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## Gibbs Grand Thermodynamic Potential in the Theory of Kinetic Crystal Properties

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In this paper, using Gibbs grand thermodynamic potential, kinetic tensors of electrical and thermal conductivity generalized equations known in non-equilibrium thermodynamics have been proven. These tensors determine calculation algorithms of the material tensors of conductor crystals and various galvanomagnetic and thermomagnetic effects coefficients. These algorithms are pragmatic formulas in calculation problems of crystals kinetic properties and in the problems for prediction of semiconductor crystals with preset properties. Their pragmatism is proven by the huge number of scientific papers dedicated to kinetic properties of semiconductor crystals study.

**Keywords:** gibbs potential, electrical conductivity, thermal conductivity, algorithm, tensor.

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### I. Elements of the general theory of crystals kinetic properties

Kinetic properties of conductor crystals are predetermined by the concentration of "free" charge carriers in crystals and their movements in the crystal lattice interstitials.

In the state of thermodynamic balance "free" charge carriers are moving randomly, their average energy remains the same and entropy of all the charge carriers has a maximum value. This is thermodynamically balanced gas of charge carriers.

Presence of drift disturbances, such as electric field with  $\vec{E}$  tension, or  $\nabla_r T$  temperature gradient (these disturbances may exist in the crystal simultaneously), within the crystal causes the gas of charge carriers left state of thermodynamic equilibrium state and makes it a non-equilibrium ensemble of particles. In this case, each particle with charge  $ze$  is affected by drift force  $\vec{F}_d$  [1-4]:

$$\vec{F}_d = ze\vec{E}_d; \quad \vec{E}_d = \vec{E} - \left( \frac{k}{ze} \right) \left( \frac{e - m}{kT} \right) \nabla_r T \quad (1)$$

where:  $z = \pm 1$  – charge denotement,  $e$  – charge of electron,  $k$  – Boltzmann constant,  $\epsilon$  – average energy of charge carrier,  $T$  – crystal temperature.

As a result of  $\vec{F}_d$  drift force, all charge carriers begin to move towards force with  $\vec{v}_d$  drift velocity,

which depends on both  $\vec{F}_d$ , and crystal properties.

The presence of  $\vec{v}_d$  drift velocity causes the formation of particles flow. At the same time, interchange of electricity, heat (energy) etc. takes place. Thus, if the drift fields are present, the set of charge carriers in crystals is converted into a grand non-equilibrium canonical ensemble with a variable number of particles.

Such a grand canonical ensemble, as shown in reference [1], is characterized by Gibbs grand thermodynamic potential, taking into account spin degeneracy:

$$\Omega = -2kT \sum_p \ln \left\{ 1 + \exp \left( \frac{m + \Delta m_p^r - e p^r}{kT} \right) \right\}, \quad (2)$$

In this formula  $p^r$  – a wave vector of the charge carrier,  $e p^r$  – charge carriers dispersion law, and  $\Delta m_p^r$  – the change of the chemical potential of a particle under the influence of disturbances, which disturbs thermodynamic equilibrium of the crystal; in the absence of such disturbances  $\Delta m_p^r = 0$ .

The value  $\Delta \mu_p^r$  is calculated in reference [1], which demonstrates that  $\Delta \mu(p^r)$  is an odd function of vector  $p^r$ , and for isotropic crystal, it has the following value:

$$\begin{aligned}
 \Delta m(\vec{p}) &= z p \left( u_{ij}(\vec{B}, \mathbf{e}) \right) E_d = z p \left( \frac{u(\mathbf{e}) d_{ij} + z u(\mathbf{e})^2 d_{ijl} B_l + u(\mathbf{e})^3 B_i B_j}{d(\vec{B})} \right) E_d = \\
 &= z p \left( u_{ij}^{(s)}(\vec{B}, \mathbf{e}) \right) E_d + z p \left( u_{ij}^{(a)}(\vec{B}, \mathbf{e}) \right) E_d; \left( u_{ij}^{(s)}(\vec{B}, \mathbf{e}) \right) = \left( \frac{u(\mathbf{e}) d_{ij} + u(\mathbf{e})^3 B_i B_j}{d(\vec{B})} \right); \\
 \left( u_{ij}^{(a)}(\vec{B}, \mathbf{e}) \right) &= \left( \frac{z u(\mathbf{e})^2 d_{ijl} B_l}{d(\vec{B})} \right); \quad d(\vec{B}) = 1 + (u(\mathbf{e}) B)^2
 \end{aligned} \tag{3}$$

The function  $u = u(\varepsilon)$ , that is included in those equations, has the same units of measurement as charge carrier mobility ( $m^2 V \cdot s$ ). This function describes the effect of charge carriers scattering mechanisms on kinetic properties of the crystals. In its physical sense,  $u(\varepsilon)$  is not averaged particle charge carrier mobility, and for crystals with isotropic dispersion law  $\varepsilon_{\vec{p}} = \varepsilon(\vec{p}) = \varepsilon(p)$ , it is [1]:

$$u = \frac{e\tau}{p} \cdot \frac{\partial \varepsilon}{\partial p}$$

Quantum mechanical calculations demonstrate, that the scattering function in isotropic crystals for important scattering mechanisms can be described by the following general formula [5, 6]:

$$u(\varepsilon) = u^{(r)}(T) p^{(2r-3)} \left( \frac{d\varepsilon}{dp} \right)^2$$

where  $u^{(r)}(T)$  - is the known values for a specific mechanism of temperature function scattering, and  $r$  - is index of scattering and has the following values:  $r = 0$  at the account of carrier scattering on acoustic phonons and on point defects of a crystal lattice;  $r = 1$  to the case with scattering on optical phonons at high temperatures above the Debye's temperature;  $r = 2$  to the case with scattering on impurity atoms or ions.

