

Thermodynamic Functions of Electron Gas in Strong Anisotropic Materials. Quantum Gas

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In this paper we report about the peculiarities of thermodynamic functions of quantum electron gas in layered crystals. In such materials the conductivity along the layers exceeds by several orders the conductivity across layers. To these structures depend layered materials: YTe_3 , $LaTe_3$, $CeTe_3$, $InSe$, which are considered at low temperatures, as well as a number of organic conductors. There are many theoretical and experimental papers, indicated coexistence of equipotential energy surfaces of electrons in the form of corrugated cylinders and corrugated sheets. The thermodynamic functions for quantum electron gas are evaluated and compared for two different dependences of energy on momentum. The same parameters are used in both models – they are effective masses and translation vectors for β -GaSe. Our investigations allowed explaining the temperature dependence of resistivity for strong anisotropic and isotropic crystals at low temperatures, received by experiment. We also analyzed the specific heat in such crystals and explained the anomaly, observed in such crystals and illustrated the imperfection of the Debye model.

Keywords: Thermodynamic Functions, Quantum Electron Gas, Layered Crystals, Specific Heat.

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1. MOTIVATION

We consider a layered material with sharp anisotropy of electrical conductivity, where electrical conductivity along the layers is several orders higher than across the layers. These structures include layered materials YTe_3 , $LaTe_3$, $CeTe_3$ [1], $InSe$ [2] at low temperatures, as well as a number of organic conductors [3]. Electron energy investigations in organic conductors indicated coexistence of equipotential surfaces in the form of corrugated cylinders and corrugated sheets [4]. In YTe_3 , $LaTe_3$, $CeTe_3$ equipotential surface energy, calculated from the first principles in [5] include weak dispersion along one direction. Two-dimensional metallic conductivity at low temperatures in $InSe$ was experimentally confirmed by magneto resistance quantum oscillations in [2].

Even for quasi classical gas of electrons the comparison thermodynamic functions obtained for parabolic dispersion (PD) (energy - quadratic function of momentum) and for strong anisotropic equipotential surfaces (SAD) done in [6], pointed to feature the electron gas in layered structures. Namely, the heat capacity plotting after the anisotropy parameter has a pronounced maximum, which was associated with the transition from closed to open equipotential surfaces. With the growth of anisotropy this maximum shifts to low temperatures, i.e. transition from closed to open surfaces occurs by lower values of energy. It was shown that the thermodynamic analysis reveals the shortcomings of the single-particle spectra of carriers [7]. A quasi-classical approximation is not applicable to materials with high concentration of carriers (metals) and semiconductors at low temperatures. This is the case we consider in this paper.

2. THE MODEL AND APPROACH

The layered crystals contain atoms of two or more layers in the unit cell. The layers are binded by Van-der-Waals interactions, which, according to [8], contain only 2 - 3% of the chemical bindings inside the layer. For such materials the one-particle energy dependence on quasi momentum was introduced in [9 - 11] (SAD):

$$E(\vec{k}) = \alpha k^2 + \gamma(1 - \cos z), \quad (2.1)$$

$$\alpha = \frac{\hbar^2}{2m_t}, \quad \gamma = \frac{\hbar^2 \pi^2}{4m_t d^2} \quad (2.2)$$

where m_t effective mass of current carrier in the plane of layer, γ - half-width of the conduction band in the direction [001], $z = k_z d$, d - translation this direction. Energy (2.1) (SAD) determines the availability of open and closed equipotential surfaces or evidence of a three- and two-dimensional electron gas. The obtained thermodynamic functions were compared with those for parabolic dispersion (when the energy depends on the square momentum (PD)). For PD the expressions for thermodynamic functions are known [12]. The same parameters are used in both models – they are effective masses and translation vectors for β -GaSe [13]. To find the density of states at the equipotential surface we used the inversion theorem of the partition function [14]. The partition function for strong anisotropic material was obtained in [15]. The resulting density of states (DS) coincides with the expressions obtained earlier [16]. Comparing this density of states, with obtained for PD we see: 1) DS of SAD is significantly greater than for isotropic materials (PD) for small energies (low frequencies), 2) For large energies (frequencies) DS of strongly anisotropic materials (SAD) is constant and much smaller than in isotropic materials (PD), where DS increases with increasing energy as $\sqrt{\epsilon}$.

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The following investigations were made using [17].

$$\begin{aligned} N &= \int_0^{\infty} g(\varepsilon) f_{FD}(\varepsilon) d\varepsilon ; \\ E &= \int_0^{\infty} \varepsilon g(\varepsilon) f_{FD}(\varepsilon) d\varepsilon ; \\ -\Omega &= \int_0^{\infty} \ln \left[1 + \exp \left(\frac{E_F - \varepsilon}{\theta} \right) \right] g(\varepsilon) d\varepsilon . \end{aligned} \quad (2.3)$$

where E_F – energy of Fermi level, $\theta = k_B T$, $g(\varepsilon)$ – density of states $f_{FD}(\varepsilon)$ – Fermi-Dirac function. Heat capacity and entropy were evaluated as derivation from energy and thermodynamic potential on temperature. They are:

$$\begin{aligned} S(T) &= k \left[\int_0^{\infty} g(\varepsilon) \ln \left(1 + e^{\frac{\mu - \varepsilon}{\theta}} \right) - \int_0^{\infty} g(\varepsilon) f_{FD}(\varepsilon) \left(\frac{\mu - \varepsilon}{\theta} \right) d\varepsilon \right] \\ C(T) &= k \int_0^{\infty} \varepsilon g(\varepsilon) f_{FD}(\varepsilon) (1 - f_{FD}(\varepsilon)) \left(\frac{\mu - \varepsilon}{\theta} \right) d\varepsilon \end{aligned} \quad (2.4)$$

Evaluations were performed for electron gas in a sample with volume of 1 cm³, which is 0.034 mols.

