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Specific thermoemf and Hall-effect in crystals with monopolar conductivity

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Abstract. The Seebeck coefficient α and Hall constant R_H are calculated for monopolar crystal as based of quantum kinetic equation. It is shown that α and R_H in the case of simple isotropic band do not depend on relaxation characteristics in contrast to the result obtained for the same crystals by calculations founded on relaxation time approximation.

Keywords: dispersion law, quantum kinetic equation, Seebeck coefficient, Hall constant.

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1. Introduction

If mobile carriers in crystal belong to several different groups there is no practical possibility to relate measured values with space flows of separate groups. The system that contains several substantially different groups of carriers has specific properties absent for crystals where unique group of carriers is actual. For instance, in a multy-group situation the state of zero total current can be provided in crystal with nonzero density of current for every group. Therefore, distribution of carriers over space of momentum in this crystal can be nonequilibrium in absence of total current.

Quite another situation appears if only one group is actual: the measured voltage drop on the total crystal length is evidently tied to the density of current for this unique group.

Below we consider two problems. The first one concerns monopolar semiconductor where carriers belong to one group (simple band) and their space distribution is nonuniform due to a small gradient of temperature T and Fermi-energy ε_F . Phenomenological relation between the density of current \vec{j} and microscopic dynamical and statistic forces in the stationary case has the form

$$\vec{E} - (1/e)\vec{\nabla}\varepsilon_F - \tilde{\alpha}\vec{\nabla}T = \tilde{\sigma}^{-1}\vec{j}. \quad (1)$$

Here e is the charge of band carriers, \vec{E} is the vector of electrical field, $\tilde{\sigma}$ is the tensor of conductivity and $\tilde{\alpha}$ is the so-called Seebeck coefficient; the latter in general is a tensor value, too.

For simplicity, we restrict our consideration in this paper by the case of band with spherical symmetry and for small divergence of equilibrium. Then the tensor values in Eq. (1) degenerate in scalars, and we obtain

$$\vec{E} - (1/e)\vec{\nabla}\varepsilon_F - \alpha\vec{\nabla}T = \sigma^{-1}\vec{j}. \quad (2)$$

Note that coefficient α is not a kinetic coefficient because it does not ensure a direct relation between some force and the density of current flow. We can call it as a structural coefficient, that depends on the band structure.

Another problem relates to an uniform crystal being in the stationary uniform external magnetic field \vec{H} of a classical value. Here, we consider again one group of carriers with the isotropic dispersion law and calculate the Hall-constant R_H .

Calculation of α and R_H can be performed using by several different methods. Usual method starts from obtaining the nonequilibrium distribution function f by the way of approximate solution of the kinetic Boltzmann equation, where the collision integral is replaced by a simple form containing relaxation time $\tau(\varepsilon) = 1/\nu(\varepsilon)$ (see, for example, Refs. [1] and [2]). Here ε is the band carrier energy. During the next step one calculates the current density based on the obtained f and marks out the values interesting for us (for instant, the coefficient α in Eq. (2)).

Another method applied here uses a set of balance equations which are moments of quantum kinetic equation in the space of wave vector (see Refs. [3] and [4]).

We will compare together α and R_H obtained by different methods and will compare the calculated values of α with some experimental data.

2. Specific thermo-emf

2.1. Seebeck coefficient α in τ -approximation

The Seebeck coefficient calculated in Refs. [1] and [2] can be presented in the form

$$\alpha_{(\tau)} = \frac{1}{eT} \left(\varepsilon_F - \frac{\langle \varepsilon \tau(\varepsilon) \rangle}{\langle \tau(\varepsilon) \rangle} \right). \quad (3)$$

Here, angle brackets denote the statistic average with equilibrium distribution function (see below Eqs. (5), (7) and (14)).