In this formula, symmetric and antisymmetric parts of the tensor  $\left( u_{ij}(\vec{B}, \mathbf{e}) \right)$  are marked by superscripts  $s$  and  $a$  in parenthesis ( $s$ ), ( $a$ ), and  $\delta_{ij}$ ,  $\delta_{ijl}$  are known Kronecker and Levi-Civita functions.

Then, with the use of statistical thermodynamics methods, total number of particles  $N$  of this non-equilibrium ensemble, its internal energy  $U$ , enthalpy  $H$ , free energy  $F$  and entropy  $S$  are calculated:

$$N = - \left( \frac{d\Omega}{dm} \right)_T = 2 \sum_{\vec{p}} f_{\vec{p}}^{\mathbf{r}}, \tag{4}$$

$$U = - \left( \frac{\partial \Omega}{\partial m} \right)_T m - \left( \frac{\partial \Omega}{\partial T} \right)_m T + \Omega = 2 \sum_{\vec{p}} \left( e_{\vec{p}}^{\mathbf{r}} - \Delta e_{\vec{p}}^{\mathbf{r}} \right) f_{\vec{p}}^{\mathbf{r}} \tag{5}$$

$$H = N m - \left( \frac{\partial \Omega}{\partial T} \right)_m T = -\Omega + 2 \sum_{\vec{p}} \left( e_{\vec{p}}^{\mathbf{r}} - \Delta e_{\vec{p}}^{\mathbf{r}} \right) f_{\vec{p}}^{\mathbf{r}}, \tag{6}$$

$$F = N m + \Omega, \tag{7}$$

$$S = - \left( \frac{d\Omega}{dT} \right)_m = -2k \sum_{\vec{p}} \left\{ f_{\vec{p}}^{\mathbf{r}} \cdot \ln \left( f_{\vec{p}}^{\mathbf{r}} \right) + \left( 1 - f_{\vec{p}}^{\mathbf{r}} \right) \cdot \ln \left( 1 - f_{\vec{p}}^{\mathbf{r}} \right) \right\}, \tag{8}$$

where  $f_{\vec{p}}^{\mathbf{r}}$  is a non-equilibrium distribution function of single particle, which non-equilibrium gas carriers statistics is based on. This feature is described by the formula:

$$f_{\vec{p}}^{\mathbf{r}} = \frac{1}{\exp \left( \frac{e_{\vec{p}}^{\mathbf{r}} - m - \Delta m_{\vec{p}}^{\mathbf{r}}}{kT} \right) + 1}, \tag{9}$$

Formula (8) displays that the entropy of a non-equilibrium gas corresponds to well known thermodynamic entropy equations for equilibrium gas. This means, that the thermodynamic potential (2) and the distribution function (9) correspond to the laws of non-equilibrium processes thermodynamics.

For a small deviation of the crystal from thermodynamic equilibrium, when Ohm's law for the current is applicable, value  $\Delta m(\vec{p})$  is smaller than  $(m - e_{\vec{p}}^{\mathbf{r}})$ , that is why thermodynamic potential  $\Omega$  (2) and non-equilibrium distribution function  $f_{\vec{p}}^{\mathbf{r}}$  (9) can be expanded in Taylor series based on this value, being limited by the linear term of the expansion. Then we have:

$$\Omega = -2kT \sum_{\vec{p}} \ln \left\{ 1 + \exp \left( \frac{m - e_{\vec{p}}^{\mathbf{r}}}{kT} \right) \right\} - 2kT \sum_{\vec{p}} \Delta e_{\vec{p}}^{\mathbf{r}} f_0(\mathbf{e}_{\vec{p}}^{\mathbf{r}}), \tag{10}$$

$$f_{\vec{p}}^{\mathbf{r}} = f_0(\mathbf{e}_{\vec{p}}^{\mathbf{r}}) + \left( - \frac{df_0(\mathbf{e}_{\vec{p}}^{\mathbf{r}})}{de_{\vec{p}}^{\mathbf{r}}} \right) \Delta m(\vec{p}), \tag{11}$$

where  $f_0(\varepsilon_{\mathbf{p}}^{\mathbf{r}}) = \frac{1}{\exp\left(\frac{\varepsilon_{\mathbf{p}}^{\mathbf{r}} - \mu}{kT}\right) + 1}$  - is Fermi-Dirac

function (it is an even function of vector  $\mathbf{p}$ ).

