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IMPACT OF LAYERED STRUCTURE EFFECTS AND CHARGE ORDERING ON THERMOEMF OF THERMOELECTRIC MATERIALS IN A QUANTIZING MAGNETIC FIELD

For the most part, the band structure of materials, thermoelectric included, and the mechanisms of charge carrier scattering in them are studied using de Haas-van Alphen and Shubnikov-de Haas effects. However, it is difficult to separate the oscillations of magnetic susceptibility, the more so, conductivity, from their total magnetic field dependence. At the same time, thermoEMF oscillations can be observed directly. By virtue of this, thermoEMF oscillations in a quantizing magnetic field can be regarded as a complementary measuring tool for the study of the band structure of materials, thermoelectric included, and the mechanisms of charge carrier scattering in them. This paper is concerned with the impact of layered structure effects and charge ordering on thermoEMF of thermoelectric materials in a quantizing magnetic field. Layered structure effects are taken into account in that the energy band spectrum of material is described by the effective mass approximation in layer plane and tight-binding approximation in a direction normal to layers. Quantizing magnetic field and temperature gradient are assumed to be normal to layers. Charge ordering is thought to be interlayer and is regarded as a simple alternation of layers with different electron density. Calculations are based on the Boltzmann kinetic equation in the approximation of constant relaxation time. In the course of calculations it has been shown that the layered structure even in the case of closed Fermi surfaces (FS) results in amplitude increase of thermoEMF oscillations and their phase delay as compared to the effective mass approximation. At the same time, the layered structure effects with closed FS affect scarcely the thermoEMF maximum in a quantizing magnetic field and cause only a slight displacement of this maximum towards weaker magnetic fields. The impact of interlayer charge ordering is manifested in a biperiodic structure of thermoEMF oscillations in quasi-classical magnetic fields and multiple reversal of their polarity in stronger fields. These reversals are synchronized with changes in chemical potential of charge carrier gas in a quantizing magnetic field. When passing into the charge-ordered state with selected parameters of a model of band spectrum of a layered crystal, thermoEMF increases as compared to the disordered state by a factor of 5.9 to 13.5 in quasi-classical magnetic fields and by a factor of 7.6 to 18.4 in stronger quantizing magnetic fields.

Key words: thermoelectric material, thermoEMF, layered structure effects, charge ordering, quantizing magnetic field, chemical potential, relaxation time, oscillations, polarity, reversal.

Introduction

A model of band spectrum of a layered crystal was proposed by R. Fivaz in 1967 [1]. In the framework of this model, the energy levels of a layered crystal in a quantizing magnetic field with induction B normal to layers are determined as:

$$\varepsilon\left(n,k_z\right)=\mu^*B\left(2n+1\right)+\Delta\left(1-\cos ak_z\right). \tag{1}$$

In this formula, n is the Landau level number, k_z is component of quasi-momentum in a direction normal to layers, $\mu^* = \mu_B m_0/m^*$, μ_B is the Bohr magneton, m_0 is free electron mass, m^* is the effective mass of electron in layer plane, Δ is half-width of a miniband describing interlayer motion of electrons, a is the distance between translation-equivalent layers. It is assumed that the layered structure effects manifest themselves only in the case of open Fermi surfaces (FS), i.e. chemical potential of the system ζ referred to the bottom of conduction band meets the condition $\zeta > 2\Delta$, i.e. when the FS is open. However, the purpose of this paper is to demonstrate manifestation of layered structure effects at $\zeta > 2\Delta$ and charge ordering effects by the examples of dependence of thermoEMF of a layered crystal on quantizing magnetic field induction at helium temperatures. The applied significance of this work is that thermoEMF oscillations in a quantizing magnetic field can be used to study the band structure of materials, thermoelectric included, and the mechanisms of charge carrier scattering in them.

Calculation and analysis of the field dependence of thermoEMF of a layered crystal without charge ordering

The use of kinetic Boltzmann equation yields the following general formula for thermoEMF of a layered crystal:

$$\alpha_{zz}\equiv\alpha=\frac{\sum\limits_{\beta}\tau_\beta v_{z\beta}^2\dfrac{\partial f^0\left(\varepsilon_\beta\right)}{\partial T}}{e\sum\limits_{\beta}\tau_\beta v_{z\beta}^2\dfrac{\partial f^0\left(\varepsilon_\beta\right)}{\partial\zeta}}. \tag{2}$$

In this formula, $\beta \equiv (n, k_z)$, T is the absolute temperature, f^0 is Fermi-Dirac distribution, e is electron charge modulus, τ_β is relaxation time, $v_{z\beta}$ is longitudinal electron velocity, the rest of notation has been explained above.