Consider the isotropic dispersion law of the following form:

$$\varepsilon(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m(\varepsilon)}. \quad (4)$$

For this case,

$$\frac{\langle \varepsilon \tau(\varepsilon) \rangle}{\langle \tau(\varepsilon) \rangle} = \frac{\int \varepsilon \tau(\varepsilon) [\partial f_0(\varepsilon) / \partial \varepsilon] [\partial \varepsilon / \partial k_i]^2 d^3 \vec{k}}{\int \tau(\varepsilon) [\partial f_0(\varepsilon) / \partial \varepsilon] [\partial \varepsilon / \partial k_i]^2 d^3 \vec{k}}. \quad (5)$$

2.1.1. Parabolic dispersion law

If the function $m(\varepsilon)$ in Eq. 4 does not depend on energy (that is dispersion law is parabolic), we have the standard simple form

$$\varepsilon(\vec{k}) = \hbar^2 \vec{k}^2 / 2m^*. \quad (6)$$

Then, it is possible to rewrite Eq. 5 in the following manner (see Ref. [1], formula (7.2) of Chapter IX):

$$\begin{aligned} \langle C(\varepsilon) \rangle &= \int_0^\infty (\partial f_0(\varepsilon) / \partial \varepsilon) C(\varepsilon) \varepsilon^{3/2} d\varepsilon \Big/ \int_0^\infty (\partial f_0(\varepsilon) / \partial \varepsilon) \varepsilon^{3/2} d\varepsilon = \\ &= \frac{2}{3} \int_0^\infty f_0(\varepsilon) \frac{\partial}{\partial \varepsilon} [C(\varepsilon) \varepsilon^{3/2}] d\varepsilon \Big/ \int_0^\infty f_0(\varepsilon) \varepsilon^{1/2} d\varepsilon. \end{aligned} \quad (7)$$

Here, $f_0(\varepsilon) = \{1 + \exp[(\varepsilon - \varepsilon_F) / k_B T]\}^{-1}$. In Ref. [1] one relates the expression (3) to an opened circuit scheme ($\vec{j} = 0$).

The expression (2) does not depend on the mode of electrical circuit and relates to an arbitrary current density in the region of small divergence of equilibrium. So, it relates to the case $\vec{j} = 0$ as well as to the case $\vec{j} \neq 0$.

If one uses the model form

$$\tau(\varepsilon) = \tau_0 \left(\frac{\varepsilon}{k_B T} \right)^r \quad (8)$$

and dispersion law (6), then he obtains from Eqs (3) and (8) the following expression for the Seebeck coefficient:

$$\alpha_{(\tau)} = \frac{1}{eT} \left[\varepsilon_F - k_B T \left(r + \frac{5}{2} \right) \frac{F_{r+3/2}(\varepsilon_F / k_B T)}{F_{r+1/2}(\varepsilon_F / k_B T)} \right], \quad (9)$$

Here, $r = -1/2$ for scattering by longitudinal acoustic phonons, $r = 3/2$ for scattering by charged impurities. The Fermi integral is introduced by the following definition:

$$F_r(\eta) = \frac{1}{\Gamma(r+1)} \int_0^\infty \frac{w^r dw}{1 + \exp(w - \eta)}. \quad (10)$$

In this formula Γ is the gamma-function.

It is very strange: Seebeck coefficients (3) and (9) don't depend absolutely on the intensity of carriers interaction with the scattering system. But it evidently depends on the energetic parameter of relaxation time r even if this interaction is very weak. One more significant objection concerns the formal record of value α . If we consider monopolar crystal with the simple band in the case $\vec{j} = 0$ (then the distribution of carriers in the space of velocities is equilibrium), the expression for thermo-emf should not contain any relaxation characteristics.

We consider these misunderstandings as a consequence of employing of the τ -approximation for rough solution of the Boltzmann equation. We think that this approach can give results of quality value only (see, for example, Ref.[4]).