In this regard, the second term on the right in formula (10) is equal to zero, as the sum of odd symmetric functions within the summation.

If the expansions (10) and (11) will be used for calculating the values (4) - (7), they will acquire such values as for grand equilibrium ensemble of particles. This physically means that, under these conditions of observation, the number of N particles and thermodynamic potentials (5) - (7) of non-equilibrium Fermi gas within the crystals have the same values as for balanced.

$$\frac{dS}{dt} = -\frac{d}{dt}\left(\frac{d\Omega}{dT}\right)_{\mathbf{m}} = \frac{1}{T}\left[2ze\sum_{\mathbf{p}}\mathbf{v}_{\mathbf{p}}^{\mathbf{r}}f_{\mathbf{p}}^{\mathbf{r}}E - 2\sum_{\mathbf{p}}\left(e\mathbf{p} - m\right)\mathbf{v}_{\mathbf{p}}^{\mathbf{r}}f_{\mathbf{p}}^{\mathbf{r}}\frac{\nabla_r T}{T}\right]. \quad (14)$$

where  $\mathbf{v} = \nabla_{\mathbf{p}} e(\mathbf{p})$  is vector of the charge carrier velocity in crystal.

Comparing this expression with formula (13), which describes the second law of thermodynamics, the conclusion that the vectors  $\mathbf{j}$  and  $\mathbf{q}$  are equal are made next expressions:

$$\mathbf{j} = 2ze\sum_{\mathbf{p}}\mathbf{v}_{\mathbf{p}}^{\mathbf{r}}f_{\mathbf{p}}^{\mathbf{r}}, \quad (15)$$

$$\mathbf{q} = 2\sum_{\mathbf{p}}\left(e\mathbf{p} - m\right)\mathbf{v}_{\mathbf{p}}^{\mathbf{r}}f_{\mathbf{p}}^{\mathbf{r}}. \quad (16)$$

The equations (15) and (16) are respectively named generalized equations of electrical conductivity and thermal conductivity in the kinetic theory.

In the field of Ohmic conductivity of the crystal deviation of its energy state from thermodynamic equilibrium is insignificant. Therefore, Taylor

In a non-equilibrium gas of charge carriers their entropy increases and electricity and heat are being transported, which is described by the first and second laws of non-equilibrium thermodynamics:

$$\frac{dU}{dt} = -\text{div}\mathbf{q} + \mathbf{j}E, \quad (12)$$

$$\frac{dS}{dt} = \frac{1}{T}\left(\mathbf{j}E - \frac{\mathbf{q}\nabla_r T}{T}\right), \quad (13)$$

where  $\mathbf{j}$ ,  $\mathbf{q}$  are the vectors of current density and heat flow.

If the formulas (8) and (9) will be used for  $\frac{dS}{dt}$  derivative calculation, the result of calculations will be:

approximation(11) can be used in the statistical calculations for non-equilibrium distribution function (9).

Further, in this approximation, with vector  $\mathbf{p}$  summing it should be counted that  $\Delta\mu(\mathbf{p})$  and charge velocity vector  $\mathbf{v}_{\mathbf{p}}^{\mathbf{r}} = \nabla_{\mathbf{p}} e(\mathbf{p})$  are odd functions of vector  $\mathbf{p}$ .

Then, in the Ohmic region of the crystal conductivity up to a quadratic terms of equation described by the disturbance that brings charge carriers gas from thermodynamic equilibrium, its concentration  $n$  and thermodynamic potentials have the same values as in the state of thermodynamic equilibrium.

Under these conditions, the vectors  $\mathbf{j}$  and  $\mathbf{q}$  are calculated in the Ohmic region of conductance taking into account (11):

$$\mathbf{j} = 2ze\sum_{\mathbf{p}}\mathbf{v}_{\mathbf{p}}^{\mathbf{r}}\Delta\mathbf{m}_{\mathbf{p}}^{\mathbf{r}}\left(-\frac{df_0}{de}\right) = ze2\sum_{\mathbf{p}}\frac{1}{p}\left(\frac{de}{dp}\right)_{\mathbf{p}}\cdot\Delta\mathbf{m}_{\mathbf{p}}^{\mathbf{r}}\left(-\frac{df_0}{de}\right), \quad (17)$$

$$\mathbf{q} = 2\sum_{\mathbf{p}}(e-m)\mathbf{v}_{\mathbf{p}}^{\mathbf{r}}\Delta\mathbf{m}_{\mathbf{p}}^{\mathbf{r}}\left(-\frac{df_0}{de}\right) = ze\left(\frac{kT}{ze}\right)2\sum_{\mathbf{p}}\left(\frac{e-m}{kT}\right)\frac{1}{p}\left(\frac{de}{dp}\right)_{\mathbf{p}}\cdot\Delta\mathbf{m}_{\mathbf{p}}^{\mathbf{r}}\left(-\frac{df_0}{de}\right), \quad (18)$$

