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A Set of the Important Kinetic Properties of Crystals and Their Dependence on the Charge Carriers’ Scattering Mechanisms

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In non-equilibrium thermodynamics, there are known the generalized equations of electrical and heat conduction. They describe the response of conducting medium to the action of drift fields in the medium as well as a magnetic field. The phenomenological tensors and coefficients in these equations describe all of the important kinetic properties of conducting crystals. Therefore, to provide an explanation for the nature of the crystal properties, the nature of a set of the kinetic tensors and coefficients must be explained. In this paper, under general observation conditions, the whole set of these quantities that are important for isotropic crystals, is calculated with the use of statistical physics methods.

Keywords: Gibbs potential, entropy, electrical conduction, heat conduction, algorithm, tensor.

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I. Kinetic properties of a crystal

Consider the conducting crystal in the presence of the electrical field \( \vec{E} \) or temperature gradient \( \nabla T \) (these perturbations may exist simultaneously), when this crystal is under the magnetic field \( \vec{B} \). According to non-equilibrium thermodynamics, in the presence of these fields, there are the electric charge and heat transport processes in this crystal. They are described by the first and second laws of nonequilibrium thermodynamics:

\[
\frac{dU_c}{dt} = -\text{div} \overrightarrow{q} + j \vec{E}, \quad \text{(the first law of non-equilibrium thermodynamics)};
\]

\[
\frac{dS_c}{dt} = \frac{1}{T} \left( j \vec{E} - q \nabla T \right), \quad \text{(the second law of non-equilibrium thermodynamics)}.
\]

In the above formulas, the vector \( \overrightarrow{j} \) is the electrical current density, the vector \( \overrightarrow{q} \) is the heat flow, \( U_c \) is the internal energy of the system, \( S_c \) is the entropy of the system.

In statistical physics it was shown that, when there is an increase of the entropy in the thermodynamic system, the processes of heat and electrical charge transport (processes of heat and electrical conduction) occur. Conversely, when the processes of heat and electrical charge occur, its entropy increases.

In nonequilibrium thermodynamics it was shown that the processes of electrical and heat conduction in the crystal are described respectively by the following generalized electrical and heat conduction equations:

\[
\begin{align*}
\overrightarrow{j} &= \left( \sigma_{ik} \left( \vec{B} \right) \right) \vec{E} - \left( \beta_{ik} \left( \vec{B} \right) \right) \nabla T, \quad (1) \\
\overrightarrow{q} &= \left( \gamma_{ik} \left( \vec{B} \right) \right) E - \left( h_{ik} \left( \vec{B} \right) \right) \nabla T. \quad (2)
\end{align*}
\]

Equations (1) and (2) describe the response of a conducting medium to the action of an electrical field, a temperature gradient and a magnetic field. The phenomenological constants \( \left( \sigma_{ik} \left( \vec{B} \right) \right), \left( \beta_{ik} \left( \vec{B} \right) \right), \left( \gamma_{ik} \left( \vec{B} \right) \right), \left( h_{ik} \left( \vec{B} \right) \right) \) in equations (1), (2) – these are the tensors of kinetic coefficients. These tensors describe numerous matter properties of the conducting medium (i.e. the crystal). They have the following properties of the Onsager symmetry:

\[
\begin{align*}
\left( \sigma_{ik} \left( \vec{B} \right) \right) &= \left( \sigma_{ki} \left( - \vec{B} \right) \right); \quad \left( \beta_{ik} \left( \vec{B} \right) \right) = \left( \beta_{ki} \left( - \vec{B} \right) \right); \quad \left( \gamma_{ik} \left( \vec{B} \right) \right) = \left( \gamma_{ki} \left( - \vec{B} \right) \right); \quad \left( h_{ik} \left( \vec{B} \right) \right) = T \left( \beta_{ki} \left( - \vec{B} \right) \right). \quad (3)
\end{align*}
\]
crystals will have the following form:

\[
\begin{align*}
\mathbf{E} & = \left( \rho_{\text{ik}} (\mathbf{B}) \right) j + R(\mathbf{B}) \left[ \mathbf{B} \times j \right] + \left( \alpha_{\text{ik}} (\mathbf{B}) \right) \mathbf{V}_T + N(\mathbf{B}) \left[ \mathbf{B} \times \mathbf{V}_T \right], \\
\mathbf{q} & = \left( \sigma_{\text{ik}} (\mathbf{B}) \right) j + P(\mathbf{B}) \left[ \mathbf{B} \times j \right] - \left( \chi_{\text{ik}} (\mathbf{B}) \right) \mathbf{V}_T + S(\mathbf{B}) \left[ \mathbf{B} \times \mathbf{V}_T \right],
\end{align*}
\]  

(4), (5)

In these equations, the vector products are denoted by the square brackets.