2.1.2. Nonparabolic dispersion law

Consider now an other dispersion law. Let in Eq.(4)

$$m(\varepsilon) = m(0)(1 + \varepsilon / \varepsilon_G). \quad (11)$$

This form is suitable for n -InSb at $\varepsilon \ll 20\varepsilon_G$ (here, $m(0) = 0.014m_0$; $\varepsilon_G = 0.17$ eV). For this case, one obtains using Eq. (8) the following expression:

$$\begin{aligned} \frac{\langle \varepsilon \tau(\varepsilon) \rangle}{\langle \tau(\varepsilon) \rangle} &= k_B T \times \\ &\frac{\int_0^\infty f_0(1974 z / T^0 K) (d/dz) [z^{5/2+r} (1+z)^{3/2} (1+2z)^{-1}] dz}{\int_0^\infty f_0(1974 z / T^0 K) (d/dz) [z^{3/2+r} (1+z)^{3/2} (1+2z)^{-1}] dz}. \end{aligned} \quad (12)$$

Results of calculations performed with the formulae (3), (9) and (12) are shown below.

2.2. Seebeck coefficient obtained from the balance equation

The quantum kinetic equation for small deviation of equilibrium for the system of uniform carriers has the form (see Ref. [3])

$$e\bar{E} \frac{1}{\hbar} \frac{\partial f_{\vec{k}}^0}{\partial k} = \text{St } f_{\vec{k}}. \quad (13)$$

Here $f_{\vec{k}}$ is the nonequilibrium distribution function, $f_{\vec{k}}^0 = f_0(\varepsilon)$ is the equilibrium distribution function, e is charge of bend carriers.

For a slightly nonuniform system, the quantum kinetic equation can be presented in the form (stationary case)

$$-\frac{1}{\hbar} \frac{\partial f_{\vec{k}}^0}{\partial k} \bar{\Lambda}(\varepsilon_{\vec{k}}) = \text{St } f_{\vec{k}}, \quad (14)$$

where

$$\bar{\Lambda}(\varepsilon_{\vec{k}}) = \bar{\nabla}(\varepsilon_F(\vec{r}) + e \varphi^{(E)}) + \frac{\varepsilon_{\vec{k}} - \varepsilon_F}{T} \bar{\nabla}T(\vec{r}) = \quad (15)$$

$$= -e \bar{E} + \bar{\nabla}\varepsilon_F(\vec{r}) + \frac{\varepsilon_{\vec{k}} - \varepsilon_F}{T} \bar{\nabla}T(\vec{r}).$$

Applying the operator

$$\frac{2}{(2\pi)^3} \int \bar{k} d^3\bar{k} \quad (16)$$

to Eq. (14), we obtain the equation that represents balance of dynamical and statistical forces:

$$e \bar{E} - \bar{\nabla}\varepsilon_F(\vec{r}) + \bar{F}_T + \bar{F}_{res} = 0. \quad (17)$$

Here,

$$\bar{F}_T = \frac{2}{(2\pi)^3 n} \int \bar{k} [\varepsilon(\bar{k}) - \varepsilon_F] \left[\frac{\partial f_{\vec{k}}^0}{\partial k} \cdot \frac{\bar{\nabla}T(\vec{r})}{T} \right] d^3\bar{k}, \quad (18)$$

n is the density of carriers. The force \bar{F}_{res} is the first moment of the scattering integral and can be presented in the form $\bar{F}_{res} = e\bar{j}/\sigma$. As a result (see Eqs. (17) and (2)), we obtain

$$\alpha = -\frac{2}{(2\pi)^3 n e T} \int k_i \frac{\partial f_{\vec{k}}^0}{\partial k_j} [\varepsilon(\bar{k}) - \varepsilon_F] d^3\bar{k}. \quad (19)$$

Note that for the linear theory this expression (in contrary to Eqs (3) and (8)) does not depend on relaxation characteristics. It contains only equilibrium values and depends only on parameters of the dispersion law.

2.2.1. Parabolic dispersion law

Introducing the law (6) in Eq. (19) and performing integration, we find (see Eq. (10)):

$$\alpha = -\frac{k_B}{e} \left[\frac{\varepsilon_F}{k_B T} - \frac{5}{2} \frac{F_{3/2}(\varepsilon_F/k_B T)}{F_{1/2}(\varepsilon_F/k_B T)} \right] \quad (20)$$

(this formula, underline it again, does not depend on the mechanism of scattering). Pay attention that expression (20) coincides with the expression (9), formally accepted at $r = 0$.