The values of the function  $\Delta\mu_p = \Delta\mu(\mathbf{p})$  will be put in those equations using formula (3). Then, known formal method of transition from summation to integration is used. After, generalized equations of electrical conductivity and thermal conductivity for vectors  $\mathbf{j}$  and  $\mathbf{q}$  look like that:

$$\mathbf{j} = \left(\mathbf{s}_{ij}(\mathbf{B})\right)_{\mathbf{E}} - \left(\mathbf{b}_{ij}(\mathbf{B})\right)_{\nabla_r T}, \quad (19)$$

$$\mathbf{q} = \left(\mathbf{g}_{ij}(\mathbf{B})\right)_{\mathbf{E}} - \left(\mathbf{h}_{ij}(\mathbf{B})\right)_{\nabla_r T}, \quad (20)$$

The coefficients  $\left(\mathbf{s}_{ij}(\mathbf{B})\right), \left(\mathbf{b}_{ij}(\mathbf{B})\right), \left(\mathbf{g}_{ij}(\mathbf{B})\right), \left(\mathbf{h}_{ij}(\mathbf{B})\right)$  are called tensors of kinetic coefficients and they, accordingly, acquire such values in those equations:

$$\left\langle s_{ij}(\mathbf{B}) \right\rangle = en \left\langle \left\langle u_{ij}(\mathbf{B}) \right\rangle \right\rangle = en \left\langle \left\langle u_{ij}^{(s)}(\mathbf{B}) \right\rangle \right\rangle + en \left\langle \left\langle u_{ij}^{(a)}(\mathbf{B}) \right\rangle \right\rangle, \quad (19, a)$$

$$\left\langle b_{ij}(\mathbf{B}) \right\rangle = en \left( \frac{k}{ze} \right) \left\langle \left\langle h \cdot u_{ij}(\mathbf{B}) \right\rangle \right\rangle = en \left( \frac{k}{ze} \right) \left\langle \left\langle h \cdot u_{ij}^{(s)}(\mathbf{B}) \right\rangle \right\rangle + en \left( \frac{k}{ze} \right) \left\langle \left\langle h \cdot u_{ij}^{(a)}(\mathbf{B}) \right\rangle \right\rangle, \quad (19, b)$$

$$\left\langle g_{ij}(\mathbf{B}) \right\rangle = en \left( \frac{k}{ze} \right) T \left\langle \left\langle h \cdot u_{ij}(\mathbf{B}) \right\rangle \right\rangle = en \left( \frac{k}{ze} \right) \left\langle \left\langle h \cdot u_{ij}^{(s)}(\mathbf{B}) \right\rangle \right\rangle + en \left( \frac{k}{ze} \right) \left\langle \left\langle h \cdot u_{ij}^{(a)}(\mathbf{B}) \right\rangle \right\rangle, \quad (20, a)$$

$$\left\langle h_{ij}(\mathbf{B}) \right\rangle = en \left( \frac{k}{ze} \right)^2 T \left\langle \left\langle h^2 \cdot u_{ij}(\mathbf{B}) \right\rangle \right\rangle = en \left( \frac{k}{ze} \right)^2 T \left\langle \left\langle h^2 \cdot u_{ij}^{(s)}(\mathbf{B}) \right\rangle \right\rangle + en \left( \frac{k}{ze} \right)^2 T \left\langle \left\langle h^2 \cdot u_{ij}^{(a)}(\mathbf{B}) \right\rangle \right\rangle, \quad (20, b)$$

In those equations  $n$  is the concentration of charge carriers

$$n = \int_0^\infty G(e) \left( -\frac{df_0}{de} \right) de, \quad (21)$$

and angle brackets, for the convenience of notes, mean averaging operator for tensor components  $\eta^l \cdot u_{ij}(\mathbf{B})$ :

$$\left\langle h^l \cdot u_{ij}(\mathbf{B}, \mathbf{e}) \right\rangle = \frac{\int_0^\infty h^l \cdot u_{ij}(\mathbf{B}, \mathbf{e}) G(e) \left( -\frac{df_0(e)}{de} \right) de}{\int_0^\infty G(e) \left( -\frac{df_0(e)}{de} \right) de}, \quad (22)$$

$$h^l = \left( \frac{e - m}{kT} \right)^l, \quad l = 0, 1, 2, \quad (23)$$

$G(e) = \int_0^e g(e) de$ , is the density of energy states in the

energy area (24)

$$u(\varepsilon) - \text{is scattering function. } u_{ij}(\mathbf{B}) = u_{ij}(u(\varepsilon), \mathbf{B}), \quad (25)$$

Equations (19) and (20) are the known equations of thermodynamics irreversible processes. They describe the reaction of conducting medium to the electric field, temperature gradient and magnetic field, characterized by the vector of induction  $\mathbf{B}$ .

In generalized electrical conductivity(19) and thermal conductivity(20) equations all the coefficients next to correspondent factors are called tensors of kinetic coefficients. The material tensors of the crystals are determined by mediation of these coefficients.