Calculation of thermoEMF of a layered crystal with a band spectrum (1) and constant relaxation time yields the following formula:

$$\alpha_{zz}=\frac{\pi\alpha_0 A}{B+C}. \tag{3}$$

In this formula, $\alpha_0 = k/e$, k is the Boltzmann constant, and the dimensionless coefficients A, B, C are determined as below:

$$\begin{aligned}A=\sum_{l=1}^{\infty}(-1)^{l-1}f_l^{th}\Bigg\{\sin\left(\pi l\frac{\zeta-\Delta}{\mu^*B}\right)\Bigg[\left(C_0-C_2\right)J_0\left(\frac{\pi l\Delta}{\mu^*B}\right)+\\ +\sum_{r=1}^{\infty}(-1)^r\left(2C_{2r}-C_{2r+2}-C_{2r-2}\right)J_{2r}\left(\frac{\pi l\Delta}{\mu^*B}\right)\Bigg]+\cos\left(\pi l\frac{\zeta-\Delta}{\mu^*B}\right)\times\\ \times\sum_{r=0}^{\infty}(-1)^r\left(2C_{2r+1}-C_{2r+3}-C_{|2r-1|}\right)J_{2r+1}\left(\frac{\pi l\Delta}{\mu^*B}\right)\Bigg\}.\end{aligned} \tag{4}$$

$$B=0.5\left(C_0-C_2\right). \tag{5}$$

$$C=\sum_{l=1}^{\infty}(-1)^l f_l^{\sigma}\left\{\cos\left(\pi l\frac{\zeta-\Delta}{\mu^* B}\right)\left[(C_0-C_2)J_0\left(\frac{\pi l\Delta}{\mu^* B}\right)+\right.\right.$$
$$+\sum_{r=1}^{\infty}(-1)^r\left(2C_{2r}-C_{2r+2}-C_{2r-2}\right)J_{2r}\left(\frac{\pi l\Delta}{\mu^* B}\right)\Bigg]-\sin\left(\pi l\frac{\zeta-\Delta}{\mu^* B}\right)\times \tag{6}$$
$$\left.\times\sum_{r=0}^{\infty}(-1)^r\left(2C_{2r+1}-C_{2r+3}-C_{|2r-1|}\right)J_{2r+1}\left(\frac{\pi l\Delta}{\mu^* B}\right)\right\}.$$

In these formulae, $J_n(x)$ are the Bessel functions of the 1-st kind, n-th order and real argument and modulating coefficients are determined as:

$$C_0=\arccos\left(1-\frac{\zeta-\mu^* B}{\Delta}\right), \tag{7}$$

$$C_m=\frac{\sin mC_0}{m}\ \text{at}\ m\neq 0. \tag{8}$$

Subtraction of $\mu^* B$ from ζ explicitly takes into account the fact of charge carrier condensation at the bottom of a subband with the number $n = 0$ in the ultraquantum limit.

Besides:

$$f_l^{th}=\left[\mathrm{sh}\left(\pi^2 lkT/\mu^* B\right)\right]^{-1}\left[1-\left(\pi^2 lkT/\mu^* B\right)\mathrm{cth}\left(\pi^2 lkT/\mu^* B\right)\right]. \tag{9}$$

$$f_l^{\sigma}=\left(\pi^2 lkT/\mu^* B\right)\left[\mathrm{sh}\left(\pi^2 lkT/\mu^* B\right)\right]^{-1}. \tag{10}$$