For nondegenerate carriers

$$\alpha = -\frac{k_B}{e} \left(\frac{\varepsilon_F}{k_B T} - \frac{5}{2} \right); \quad (21)$$

For high degeneration

$$\alpha = \frac{k_B^2 T \pi^2}{2e\varepsilon_F}. \quad (22)$$

Results of numerical calculations performed for n -GaAs shown in Figs 1, 2 and 3. Here and further curves 1 relate to the formula (20), curves 2 and 3 – to the formulae (9) at $r = 3/2$ and $r = -1/2$ consequently (see Ref. [1]). Fig. 1 relates to density $n = 3.5 \times 10^{17} \text{ cm}^{-3}$, Fig. 2 relates to the density $n = 7.7 \times 10^{18} \text{ cm}^{-3}$. Black points in Fig. 3 represent the experimental data at $T = 300 \text{ K}$ (see Ref. [5]).

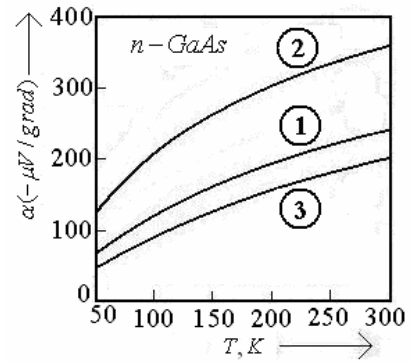


Fig. 1.

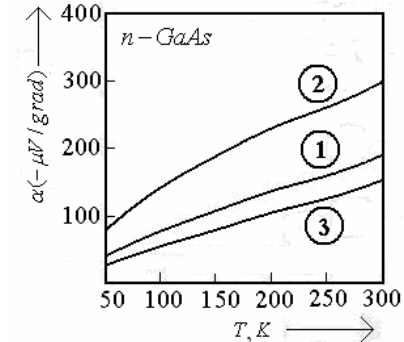


Fig. 2.

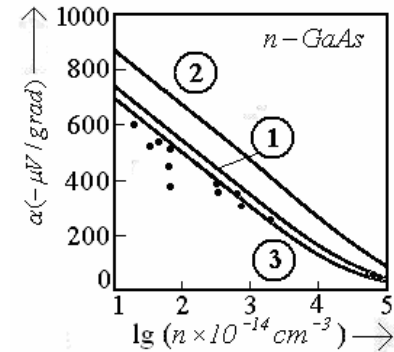


Fig. 3.

2.2.2. Nonparabolic dispersion law

Consider now the dispersion law (11) and apply it to n -InSb. Then it follows from (19):

$$\alpha = \frac{2\sqrt{2m^3(0)}}{3\pi^2 neT\hbar^3} \times \int_0^\infty \varepsilon^{3/2} \frac{\partial f^0(\varepsilon)}{\partial \varepsilon} (\varepsilon - \varepsilon_F) (1 + \varepsilon/\varepsilon_G)^{1/2} (1 + 2\varepsilon/\varepsilon_G) d\varepsilon. \quad (23)$$

Fig. 3 represents the dependences $\alpha(n)$ calculated for different temperatures as based on the formula (23) (see curves 1) and on formulae (8), (12) at $r = 3/2$ (see curves 2). The curves (a) relate to temperature $T = 50 K$, the curves (b) relate to temperature $T = 100 K$, the curves (c) relate to temperature $T = 150 K$, the curves (d) relate to temperature $T = 200 K$, the curves (e) relate to temperature $T = 300 K$, the curves (f) relate to temperature $T = 400 K$. Distinction between the curves 1 and 2 calculated with the different approaches is quite evident.