Equations (19) and (20) can result in the following with linear transformation:

$$\mathbf{E} = \left( \sigma_{ij}(\mathbf{B}) \right)^{-1} \mathbf{j} + \left( \sigma_{ij}(\mathbf{B}) \right)^{-1} \cdot \left( \beta_{ij}(\mathbf{B}) \right) \nabla_{\mathbf{r}} T, \quad (26)$$

$$\mathbf{q} = \left( g_{ij}(\mathbf{B}) \right) \cdot \left( s_{ij}(\mathbf{B}) \right)^{-1} \mathbf{j} - \left( \left( h_{ij}(\mathbf{B}) \right) - \left( g_{ij}(\mathbf{B}) \right) \cdot \left( s_{ij}(\mathbf{B}) \right)^{-1} \cdot \left( b_{ij}(\mathbf{B}) \right) \right) \nabla_{\mathbf{r}} T, \quad (27)$$

The tensors, multiplied by the vectors  $\mathbf{j}$  and  $\nabla_{\mathbf{r}} T$ , according to Onsager symmetry theory, have the

following values in those equations:

$$\left( r_{ij}(\mathbf{B}) + R_{ij} d_{ijl} B_l \right) = \left( s_{ij}(\mathbf{B}) \right)^{-1} = \frac{1}{en} \left\langle \left\langle u_{ij}(\mathbf{B}) \right\rangle \right\rangle^{-1} \quad (28)$$

$$\left( a_{ij}(\mathbf{B}) + N_{ik} d_{ijl} B_l \right) = \left( s_{ij}(\mathbf{B}) \right)^{-1} \cdot \left( b_{ij}(\mathbf{B}) \right) = \left( \frac{k}{ze} \right) \left\langle \left\langle u_{ij}(\mathbf{B}) \right\rangle \right\rangle^{-1} \left\langle \left\langle h \cdot u_{ij}(\mathbf{B}) \right\rangle \right\rangle \quad (29)$$

$$\left( p_{ij}(\mathbf{B}) + P_{ij} d_{ijl} B_l \right) = \left( g_{ij}(\mathbf{B}) \right) \cdot \left( s_{ij}(\mathbf{B}) \right)^{-1} = \left( \frac{k}{ze} \right) T \left\langle \left\langle u_{ij}(\mathbf{B}) \right\rangle \right\rangle^{-1} \left\langle \left\langle h \cdot u_{ij}(\mathbf{B}) \right\rangle \right\rangle \quad (30)$$

$$\left( c_{ij}(\mathbf{B}) + S_{ij} d_{ijl} B_l \right) = \left( h_{ij}(\mathbf{B}) \right) - \left( g_{ij}(\mathbf{B}) \right) \cdot \left( s_{ij}(\mathbf{B}) \right)^{-1} \cdot \left( b_{ij}(\mathbf{B}) \right) =$$

$$\begin{aligned}
 &= \left( \frac{k}{ze} \right)^2 T \left( s_{ij}(\mathbf{B}) \right) \left\{ \left( \langle u_{ij}(\mathbf{B}) \rangle \right)^{-1} \left( \frac{e^2}{(kT)^2} u_{ij}(\mathbf{B}) \right) - \left[ \left( \langle u_{ij}(\mathbf{B}) \rangle \right)^{-1} \left( \frac{e}{kT} u_{ij}(\mathbf{B}) \right) \right]^2 \right\} = \\
 &= \left( \frac{k}{ze} \right)^2 T \left( s_{ij}(\mathbf{B}) \right) \cdot \left\{ K_{ij}(\mathbf{B}) \right\}
 \end{aligned} \tag{31}$$

Formula (31) is cumbersome and difficult to analyze, because it is written in abbreviated form and in this form it describes the Wiedemann-Franz law for charge carriers thermal conductivity in the crystal in the presence of a magnetic field.

There are symmetric tensors  $\left( \rho_{ij}(\mathbf{B}) \right)$ ,  $\left( \alpha_{ij}(\mathbf{B}) \right)$ ,  $\left( \pi_{ij}(\mathbf{B}) \right)$ ,  $\left( \chi_{ij}(\mathbf{B}) \right)$  in the equations (28)-(31), namely material tensors of resistivity, Seebeck coefficient, Peltier and thermal conductivity of the crystal efficient, which must be either experimentally measured or theoretically calculated. They are the even functions of magnetic induction vector.

The coefficients  $R_{ij}(\mathbf{B})$  and  $P_{ij}(\mathbf{B})$  are the

coefficients of transverse galvanomagnetic effects of Hall and Ettingshausen, and the coefficients  $N_{ij}(\mathbf{B})$ , and  $S_{ij}(\mathbf{B})$  are the Nernst-Ettingshausen's and Righi-Leduc's coefficients of transverse thermomagnetic effects. They are the even functions of the magnetic induction vector, and within isotropic crystals, these coefficients are scalar even magnetic induction functions, i.e.:

$$\begin{aligned}
 R_{ij}(\mathbf{B}) &= R(\mathbf{B}) = R(-\mathbf{B}); \quad P_{ij}(\mathbf{B}) = P(\mathbf{B}) = P(-\mathbf{B}), \\
 N_{ij}(\mathbf{B}) &= N(\mathbf{B}) = N(-\mathbf{B}), \quad S_{ij}(\mathbf{B}) = S(\mathbf{B}) = S(-\mathbf{B}).
 \end{aligned}$$