It is easy to show the physical sense of the phenomenological tensors and coefficients in equations (4), (5) with the use of the different phenomenological laws of non-equilibrium thermodynamics. These laws describe all set of the galvanomagnetic and thermomagnetic phenomena.

It can be seen from this analysis that in equations (4), (5), \( \rho_{\text{ik}}, \alpha_{\text{ik}}, \sigma_{\text{ik}}, \chi_{\text{ik}} \) – these are respectively, the material tensors of the resistivity, Seebeck effect, Feltier effect, conductivity of the crystal, and \( R, N, P, S \) – these are respectively, the coefficient of the Hall effect, Nernst-Ettingshausen, Nernst and Righi-Leduc effects.

Accordingly to the Onsager symmetry principle for the kinetic coefficients, all these tensors and coefficients can only be even functions of the magnetic inductance vector \( \mathbf{B} \).

Formulas (4), (5) provide a possibility to compare the results of experimental measurements with the results of macroscopic theory of non-equilibrium thermodynamics. They show that in the presence of a magnetic field in a crystal, the relatively simple processes of the electrical and heat conduction will become more complicated.

In this case, additional effects occur, these are known as the galvanomagnetic and thermomagnetic effects. The first effects are produced by the action of a magnetic field on the ohmic part and the second effect – by its action on thermal part of the electrical current, accordingly to the generalized equation of the electrical conduction (1). It is clear from equation (1), that the electrical current is composed of two parts: the ohmic part that is proportional to the strength of electrical field \( \mathbf{E} \), the thermal part that is proportional to the temperature gradient \( \mathbf{V}_T \).

All tensors and coefficients in equations (4), (5) are of pragmatic significance for modern solid state electronics, in that they described different crystals’ properties – these are used in the manufacture of solid-state electronic equipment.

II. Statistical computations of crystals’ kinetic properties

In works [1, 2, 5] was shown that all kinetic properties of a crystal may be statistically calculated with the use of the Gibbs grand canonical potential:

\[
\Omega = -2kT \sum \ln \left\{ 1 + \exp \left( \frac{\mu + \Delta \mu}{kT} - \frac{\epsilon}{kT} \right) \right\},
\]  

(6)

This potential was described thoroughly in the cited works, where having it, the calculations of all set of the important kinetic properties of the isotopic semiconductor 3D, 2D and 1D crystals were given.

In modern literature, the symbols 3D, 2D, 1D denote the macroscopic three dimensional crystals, thin films with a microscopic thickness \( d \), nanowire crystals with a microscopic thickness \( d \), respectively.

Calculations presented in the cited works show that the kinetic properties of 3D crystals, in the presence of a weak magnetic field, or when the magnetic field is absent, are described by the following algorithmic formulas:

\[
\rho (\mu^*, T) = \frac{1}{en} \frac{U(0,0,\mu^*, T)}{I(0,1,\mu^*, T)},
\]  

(7)

\[
R(\mu^*, T) = \frac{1}{zen} \frac{I(0,0,\mu^*, T)}{I(0,1,\mu^*, T)^2},
\]  

(8)

\[
\alpha (\mu^*, T) = \left( \frac{k}{ze} \right) \frac{I(1,1,\mu^*, T)}{I(0,1,\mu^*, T)} - \mu^*,
\]  

(9)

\[
N(\mu^*, T) = \left( \frac{k}{e} \right) U_H(\mu^*, T) \left[ \frac{I(1,1,\mu^*, T)}{I(0,1,\mu^*, T)} - \frac{I(2,1,\mu^*, T)}{I(0,2,\mu^*, T)} \right],
\]  