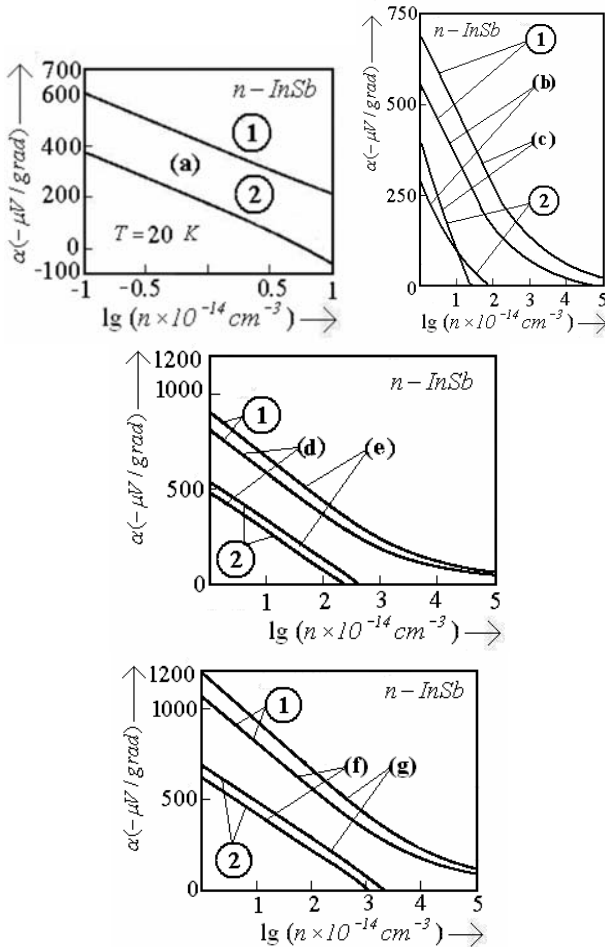


Fig. 4.

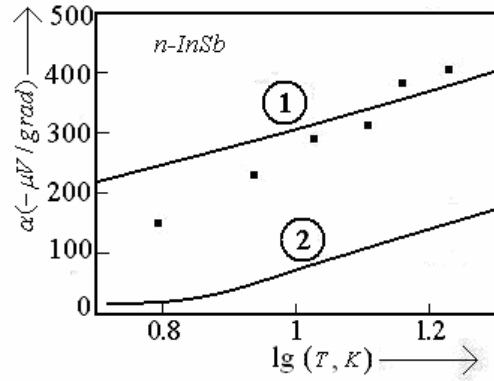


Fig. 5.

Fig. 5 represents the dependences $\alpha(T)$ calculated at $n = 10^{14} \text{ cm}^{-3}$. Here and further the curve 1 relates to the formula (23), the curve 2 – to the formulae (9) and (12) at $r = 3/2$. One can see that the model which uses τ -approximation is not suitable for electron indium antimonide.

3. Hall-effect

In the presence of uniform magnetic field \vec{H} , the quantum kinetic equation for band carriers has the form (stationary case)

$$-\vec{v}(\vec{k}) \frac{\partial f_{\vec{k}}^0}{\partial \varepsilon} \bar{\Lambda}(\varepsilon) + \frac{e}{\hbar} \left\{ \frac{1}{c} \left[\left(\vec{H} \times \frac{\partial}{\partial \vec{k}} \right), \vec{v}(\vec{k}) \right]_+ f_{\vec{k}} \right\} = \text{St } f_{\vec{k}}. \quad (24)$$

Here, $\vec{v} = \frac{1}{\hbar} \frac{\partial \varepsilon_{\vec{k}}}{\partial \vec{k}}$; $[A, B]_+ = (1/2)(AB + BA)$; $\bar{\Lambda}(\varepsilon)$ is represented by Eq. (15). The magnetic field is supposed to be classical: $|\hbar e H| / m^* c \ll \langle \varepsilon \rangle$.

Apply to Eq. (24) the operator (16). Then, we obtain the equation that represents balance of forces (see Eq. (18)):

$$e [\vec{E} + (1/c)(\vec{H} \times \vec{u})] - \vec{\nabla} \varepsilon_F(\vec{r}) + \vec{F}_T + \vec{F}_{res} = 0. \quad (25)$$

Here, $\vec{F}_{res} = -e^2 n \vec{u} / \sigma = -e \vec{j} / \sigma$ (we denote the average drift velocity of carriers as \vec{u}). In Eq. (25), we have omitted the term

$$\vec{C}(\vec{H}) = -\frac{e}{(2\pi)^3 n c} \times \int \vec{u} \frac{\partial \varepsilon}{\partial \vec{v}} \frac{\partial f_{\vec{k}}^0}{\partial \varepsilon} \vec{k} \left[\left(\vec{H} \times \frac{\partial}{\partial \vec{k}} \right) \cdot \vec{v}(\vec{k}) \right] d^3 \vec{k},$$

because further we use the simple dispersion law (6). For this case $\vec{C}(\vec{H}) = 0$. Note that Eq. (25) was obtained from the quantum kinetic equation (24) without any approximation.