So, the equations (26) and (27) can be formulated for isotropic crystals:

$$\mathbf{E} = \left( r_{ij}(\mathbf{B}) \right) \mathbf{j} + R(\mathbf{B}) \cdot \left[ \mathbf{B} \times \mathbf{j} \right] + \left( a_{ij}(\mathbf{B}) \right) \nabla_r \mathbf{T} + N(\mathbf{B}) \left[ \mathbf{B} \times \nabla_r \mathbf{T} \right], \tag{32}$$

$$\mathbf{q} = \left( p_{ij}(\mathbf{B}) \right) \mathbf{j} + P(\mathbf{B}) \cdot \left[ \mathbf{B} \times \mathbf{j} \right] - \left( c_{ij}(\mathbf{B}) \right) \nabla_r \mathbf{T} + S(\mathbf{B}) \left[ \mathbf{B} \times \nabla_r \mathbf{T} \right], \tag{33}$$

Vector products of corresponding vectors are put inside the square brackets, and symmetrical tensors and corresponding coefficients of transverse galvanomagnetic and thermomagnetic effects are described by the formulas (28)-(31) in these equations.

Analysis of equations (32), (33) and relationships (28)-(31) shows, that the isotropic crystal, when being placed in a magnetic field, becomes anisotropic and relatively simple phenomena of electrical conductivity and thermal conductivity in the crystal become more complex. In this case, additional transverse galvanomagnetic and thermomagnetic effects appear.

Galvanomagnetic effects are caused by the influence of magnetic field on the Ohmic part of electric current, and thermomagnetic - on the thermal part, according to the generalized conductivity equation (19).

Kinetic tensors and coefficients, included in the equations and relations (28)-(33), in addition to determining the nature of the conducting environment important material properties, are widely applied in the modern solid-state electronics, which uses crystals of different nature in its production.

All the kinetic coefficients, included in generalized electrical conductivity (26) and thermal conductivity (27) equations, according to the formulas (19,a), (19,b), (20,a), (20,b) consist of symmetric and antisymmetric parts of the tensor. Symmetric part, according to the

formula (3), is an even function of magnetic induction vector  $\mathbf{B}$ , and antisymmetric is an odd function.

Now, the inverse tensor  $\left( \left( u_{ij}(\mathbf{B}) \right) \right)^{-1}$  is calculated under the rules of tensor algebra and the calculations will be presented in the following manner:

$$\left( \left( u_{ij}(\mathbf{B}) \right) \right)^{-1} = \left( \rho_{ij}(\mathbf{B}) \right) = \left( \rho_{ij}^{(s)}(\mathbf{B}) \right) + \left( \rho_{ij}^{(a)}(\mathbf{B}) \right)$$

The values of the inverse tensor are put in the equations (28)-(31). Then, all the tensors of the equations are split into symmetric and antisymmetric parts, basic tensor multiplications are done in the right part of the equations and this part is split into symmetric and antisymmetric parts. After, with the simple identification method, it is easy to prove such common basic formulas for symmetric tensors and different coefficients of transverse galvanomagnetic and thermomagnetic effects:

$$\left( r_{ij}(\mathbf{B}) \right) = \left( r_{ij}^{(s)}(\mathbf{B}) \right) \tag{34}$$

$$R(\mathbf{B}) \left( d_{ijl} B_l \right) = \left( r_{ij}^{(a)}(\mathbf{B}) \right) \tag{35}$$

$$\left( a_{ij}(\mathbf{B}) \right) = \left( r_{il}^{(s)}(\mathbf{B}) b_{lj}^{(s)}(\mathbf{B}) + r_{jl}^{(a)}(\mathbf{B}) b_{li}^{(a)}(\mathbf{B}) \right) \tag{36}$$

$$N(\vec{B})\left(d_{ijl}B_l\right)=\left(r_{il}^{(s)}(\vec{B})b_{lj}^{(a)}(\vec{B})+r_{il}^{(a)}(\vec{B})b_{lj}^{(s)}(\vec{B})\right), \quad (37)$$

$$\left(p_{ij}(\vec{B})\right)=\left(g_{il}^{(s)}(\vec{B})r_{lj}^{(s)}(\vec{B})+g_{il}^{(a)}(\vec{B})r_{lj}^{(a)}(\vec{B})\right), \quad (38)$$

$$P(\vec{B})\left(d_{ijl}B_l\right)=\left(g_{ii}^{(s)}(\vec{B})r_{ij}^{(a)}(\vec{B})+g_{ij}^{(a)}(\vec{B})r_{jj}^{(s)}(\vec{B})\right), \quad (39)$$

$$\left(c_{ij}(B_3)\right)=\left(\frac{k}{ze}\right)^2 \cdot T \cdot \left[\left(s_{ij}(B_3)\right)^{(s)} \cdot \left(K_{ij}(B_3)\right)^{(s)} + \left(s_{ij}(B_3)\right)^{(a)} \cdot \left(K_{ij}(B_3)\right)^{(a)}\right], \quad (40)$$

$$P(\vec{B})\left(d_{ijl}B_l\right)=\left(\frac{k}{ze}\right)^2 \cdot T \cdot \left[\left(s_{ij}(B_3)\right)^{(s)} \cdot \left(K_{ij}(B_3)\right)^{(a)} + \left(s_{ij}(B_3)\right)^{(a)} \cdot \left(K_{ij}(B_3)\right)^{(s)}\right] \quad (41)$$

Equation (40) is the Wiedemann-Franz law for charge carriers thermal conductivity in the crystal in the presence of a magnetic field, and the formula (41) defines the coefficient  $P(\vec{B})$  of transverse thermomagnetic Righi-Leduc effect.

