

$$\hat{\Delta}^{-}\left(\vec{H}\right)=\frac{k}{e}\left[\hat{I}_3\left(\hat{e}\,\vec{h}\right)-\left(\hat{e}\,\vec{h}\right)\hat{I}_3\right]F_{-}\left(\vec{H}\right)+\frac{k}{e}\left(\hat{\gamma}+\hat{\tilde{\gamma}}\right)f\left(\vec{H}\right), \tag{25}$$

where $\gamma_{ik}=\begin{vmatrix} h_1 h_2 h_3 & h_2^2 h_3 & 0 \\ -h_1^2 h_3 & -h_1 h_2 h_3 & 0 \\ 0 & 0 & 0 \end{vmatrix}$; $\hat{e}$ is anti-symmetric Levi-Chivita pseudotensor of rank three; $\hat{\tilde{\gamma}}$ is a matrix transposed to $\hat{\gamma}$; $F_{-}\left(\vec{H}\right)$ and $f\left(\vec{H}\right)$ are known functions (combinations of average products) [6].

Assuming that $\hat{\mu}\left(\mathcal{E}\right)$ has the form of (4) (that is, scattering is anisotropic), then $f\left(\vec{H}\right)\neq 0$, and it means that even the value of diagonal components of the tensor $\hat{\alpha}\left(\vec{H}\right)$ depends on the sign (i.e., direction) of a magnetic field, and it is caused by anisotropic scattering.

In the case when $\hat{\mu}\left(\mathcal{E}\right)$ is described by power dependence, the function $f\left(\vec{H}\right)=0$, and for the electron part of $\hat{\alpha}\left(\vec{H}\right)$ the following relations are valid:

$$\left.\begin{aligned}\alpha_{31}\left(-\vec{H}\right)=K\,\alpha_{13}\left(\vec{H}\right)\\ \alpha_{32}\left(-\vec{H}\right)=K\,\alpha_{23}\left(\vec{H}\right)\end{aligned}\right\}, \tag{26}$$

and the other components meet the symmetry relation (21).

In the region of electron-phonon drag the proportionality factor in commutation relations of the type (26) is equal to K/K_j, where $K_j=\frac{\alpha_{\parallel}^{(j)}}{\alpha_{\perp}^{(j)}}$ is the anisotropy parameter of the drag thermoEMF caused by the drag of electrons by polarization phonons j.

The above peculiarities of tensor $\hat{\alpha}$ in one valley, no doubt, should be also exhibited in the case of a multi-valley semiconductor located in a magnetic field, the more so in the presence of uniaxial elastic strain. Moreover, in a semiconductor with several valleys the multi-valley effects should be exhibited as well (in addition to the above peculiarities).

Let us consider those of them which vividly illustrate the role of micro- and macrolevel anisotropy (mobility and drag thermoEMF) under the influence of macroscopic external effects from magnetic fields and uniaxial elastic deformation. Typical in this respect are unpaired thermomagnetic effects in strained semiconductors of cubic symmetry in a weak magnetic field.

Let us consider as an example the strained *n-Ge* and *n-Si*. For a linear dependence $\hat{\alpha}^{-}\left(\vec{H}\right)$ it can be written

$$\hat{\alpha}^{-}\left(\vec{H}\right)=-\hat{N}\,\vec{H}, \tag{27}$$

where $\hat{N}$ is a generalized Nernst-Ettingshausen tensor (nonsymmetrical pseudotensor of rank three). Let us separate from tensor $\hat{N}$ the anti-symmetrical and symmetrical parts, that is, present the tensor in the form

$$\hat{N}=\hat{e}\,\hat{Q}+\hat{S}. \tag{28}$$

Then, with regard to (27) and (28), the Nernst-Ettingshausen field

$$\vec{E}_{N\text{-}E}=\left[\,\hat{Q}\,\vec{H},\nabla T\,\right]-\hat{S}\,\vec{H}\,\nabla T. \tag{29}$$

The presence of other summand in expression (29) means that the field $\vec{E}_{N\text{-}E}$ is not perpendicular to vectors $\vec{H}$ and ∇T. A deviation of field $\vec{E}_{N\text{-}E}$ from the perpendicular in the plane that passes through $\vec{H}$ and ∇T, occurs in the case when tensor $\hat{Q}$ is nonsymmetrical. Indeed, separating from $\hat{Q}$ the antisymmetrical part and comparing to its dual vector $\vec{Q}$ for which the relation $Q_i=\frac{1}{2}e_{ikl}\,Q^{a}_{kl}$ is valid, expression (29) can be written as

$$\vec{E}_{N\text{-}E}=\left[\,\hat{Q}^{s}\,\vec{H},\nabla T\,\right]+\left[\,\left[\,\vec{Q}\,\vec{H}\,\right]\,\nabla T\,\right]-\hat{S}\,\vec{H}\,\nabla T.$$