In these formulae, sh(x) and cth(x) are hyperbolic sinus and cotangent, respectively. In the effective mass approximation the coefficients A, B, C are determined as follows:

$$A=\sum_{l=1}^{\infty}(-1)^{l-1} f_l^{th}\left\{\frac{\mu^* B}{\pi l\Delta}\sqrt{\frac{2\left(\zeta-\mu^* B\right)}{\Delta}}-\frac{1}{\pi}\left(\frac{\mu^* B}{l\Delta}\right)^{3/2}\left[\cos\left(\frac{\pi l\zeta}{\mu^* B}\right)\times\right.\right.$$
$$\left.\left.\times C\left(\sqrt{2l\left(\frac{\zeta}{\mu^* B}-1\right)}\right)+\sin\left(\frac{\pi l\zeta}{\mu^* B}\right)S\left(\sqrt{2l\left(\frac{\zeta}{\mu^* B}-1\right)}\right)\right]\right\}. \tag{11}$$

$$B=\frac{1}{6}\left[2\left(\frac{\zeta-\mu^* B}{\Delta}\right)\right]^{3/2}. \tag{12}$$

$$C=\sum_{l=1}^{\infty}(-1)^l\frac{f_l^{\sigma}}{\pi}\left(\frac{\mu^* B}{l\Delta}\right)^{3/2}\left[\sin\left(\frac{\pi l\zeta}{\mu^* B}\right)\times C\left(\sqrt{2l\left(\frac{\zeta}{\mu^* B}-1\right)}\right)-\cos\left(\frac{\pi l\zeta}{\mu^* B}\right)S\left(\sqrt{2l\left(\frac{\zeta}{\mu^* B}-1\right)}\right)\right]. \tag{13}$$

In formulas (11) and (13) $C(x)$ and $S(x)$ – cosine- and sine- Fresnel integrals, respectively.

Equations defining the chemical potential of electron gas in a quantizing magnetic field for a real layered crystal and in the effective mass approximation are given in [2]. The results of calculation of thermoEMF of a layered crystal in a quantizing magnetic field are presented in Figs. 1 and 2.

From the plots it is apparent that in quasi-classical magnetic fields the layered structure effects are manifested in phase delay and increase of a relative contribution of thermoEMF oscillations with a

reduction of its value as a whole. In stronger magnetic fields there is an optimal range of these fields wherein the layered structure effects are most pronounced, but thermoEMF maximum is affected scarcely by these effects that only cause its slight displacement towards weaker magnetic fields.