Calculation formulas (34)-(41) have a very complex structure and symmetry in any direction of magnetic induction vector in the crystal.

These formulas have the simplest structure and symmetry when magnetic induction vector is directed along the main axis of the crystal energy valley. Then, all the symmetric tensors become diagonal, and antisymmetric tensors have the simplest form. Any axis can be considered as the main within isotropic crystals.

For example, if the main axes of Cartesian coordinates system are designated by the indices "123", and the magnetic induction vector is directed along "3" axis, which is parallel to the main axis of the energy valley of the crystal and is normal to the vectors  $\vec{E}_d$  and

$\nabla_{\vec{r}}T$ , all the tensors and coefficients in the equations (34)-(40) depend on the induction vector  $B_3$ , symmetric tensors become diagonal, and antisymmetric have the simplest form. In this case, the equations (34) - (41) look like this, taking into account the structure of electrical conductivity and thermal conductivity generalized equations tensors (19) (20):

$$\left(r_{ij}(B_3)\right)=\left(r_{ii}(B_3)d_{ij}\right),$$

$$r_{11}(B_3)=r_{22}(B_3)=\frac{1}{en} \cdot \frac{J(0,0,\vec{m},T)}{J(0,1,B_3,\vec{m},T)\Delta(B)},$$

$$r_{33}(0)=\frac{1}{en} \cdot \frac{J(0,0,\vec{m},T)}{J(0,1,\vec{m},T)}, \quad (34, a)$$

$$R(B_3)=\frac{1}{zen} \cdot \frac{J(0,0,\vec{m},T)J(0,2,B_3,\vec{m},T)}{J(0,1,B_3,\vec{m},T)^2\Delta(B_3)}, \quad (35, a)$$

$$\left(a_{ij}(B_3)\right)=\left(a_{ii}(B_3)d_{ij}\right), \quad a_{11}(B_3)=a_{22}(B_3)=$$

$$=\frac{k}{ze} \cdot \left\{ \left[ \frac{J(1,1,B_3,\vec{m},T)}{J(0,1,B_3,\vec{m},T)} - \vec{m} \right] + \frac{J(0,2,B_3,\vec{m},T)^2}{J(0,1,B_3,\vec{m},T)^2} \cdot \left[ \frac{J(1,2,B_3,\vec{m},T)}{J(0,2,B_3,\vec{m},T)} - \vec{m} \right] \cdot B_3^2 \right\} \frac{1}{\Delta(B_3)}$$

$$\left(a_{33}(0)\right)=\frac{k}{ze} \cdot \left[ \frac{J(1,1,\vec{m},T)}{J(0,1,\vec{m},T)} - \vec{m} \right], \quad (36, a)$$

$$N(B_3)=\left(\frac{k}{e}\right) \cdot \frac{J(0,2,B_3,\vec{m},T)}{J(0,1,B_3,\vec{m},T) \cdot \Delta(B_3)} \cdot \left[ \frac{J(1,2,B_3,\vec{m},T)}{J(0,2,B_3,\vec{m},T)} - \frac{J(1,1,B_3,\vec{m},T)}{J(0,1,B_3,\vec{m},T)} \right], \quad (37, a)$$

$$\left(p_{ij}(B_3)\right)=T \cdot \left(a_{ij}(B_3)\right), \quad (38, a)$$

$$P(B_3)=T \cdot N(B_3), \quad (39, a)$$

$$\left(c_{ij}(B_3)\right)=\left(\frac{k}{ze}\right)^2 \cdot T \cdot \left[\left(s_{ij}(B_3)\right)^{(s)} \cdot \left(K_{ij}(B_3)\right)^{(s)} + \left(s_{ij}(B_3)\right)^{(a)} \cdot \left(K_{ij}(B_3)\right)^{(a)}\right], \quad (40, a)$$

$$P(\vec{B})\left(d_{ijl}B_l\right)=\left(\frac{k}{ze}\right)^2 \cdot T \cdot \left[\left(s_{ij}(B_3)\right)^{(s)} \cdot \left(K_{ij}(B_3)\right)^{(a)} + \left(s_{ij}(B_3)\right)^{(a)} \cdot \left(K_{ij}(B_3)\right)^{(s)}\right], \quad (41, a)$$