It turns out that in elastically strained *n-Ge* and *n-Si* both vector $\vec{Q}$ and tensor $\hat{S}$ are different from zero, the tensor $\hat{S}$ describing the so-called commutation effect for the nondiagonal components of the tensor of thermoEMF which is reflected in the fact that under conditions when a magnetic field is not directed along the principal ellipsoid axis and does not lie in the plane which is perpendicular to it, $\alpha_{ik}\left(\vec{H}\right)\neq\alpha_{ki}\left(-\vec{H}\right)$. If we introduce the measure of commutation effect

$$\Delta^{-}_{ik}\left(\vec{H}\right)=\alpha^{-}_{ik}\left(\vec{H}\right)-\alpha^{-}_{ki}\left(-\vec{H}\right),$$

then

$$\hat{\Delta}^{-}\left(\vec{H}\right)=2\,\hat{S}\,\vec{H}.$$

Dissimilarity from zero of vector $\vec{Q}$ is a direct consequence of the multi-valley character of semiconductor ($Q_i\sim\Phi$), since for $\vec{Q}\neq 0$ it is necessary that the Brillouin zone be characterized at least by three groups of nonequivalent valleys.

A basically different situation will be created when in quadratic with respect to components of vector $\vec{H}$ approximation the strain nonequivalence of valleys will be imposed by the nonequivalence due to distinctions in the orientation of vector $\vec{H}$ with respect to the principal axes of mass ellipsoids (orientation nonequivalence). Under these conditions, one can introduce the tensor

$$\hat{U}=\sum_{k=1}^{s}\overline{n}_k\,\hat{Q}^{(k)},$$

which is the analog of tensor $\hat{C}$, and the value

$$\overline{n}_k = n_k \ \mathrm{Sp}\, \hat{a}^{(k)}\, \hat{\mathcal{H}}$$

can be referred to as parameter of nonequivalence of *k*-th valley (in low-intensity magnetic fields). From the designation of tensor $\hat{U}$ it follows that it does not degenerate into a scalar even in the absence of strain. It means that in quadratic with respect to H_i approximation the thermomagnetic effect (even in unstrained multi-valley semiconductors) should exhibit tensor properties. Exactly this accounts for the origination of paired Nernst-Ettingshausen effect and paired thermomagnetic analog of the Grabner effect, anticipated and experimentally measured in [7, 8].

However, under conditions in hand (i.e. at $X = 0$) the relation $\alpha_{ik}\left(\vec{H}\right) = \alpha_{ki}\left(-\vec{H}\right)$ is still met. And it is violated at $X \neq 0$ (i.e. in the presence of strain). Here it should be noted that even in the absence of strain (i.e. at $X = 0$), if in the expansion in H_i of tensor $\hat{\alpha}\left(\vec{H}\right)$ we consider higher than quadratic terms, then the nonequivalence of valleys in a magnetic field ($\vec{H} \neq 0$) leads to origination of new effects, such as unpaired thermomagnetic analog of the Grabner effect, commutation effect, etc.

In a classically strong magnetic field a parameter of the nonequivalence of the valleys

$$\overline{n}_k = \frac{n_k}{1 + \left(K - 1\right)\ Sp\, \hat{a}^{(k)}\, \hat{\mathcal{H}}}$$

more drastically depends on the anisotropic characteristics of a semiconductor on the microlevel, so the thermomagnetic effects on the macrolevel in this case are characterized by the most pronounced anisotropy. Moreover, planar thermomagnetic effects arise in a classically strong magnetic field [9].

It should be noted that the nonequivalence of valleys caused by strain introduces even qualitative changes into the field dependence of thermomagnetic coefficients. For this same reason the thermomagnetic analog of the Grabner effect or the longitudinal Nernst-Ettingshausen effect under strong uniaxial elastic strain in a classically strong magnetic field essentially depends on the value of anisotropy parameter of the drag thermoEMF *M* (the electronic part of these effects is equal to zero). Moreover, the efficiency of electron drag by polarization phonons *j* depends differently on the value of mechanical strain *X* for phonons of different polarizations, which, if necessary, can be rather reliably substantiated.

The anisotropic thermoelectric effects (for instance, thermoEMF anisotropy in a multi-valley semiconductor of cubic symmetry under uniaxial elastic strain) are due to the deformation nonequivalence of valleys. In a classically strong magnetic field due to "magnetic" (or orientation) nonequivalence, there arises a longitudinal Nernst-Ettingshausen effect in a longitudinal magnetic field. Both in the former and the latter cases the same reasons bring about a change in resistivity.