Consider here uniform crystal with n -conductivity and simple band. For this case $-\vec{\nabla}\varepsilon_F(\vec{r}) + \vec{F}_T = 0$ and Eq. (25) has the form (here and further $e > 0$)

$$\vec{E} + (1/enc)(\vec{H} \times \vec{j}) - (1/\sigma)\vec{j} = 0. \quad (26)$$

Let z -axis is directed along the vector \vec{j} and vector \vec{H} is disposed in $\{xy\}$ -plane:

$$\vec{j} = (0, 0, j_z), \quad \vec{H} = (H_x, H_y, 0). \quad (27)$$

It follows from Eqs (26) and (27):

$$\begin{aligned} E_x + (H_y/enc)j_z = 0; \quad E_y - (H_x/enc)j_z = 0; \\ E_z - (1/\sigma)j_z = 0. \end{aligned} \quad (28)$$

We consider here the vector $\vec{e}_z E_z$ as applied electric field and the vector $\vec{E}_H = \vec{e}_x E_x + \vec{e}_y E_y$ as Hall-field.

The following relation determines the Hall constant R_H :

$$\begin{aligned} E_\perp = \sqrt{E_x^2 + E_y^2} = R_H \sqrt{H_x^2 + H_y^2} j = R_H H_\perp j; \\ j = |j_z| = \sigma_{||} |E_z|. \end{aligned} \quad (29)$$

As a result, one obtains:

$$R_H = \frac{1}{enc}. \quad (30)$$

We can see that in the classical limit for magnetic field the constant R_H does not depend on magnetic field. We can see also that the Hall constant does not depend on the form of dispersion law $\varepsilon(\vec{k})$, if this law is isotropic. These results completely differ from results obtained in Ref. [1] for τ -approximation. There

$$R_H = \frac{1}{enc} \frac{\left\langle \frac{\tau^2(\varepsilon)}{1 + (e\tau(\varepsilon)H/m^*c)^2} \right\rangle}{\left\langle \frac{\tau(\varepsilon)}{1 + (e\tau(\varepsilon)H/m^*c)^2} \right\rangle^2 + \left\langle \frac{e\tau^2(\varepsilon)H/m^*c}{1 + (e\tau(\varepsilon)H/m^*c)^2} \right\rangle^2}. \quad (31)$$

Results of numerical calculations performed using of Eqs (31) – (34) and (8) at different densities and temperatures are shown in Fig. 6. Here $T = 300$ K and $n = 10^{15} \text{ cm}^{-3}$ for (a), $T = 300$ K and $n = 10^{18} \text{ cm}^{-3}$ for (b), $T = 300$ K and $e\tau_0 H/m^*c \rightarrow 0$ for (c), $T = 300$ K and $e\tau_0 H/m^*c = 1$ for (d), $T = 300$ K and $e\tau_0 H/m^*c = 4$ for (e), $n = 3.5 \times 10^{17} \text{ cm}^{-3}$ and $e\tau_0 H/m^*c \rightarrow 0$ for (f), $n = 3.5 \times 10^{17} \text{ cm}^{-3}$ and $e\tau_0 H/m^*c = 1$ for (g), $n = 3.5 \times 10^{17} \text{ cm}^{-3}$ and $e\tau_0 H/m^*c = 4$ for (h).

APPENDIX

Nernst-Ettingsgauzen effect in nonuniform crystal

Consider the case when external magnetic field and constant gradient of temperature are applied to monopolar crystal with a simple isotropic band. Then, Eq. (26) changes to (here and below $e > 0$)

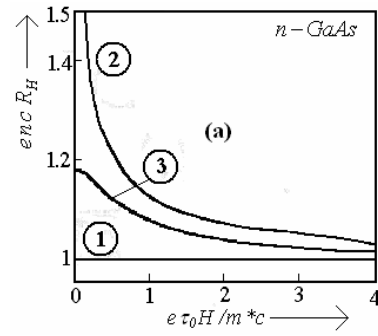


Fig. 6 (a).