3. THE RESULTS AND DISCUSSION

The concentration of carriers plotting again the temperature for (SAD) shows stronger dependence on the temperature than in (PD).

The number of carriers increases considerably stronger with the temperature for layered materials at low temperatures. It consists with a number of experimental works on resistivity of layer materials at low temperatures [18, 19]. This property is used in [19] for temperature sensor based on GaSe. The received dependences of heat capacity of the electron gas point to its linear temperature dependence $C_p = \gamma T$ with $\gamma = 0.052 \text{ mJ} \cdot \text{mol}^{-1} \text{K}^{-2}$. For all cases entropy and heat capacity are well interpolated by linear dependences on temperature with different tangent angles, depending on the Fermi energy. At small Fermi energies (0.014 eV) the heat capacity of SAD electron gas depends stronger on the temperature than in PD materials. For large values of E_F (1 eV) – on the contrary. The same tendency occurs for the temperature dependences of entropy. These contradictorally depending can be explained by the Lifshitz phase transition – the transition from closed to open equipotential surfaces [21]. Figure 1 shows the dependence of heat capacity and entropy of the Fermi energy evaluated at $T = 10 \text{ K}$.

As we see from Fig. 1, a topological phase transition is noticeable in specific heat and entropy. The analyzed dependences for the internal energy and thermodynamic potential did not have any features. In experimental data [22] the anomalies in the Specific heat of the layered material were observed, and they may have the same nature as in our investigations. Both these results conclude the limited possibility of using Debye theory of heat capacity in layered materials. The entropy dependence of the Fermi energy (Fig. 1b) is in good agreement with [23], where the entropy on two-dimensional gas was analyzed.

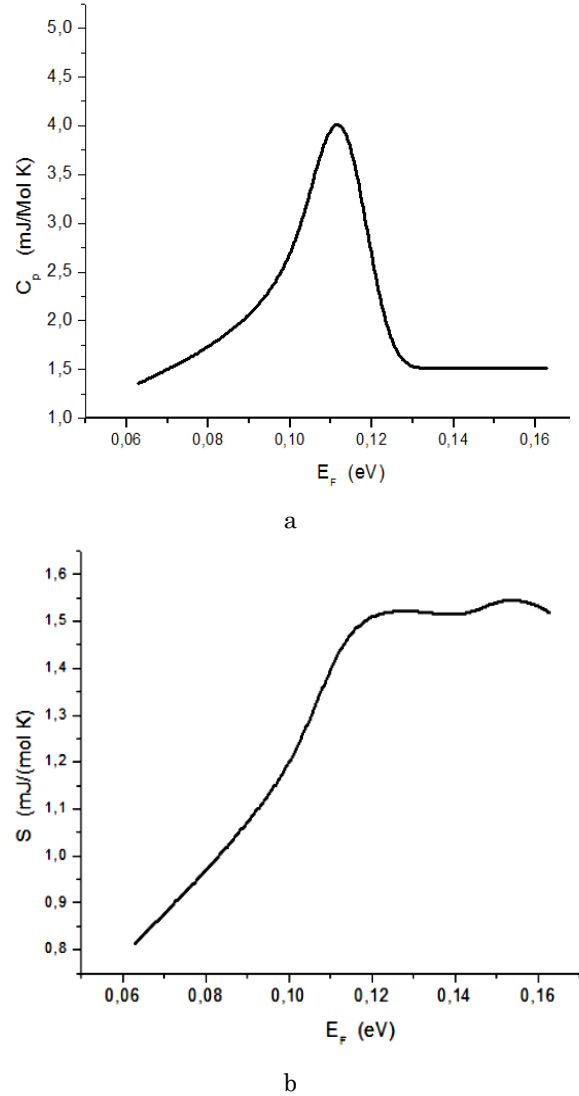


Fig. 1 – The dependence of specific heat (a) and entropy (b) of the Fermi energy

4. CONCLUSIONS

The thermodynamic functions for quantum electron gas are evaluated and compared for two different dependences of energy on momentum. The same parameters are used in both models – they are effective masses and translation vectors for β - GaSe.

The temperature dependences of electron concentration for strong anisotropic case allowed us to explain the experimental data for resistivity, more increasing with temperature in strongly anisotropic materials (for low temperatures).

We obtain the contradictory dependences of the thermodynamic functions on temperature: bigger for strong anisotropic case for small Fermi - energies (with closed equipotential surfaces) and vice versa for big Fermi - energies (with opened equipotential surfaces). It was shown that this contradiction can be explained by topological transition from closed to opened equipotential surfaces (Lifshitz's transition). Our analyzing of heat capacity allowed to explain the anomaly, obtained experimentally. It also illustrates the imperfection of the Debye model of heat capacity for strong anisotropic materials.

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