(10)

\[
\pi (\mu^*, T) = T \alpha (\mu^*, T),
\]  

(11)

\[
P(\mu^*, T) = TN (\mu^*, T),
\]  

(12)

\[
\chi(\mu^*, T) = \left( \frac{k}{e} \right)^2 \frac{T}{\rho (\mu^*, T)} \left[ \frac{I(2,1,\mu^*, T)}{I(0,1,\mu^*, T)} - \left( \frac{I(1,1,\mu^*, T)}{I(0,1,\mu^*, T)} \right)^2 \right],
\]  

(13)

\[
U_H(\mu^*, T) = U(r,T) \frac{I(0,2,\mu^*, T)}{I(0,1,\mu^*, T)}; U_D(\mu^*, T) = U(r,T) \frac{I(1,0,\mu^*, T)}{I(0,1,\mu^*, T)};
\]  

(14)

\[
n(\mu^*, T) = Nc(T) I(0,0,\mu^*, T),
\]  

(15)
A Set of the Important Kinetic Properties of Crystals…

Analysis of formulas (7) - (15) shows that the anisotropy of a crystal (when it has arisen from the action of a magnetic field) will disappear when the magnetic field is absent, or in the presence of a weak magnetic field \( \left( u(\varepsilon, T)B_3 \right)^2 << 1 \).

In formulas (7) - (15), the following notations were used:

\[ U_H(\mu^*, T) \] and \( U_{J_0}(\mu^*, T) \) are respectively, the Hall and carrier mobility of a crystal,

\[ I(i, j, \mu^*, T) \] is the main algorithmic functional during calculations of the properties of a crystal,

\[ U(r, T) \] and \( N_c(T) \) are respectively, the coefficients in calculated functions.

The main algorithmic functional \( I(i, j, \mu^*, T) \) is calculated for an arbitrary isotropic energy spectrum of the current carriers:

\[
\frac{p_x^2 + p_y^2 + p_z^2}{2m^*} = \frac{p^2}{2m} = E(\varepsilon), \quad (16)
\]

where \( m \) is the mass of the free electron, \( m^* \) is the carrier reduced effective mass in a crystal.

In formula (16), \( E(\varepsilon) \) is the first order homogeneous quantum-mechanical function of energy. For an isotropic parabolic energy spectrum and for an isotropic non-parabolic Kane’s formula, respectively, this function is given by:

\[
U(r, T) = \left[ \frac{1}{T} \left( U_A \delta(0, r) + U_O \delta(1, r) \right) + U_I \delta(2, r) \right] m^* (r^{3/2}) T(r^{-1/2}), \quad (18)
\]

where \( U_A, U_O, U_I \) are the crystal constants – they depend on the crystal nature and the nature of the scattering mechanisms of the current carriers, \( \delta(m, n) \) is the Kronecker symbol.

and the coefficient \( N_c(T) \) is given by:

\[
N_c(T) = \frac{8}{3\sqrt{\pi}} \left( \frac{2mm^*kT}{h^2} \right)^{3/2}, \quad (20)
\]

The algorithmic formulas (7)-(15) together with functional (19) provide a full explanation of the nature of all set of the actual crystal kinetic properties.

Therefore it stands to reason that they have a practical implementation in research laboratories, where the different semiconductor crystals are synthesized and their kinetic properties are investigated.

For the energy dispersion relation (16), the main algorithmic functional \( I(i, j, \mu^* T) \) takes form:

\[
I(i, j, \mu^* T) = \int_0^\infty x^j u(x)^j E(x)^{3/2} \left( -\frac{\partial\varepsilon}{\partial x} \right) dx = \int_0^\infty x^j \left( \frac{E(x)^{r-j+1/2+3/2}}{2j} \right) \left( -\frac{\partial\varepsilon}{\partial x} \right) dx, \quad (19)
\]

and the coefficient \( N_c(T) \) is given by:

\[
N_c(T) = \frac{8}{3\sqrt{\pi}} \left( \frac{2mm^*kT}{h^2} \right)^{3/2}, \quad (20)
\]

Conclusions

For the energy dispersion relation (16), the dimensionless functional \( I(i, j, \mu^* T) \) takes form:

\[
E(\varepsilon) = \varepsilon, \quad E(\varepsilon) = \varepsilon + \frac{\varepsilon^2}{E_G}, \quad (16a)
\]

where \( E_G \) is the energy gap width for the charge carriers in a crystal.