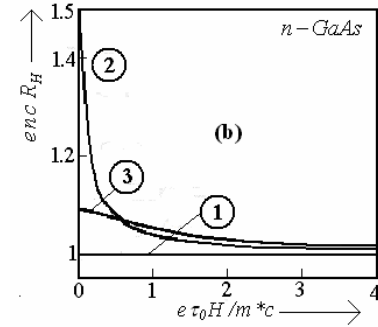


Fig. 6 (b).

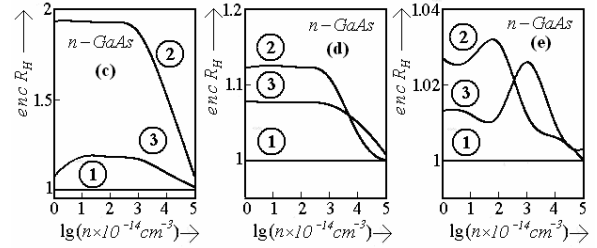


Fig. 6 (c, d, e).

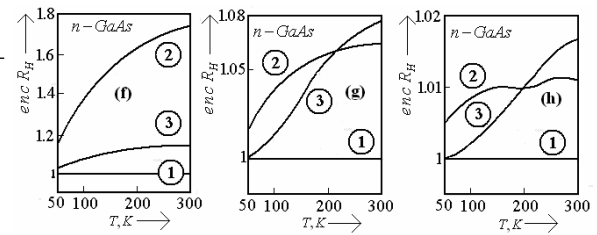


Fig. 6 (f, g, h).

$$\vec{E}^* + (1/enc)(\vec{H} \times \vec{j}) + \alpha \vec{\nabla} T(\vec{r}) - (1/\sigma)\vec{j} = 0. \quad (A1)$$

Here (see Eqs. (18), (10) and (6)),

$$\vec{E}^* = \vec{E} + (1/e)\vec{\nabla}\varepsilon_F; \quad (A2)$$

$$\alpha = -\frac{4}{3(2\pi)^3 n e T} \int \varepsilon(\vec{k}) \frac{\partial f_{\vec{k}}^0}{\partial \varepsilon(\vec{k})} [\varepsilon(\vec{k}) - \varepsilon_F] d^3 \vec{k} = \quad (A3)$$

$$= -\frac{\varepsilon_F}{k_B T} + \frac{5 F_{3/2}(\varepsilon_F/k_B T)}{2 F_{1/2}(\varepsilon_F/k_B T)}.$$

Using Eq. (A1) consider Nernst-Ettingsgauzen effect showing relation of the measured voltage drop with the crossed gradient of temperature $\vec{\nabla} T$ and

magnetic field \vec{H} . Choose the following orientation of fields and current:

$$\vec{H} = (H_x, 0, 0) ; \vec{\nabla}T = (0, 0, \nabla_z T) ; \vec{j} = (0, 0, j_z) . \quad (\text{A4})$$

It follows from (A1) – (A4):

$$E_y^* = (H_x \sigma / e c n) \alpha \nabla_z T . \quad (\text{A.5})$$

Determine the Nernst-constant Нернста Q by the relation:

$$Q = \left| E_y^* / H_x \nabla_z T \right| . \quad (\text{A.6})$$

Then,

$$Q = \alpha \sigma / e c n . \quad (\text{A.7})$$

Using Eq. (20) one obtains:

$$Q = \frac{k_B \sigma(H=0)}{e^2 n c} \left| \frac{\varepsilon_F}{k_B T} - \frac{5}{2} \frac{F_{3/2}(\varepsilon_F / k_B T)}{F_{1/2}(\varepsilon_F / k_B T)} \right| . \quad (\text{A.8})$$

The value Q/σ does not depend on relaxation characteristic (in contrary to subsequent result obtained in Ref. [1]).

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