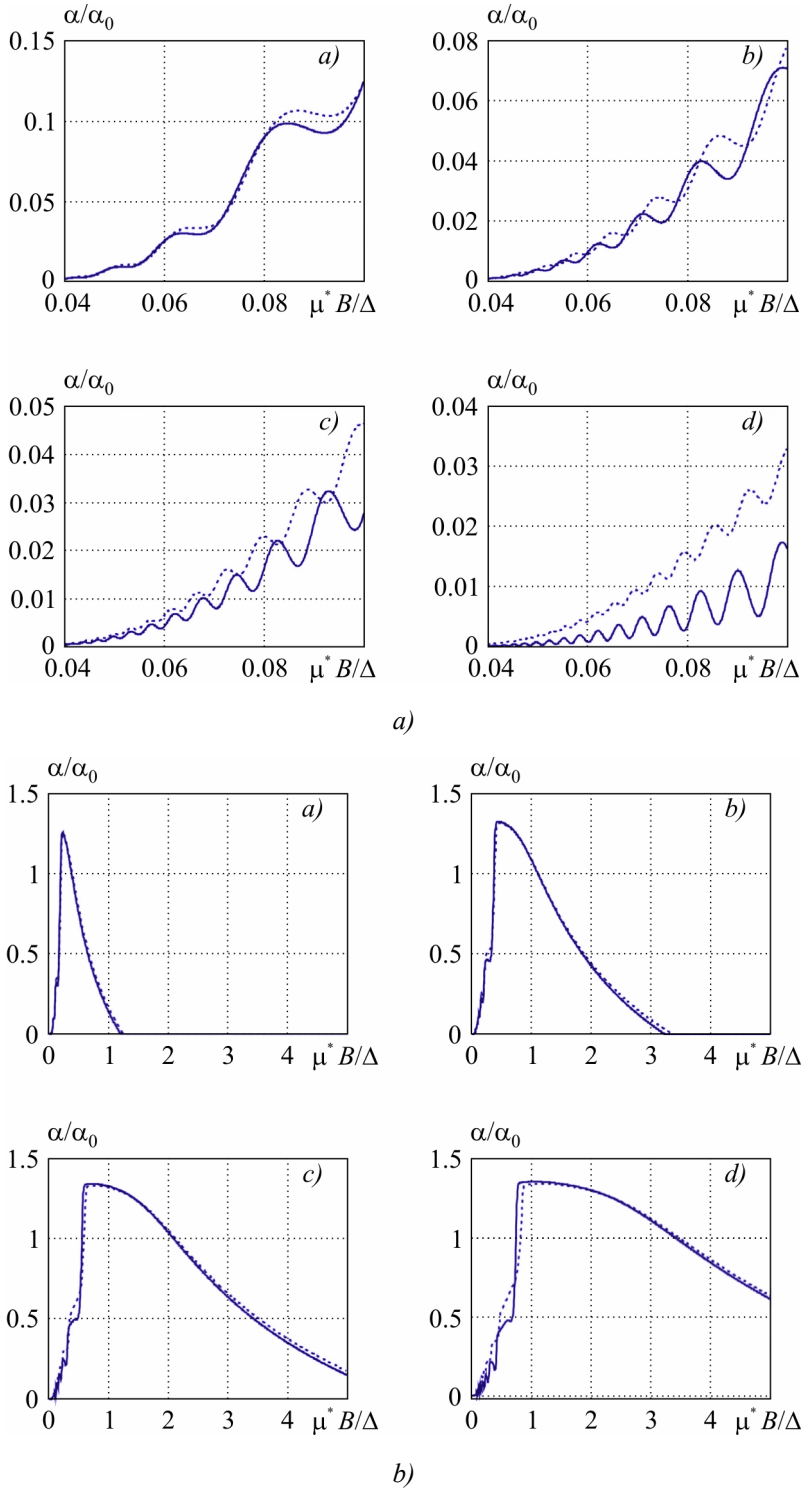


Fig. 1. Field dependences of thermoEMF of a layered crystal: a) in quasi-classical approximation, b) in a wide range of magnetic fields at $kT/\Delta = 0.03$. Solid curves correspond to a real layered crystal, dashed curves – to the effective mass approximation. In the plots, the Latin letter a corresponds to the ratio ζ_0/Δ equal to 0.5, b – 1, c – 1.5, d – 2.

Impact of charge ordering on thermoEMF of layered crystals in a quantizing magnetic field

If charge ordering in a layered crystal is considered as a simple alternation of layers more or less filled with electrons, then the coefficients A, B, C in the approximation of constant relaxation time are determined as follows [3]:

$$A = \sum_{l=1}^{\infty} (-1)^l f_l^{th} \int_{-(\gamma-b)}^{\sqrt{w^2\delta^2+1}} \left| y^{-1} \right| \sqrt{\left(1 + w^2\delta^2 - y^2\right)\left(y^2 - w^2\delta^2\right)} \sin\left[\pi l b^{-1}(\gamma - y)\right] dy, \tag{14}$$

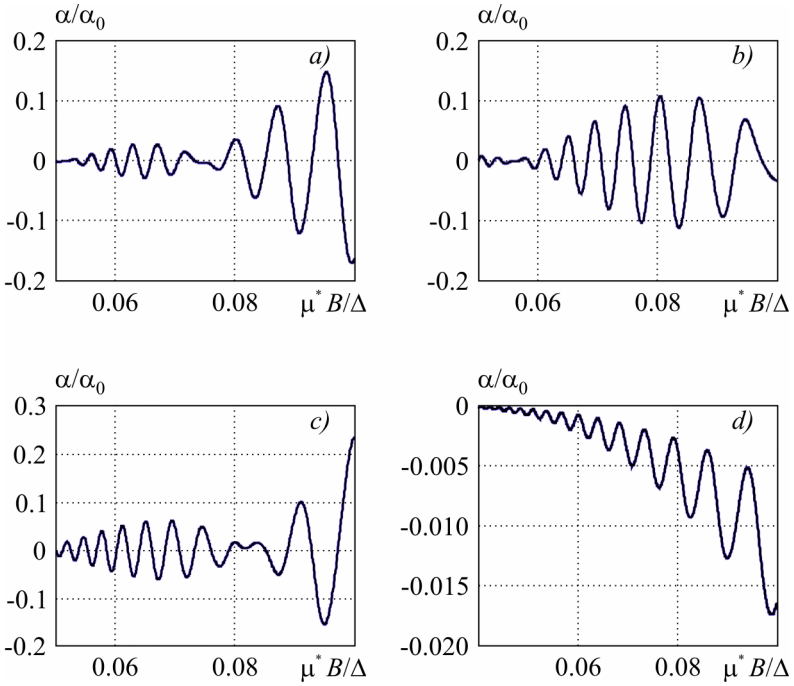
$$B = 0.5 \int_{-(\gamma-b)}^{\sqrt{w^2\delta^2+1}} \left| y^{-1} \right| \sqrt{\left(1 + w^2\delta^2 - y^2\right)\left(y^2 - w^2\delta^2\right)} dy, \tag{15}$$