Research on thermoEMF in semiconductors (as in metals) is inseparably related to the use of temperature gradient. As long as it is impossible to grow ideally homogeneous crystals (without any inhomogeneities in the volumetric distribution of doping and residual impurities and free from inhomogeneous distribution of internal mechanical strains), the question now arises as to whether it is possible to use a relation of thermoEMF tensor $\hat{\alpha}$ (or drag thermoEMF anisotropy $\Delta\alpha$) to a change in some less sensitive to the presence of parameter impurity inhomogeneities for a more detailed study of $\hat{\alpha}$ (or $\Delta\alpha$) according to a change in selected parameter .

As is shown by theory [2], for the case of strain nonequivalence of valleys in a multi-valley semiconductor (of *n-Si* or *n-Ge* type) caused by directional pressure, as well as for the case of "magnetic" (or orientation) nonequivalence of valleys (due to the use of an external magnetic field),

between the relative changes in electron-phonon drag thermoEMF ($\Delta\alpha^{ph}/\alpha_0^{ph}$) and resistivity (($\Delta\rho/\rho_0$) there is a linear relationship:

$$\frac{\Delta\alpha^{ph}}{\alpha_0^{ph}} = \frac{M-1}{K-1}\cdot\frac{3K}{2K+M}\cdot\frac{\Delta\rho}{\rho_0},$$

where

$$K = \frac{\mu_\perp}{\mu_\parallel} = \frac{3}{2}\frac{\rho_\infty}{\rho_0} - \frac{1}{2},$$

$$M = \frac{\alpha_\parallel^{ph}}{\alpha_\perp^{ph}} = \frac{2K}{(2K+1)\dfrac{\alpha_0^{ph}}{\alpha_\infty^{ph}} - 1} = \frac{2K}{(2K+1)\dfrac{\alpha_0 - \alpha_{(6)}^{e}}{\alpha_\infty - \alpha_{(2)}^{e}} - 1},$$

and the differences $\alpha_0 - \alpha_{(6)}^{e} = \alpha_0^{ph}$ and $\alpha_\infty - \alpha_{(2)}^{e} = \alpha_\infty^{ph}$ are used to mean the phonon components of the electron-phonon drag thermoEMF in an unstrained and in a heavily strained *n-Si* crystal, respectively.

For a practical use of thermoelectric characteristics of material one should not only know some of thermoEMF components, but have at one's disposal information on the thermoEMF anisotropy $\Delta\alpha$, typical of this material (if it is thermoelectrically anisotropic) or induced due to unidirectional elastic deformation or classically strong magnetic field.

In the case of multi-valley semiconductors (of the type *n-Ge* or *n-Si*), having the values of phonon components of thermoEMF for the unstrained (α_0^{ph}) and heavily strained crystal (α_∞^{ph}), as well as the values of the anisotropy parameters *K* and M, one can also calculate the thermoEMF anisotropy using the relation

$$\Delta\alpha = \alpha_\infty^{ph}\left(1 - \frac{1}{M}\right),$$

or

$$\Delta\alpha = \left(\alpha_\infty^{ph} - \alpha_0^{ph}\right)\left(1 + \frac{1}{2K}\right).$$

Conclusions

1. A universal relationship between the relative changes in electron-phonon drag thermoEMF $\Delta\alpha^{ph}/\alpha_0^{ph}$ and resistivity $\Delta\rho/\rho_0$ in a field of directional pressure or in a classically strong magnetic field has been established.
2. The results obtained are valid not only for conditions of carrier scattering on crystal lattice vibrations, but in the case of mixed scattering (on crystal lattice vibrations and on doping impurities). They also can experience only some quantitative modification, rather than qualitative changes.
3. The calculations cover the cases when under the influence of external effects only inter-minima migration of electrons takes place, but all of them remain in conduction band, i.e. neither strain nor magnetic carrier "freeze-out" of conduction band is present.
4. Under conditions when a magnetic field $\vec{H}$ is directed at an angle to revolution axis of mass ellipsoid and does not lie in the plane normal to it, the symmetry relations for the nondiagonal components of tensor $\hat{\alpha}(\vec{H})$ even in the case of one valley are not fulfilled and, as a result, a commutation effect $\alpha_{ik}(\vec{H}) \neq \alpha_{ki}(-\vec{H})$ becomes apparent.

5. Significant role of scattering anisotropy in a one-valley semiconductor causes a dependence of the value of diagonal components of the tensor $\hat{\alpha}\left(\vec{H}\right)$ on magnetic field direction, and in the presence of several valleys the multi-valley effects also make their contribution to the considered effect for the diagonal components.

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