For the energy dispersion relation (16), the main algorithmic functional \( I(i, j, \mu^* T) \) takes form:

\[
I(i, j, \mu^* T) = \int_0^\infty x^j u(x)^j E(x)^{3/2} \left( -\frac{\partial\varepsilon}{\partial x} \right) dx, \quad (17)
\]

In functional (17), the function \( U(r, T)u(x) \) is called the scattering function. It describes the action of the current carriers’ scattering mechanisms (modes) on the kinetic properties of a crystal. This scattering is by the crystal lattice defects and the scattering parameter \( r \) depends on the nature of the crystal and its defects.

According to the quantum-mechanical calculations [1, 3-5], for the energy dispersion relation (16),

\[
U(r, T)u(x) = U(r, T) \left( \frac{dE(x)}{dx} \right)^2,
\]

where \( U(r, T) \) is the temperature function, it has dimension of the mobility. This scattering function is given by the following formula:

\[
U(r, T) = \frac{1}{T} \left( U_A \delta(0, r) + U_O \delta(1, r) \right) + U_I \delta(2, r) \left( m^* (r^{3/2}) T(r^{-1/2} \right), \quad (18)
\]

The main objective of these investigations is to explain the nature of the crystals’ properties and give the prediction during synthesis of the crystals having the specified properties.

In actual practice, during these investigations, the dispersion relation of the current carriers in the crystal is assumed to be known. Thus, to explain the nature of the crystal properties (using the algorithmic formulas (7)-(15)), the described above scattering function should be known. This function depends on the scattering mechanisms of the current carriers in the crystal lattice defects and it is described by the parameter of
When the parameter \( r \) is determined and the dispersion relation (16) is known, the scattering function has the known value, and (as it was thoroughly described in works [2, 5]) all kinetic coefficients (7)-(15) can be theoretically calculated.

In practice, with the use of regression analysis method, the parameter of scattering \( r \) can be established from the relationship between the logarithm of the Hall mobility and the logarithm of the crystal temperature (it is in Kelvin degrees). It should be noted that the Hall mobility \( U_r(T) \) is given by
\[
U_r(T) = \frac{R(T)}{\rho(T)}.
\]

The mobility \( U_r(T) \) is experimentally measured. Having a set of the relationships between values of \( U_r(T) \) and different values of temperature \( T \), we will construct the plot \( \ln(U_r(T)) \) vs. \( \ln(T) \). Theoretical analysis of this plot shows that it is given by the following analytical form:
\[
\ln(U_r(T)) = a + b \cdot \ln(T),
\]
where \( a \) and \( b \) are the regression coefficients. There is a correlation between these coefficients and the scattering parameter \( r \), thus the value \( r \) can be easily established, as it was described in work [5]. Once this value has been established, all kinetic coefficients \( K_i(T) \) may be theoretically calculated and they may be compared with the experimental coefficients \( K_e(T) \). To make an estimation of a convergence between the experimental and theoretical data, there is the Pearson’s correlation coefficient \( corr(K_e(T), K_i(T)) \leq 1 \) in Mathcad environment.

If there is a good convergence between these data, then the Pearson’s coefficient of correlation is equal to one, or very nearly one. On the opposite, if the convergence is poor, this correlation coefficient is considerable less than one.

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Множина важливих кінетичних властивостей кристалів та їх залежність від механізмів розсіювання носіїв зарядів

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В нерівноважній термодинаміці відомі узагальнені рівняння електропровідності та теплопровідності. Вони описують відгук провідного середовища на дію дрейфових полів в ньому та магнітного поля. В ці рівняння входять феноменологічні тензори та коефіцієнти, які визначають всю множні важливих кінетичних властивостей провідних кристалів. Отже, для виявлення природи властивостей кристала необхідно використати природу множини кінетичних тензорів і коефіцієнтів, які входять в узагальнені рівняння електропровідності та теплопровідності. В даній роботі вся множна цих важливих величин для ізотропних кристалів методами статистичної фізики розраховуються при загальних умовах спостереження.

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