$$C = \sum_{l=1}^{\infty} (-1)^l f_l^{\sigma} \int_{-(\gamma-b)}^{\sqrt{w^2\delta^2+1}} \left| y^{-1} \right| \sqrt{\left(1 + w^2\delta^2 - y^2\right)\left(y^2 - w^2\delta^2\right)} \cos\left[\pi l b^{-1}(\gamma - y)\right] dy. \tag{16}$$

In these formulae, $\gamma = \zeta / \Delta$, $b = \mu^* B / \Delta$, $w = W_0 / \Delta$. Moreover, δ is order parameter varying in the range from 0 to 1, W_0 is the effective interaction that results in charge ordering. With such ordering, charge carrier motion in the direction normal to layers is described by the formula:

$$W(k_z) = \pm\sqrt{W_0^2\delta^2 + \Delta^2 \cos^2 ak_z}. \tag{17}$$

Equations defining the field dependences of chemical potential and the order parameter are given in [4]. The results of calculating thermoEMF of a charge-ordered layered crystal are depicted in Fig. 2.



a)

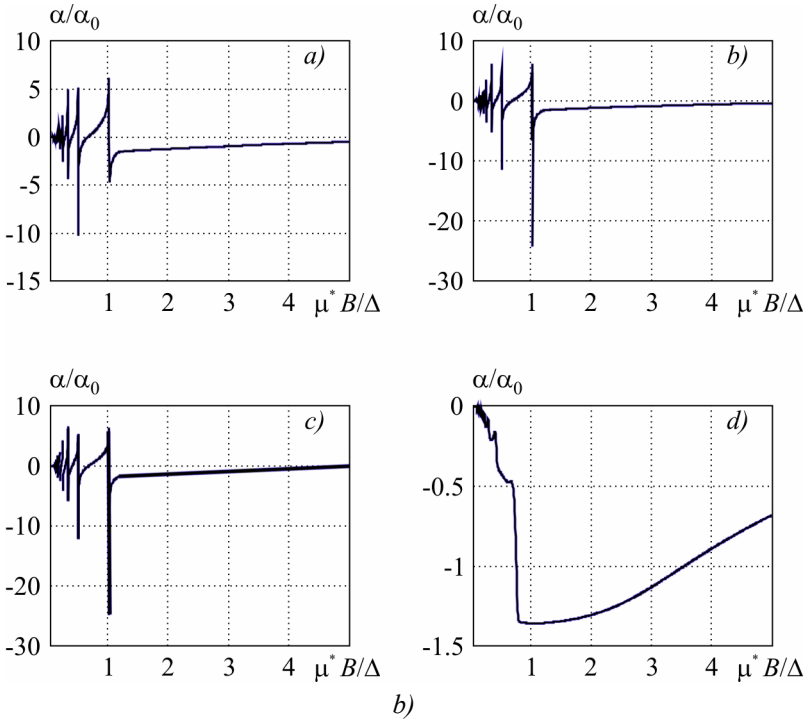


Fig. 2. Field dependences of thermoEMF of a layered charge-ordered crystal: a) in quasi-classical magnetic fields; b) in a wide range of magnetic fields. In the plots the Latin letter a corresponds to the ratio W_0 / ζ_{02D} equal to 1.5, b – 2, c – 2.5, d – 0 (disordered state).

From the plots it is seen that charge ordering is manifested in a biperiodic structure of oscillations in quasi-classical magnetic fields, their polarity reversal in stronger magnetic fields and a drastic drop of thermoEMF value after the point of a topological transition matched by the last polarity reversal.

Conclusions and recommendations

1. The layered structure effects are manifested in the reduction of relative contribution and phase delay of thermoEMF oscillations in quasi-classical magnetic fields, the existence of optimal range where they are most pronounced in the intermediate magnetic fields and a slight displacement of thermoEMF maximum toward weaker magnetic fields.
2. Charge ordering is manifested in the origination of a biperiodic structure of oscillations, thermoEMF polarity reversal in strong magnetic fields and a drastic drop of thermoEMF value after the point of a topological transition from an open FS into a closed one.

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