В цих рівняннях для головного розрахункового функціонала використано таке позначення :

$$J(i, j, B_3, \mathbf{m}^\bullet, T) = \int_0^\infty \left( \frac{e}{kT} \right)^i \frac{u(e)^j}{d(B_3)} G(e) \left( -\frac{df_0}{de} \right) de, \quad (42)$$

Цей функціонал має такі очевидні властивості:

$$J(i, j, B_3, \mathbf{m}^\bullet, T)_{(uB_3) \gg 1} = \frac{1}{B_3^2} \int_0^\infty \left( \frac{e}{kT} \right)^i u(e)^{(j-2)} G(e) \left( -\frac{df_0}{de} \right) de = \frac{1}{B_3^2} J(i, (j-2), \mathbf{m}^\bullet, T) \quad (42, a)$$

$$J(i, j, B_3, \mathbf{m}^\bullet, T)_{(uB_3) \ll 1} = \int_0^\infty \left( \frac{e}{kT} \right)^i u(e)^j G(e) \left( -\frac{df_0}{de} \right) de = J(i, j, \mathbf{m}^\bullet, T) \quad (42, b)$$

$$J(0, 0, \mathbf{m}^\bullet, T) = \int_0^\infty G(e) \left( -\frac{df_0}{de} \right) de = \int_0^\infty g(e) f_0 de = n(\mathbf{m}^\bullet, T), \quad G(e) = \int_0^e g(e) de, \quad (41, c)$$

The equations (34)-(41) with the functionality (42) prove common calculation algorithms of important kinetic properties of one-valley crystals with any isotropic dispersion law  $\varepsilon_p^\mathbf{r} = \varepsilon(p)$  of charge carriers,

that are scattered at any defects of the crystal lattice. (42,a) functionality should be used for the calculations of (34,a)-(41,a) properties within a strong magnetic field, and (42,b) functionality should be used within a weak magnetic field. In this regard, it is possible to name these equations as determinative equations.

The algorithms of these equations allow calculations of kinetic properties of 2D (with a microscopic film thickness) crystals, which spatial quantization of charge carriers energy spectrum can be observed in [11].

## II. The kinetic properties of isotropic crystals within magnetic field

It is shown that non-equilibrium grand canonical ensemble of particles is characterized by the grand thermodynamic potential (2), entropy (8) and a derivative of time entropy, describing the second law of non-equilibrium thermodynamics(13). According to this law, non-equilibrium ensemble of charge carriers in the crystal causes electricity flow with density  $\mathbf{j}$  and heat flow with density  $\mathbf{q}$  in the crystal. These flows are described by the equations (19) (20).

According to the theory of Onsager symmetry, the tensors of kinetic coefficients included in this equation, describe material tensors of the kinetic properties of the crystal, which should be either theoretically calculated or experimentally measured, with the determinative equations (34)-(41).

The analysis of these formulas shows, that with the presence of the electronic spectrum parameters, chemical potential  $\mu$ , and mechanism of charge carriers

scattering at crystal lattice defects, i.e. the scattering functions with the scattering indicator  $r$ , it is possible to theoretically calculate and experimentally measure all the kinetic properties of the crystals described with the formulas (34,a)-(41,a). In addition, these formulas show, that the anisotropy acquired by the crystal under the influence of a magnetic field disappears, when the magnetic induction vector  $\mathbf{B}$  of this field is equal to zero.

Such methods of calculations and measurements in a weak magnetic field are described in detail in [8- 11] for selenious lead with isotropic Kane dispersion law. All the calculations in these works have been done with the use of MathCAD computer package, and the closeness of the calculated and experimental values of various kinetic properties of the crystal was estimated with the help of Pearson's correlation coefficient  $corr(K_e, K_t)$ , inscribed into the package.  $K_e$  is the vector of experimental values of the kinetic property  $K$ , and  $K_t$  is the vector of the theoretical values of this property within this correlator.

In the case of good correlation between experimental and calculated values, i.e. closeness between these values, Pearson's correlation coefficient is very close to 1, while in the case of weak convergence the coefficient is significantly smaller than 1.

Pearson correlation coefficient in the analysis was important in this numerical range:  $corr(K_e, K_t) \cong 0.975 \div 0.99$  in the cited works [8-11]. These values of correlation coefficient proved closeness between experimental and theoretical data in the analysis of the relevant works.

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## **Великий термодинамічний потенціал Гіббса в теорії кінетичних властивостей кристалів**

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В даній роботі за допомогою великого термодинамічного потенціалу Гіббса були обґрунтовані кінетичні тензори відомих в нерівноважній термодинаміці узагальнених рівнянь електропровідності та теплопровідності. Ці тензори визначають розрахункові алгоритми матеріальних тензорів провідних кристалів та коефіцієнтів різних гальваномагнітних і термомагнітних ефектів. Ці алгоритми – прагматичні формули в розрахункових задачах кінетичних властивостей кристалів та в задачах прогнозування напівпровідникових кристалів із заданими властивостями. Їх прагматичність підтверджується величезною кількістю наукових робіт присвячених дослідженням кінетичних властивостей напівпровідникових кристалів.

**Ключові слова:** потенціал Гіббса, електропровідність, теплопровідність, алгоритм, тензор.