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Thermodynamic functions of an electron gas in strongly anisotropic crystals for different models of electron spectrum

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Different models of electron energy for *GaSe* are considered for the purpose of deriving thermodynamic functions for an electron gas at low and high temperatures. Their common features and differences are pointed out and their agreement with existing data is analyzed. The results show cases where the two models are equivalent. We also show conditions at which they yield different results and therefore peculiarities of the chemical bonding are to be taken into consideration.

GaSe / Thermodynamic functions / Layered structure

1. Introduction

We have considered two simulations of the electron energy as a function of the quasi-momentum: the parabolic one, typical of isotropic semiconductors, and the Fivaz one, which was introduced in [1,2] for layered semiconductors with specific chemical bonding in one of the crystallographic directions. Using parameters known for *GaSe* we find the thermodynamic functions for an electron gas and compare them for both high (quasi-classical) and low (Fermi gas) temperatures. This enables us to identify the cases where a parabolic dependence of the energy on the quasi-momentum (which is appreciable for many particle interaction problems due to its simplicity) can also be used for layered semiconductors.

For Fivaz' model we analyzed the dependences of the thermodynamic functions on parameters that can be affected by intercalation or pressure, as well as the transition from closed to open energy surfaces.

2. Thermodynamic functions for a quasi-classical electron gas

We consider a quasi-classical electron gas when $e^{\frac{\mu}{\theta}} << 1$ (μ denotes the chemical potential, θ = kT, where T – the temperature of the sample, k – the Boltzmann constant).

In [3], the statistical sum for such a gas was expressed as follows:

$$Z(\theta) = A\theta \exp\{-\delta\}\int_0^{\pi} \exp\{\delta\cos(x)\}dx \qquad (1)$$

with

$$A = \frac{4VL_z m_t}{h^2 d^2}, \quad \delta = \gamma / \theta \qquad (2)$$

$$I_n(\delta) = \int_0^{\pi} (\cos(x))^n \exp\{\delta\cos(x)\}dx, \qquad (3)$$

which is very similar to the modified Bessel functions. In (2) V denotes the crystal volume (1 cm^3), L_z the thickness of the sample (1 cm), d the crystal cell constant in the [001] direction, m_t the effective mass of electrons in the layer [4], γ denotes the parameter introduced in [1,2] for the energy dependence:

$$E(k) = \alpha k_{\perp}^2 + \gamma(1 - \cos z) \text{ with } 0 < z < \pi, \qquad (4)$$

$\alpha = \hbar^2/(2m_t)$, $k_{\perp} = (k_x, k_y)$ – quasi-momentum of an electron in the plane of the layer, $z = k_z d''$, k_z – quasi-momentum of an electron in the direction normal to the plane. We use the expression for the thermodynamic potential for a quasi-classical electron gas from [5]:

$$-\Omega = pV = N\theta\left[1 + \frac{N}{2}\frac{Z\left(\frac{2}{\theta}\right)}{Z^2\left(\frac{1}{\theta}\right)}\right], \qquad (5)$$

where p denotes pressure, V volume, and N the number of particles.

After using (4) in (5), the expressions for the thermodynamic potential and entropy become:

$$-\Omega = N\theta\left(1+\frac{N}{4A\theta}\frac{I_0(2\delta)}{\left(I_0(\delta)^2\right)}\right)$$
$$S = Nk\left(1+\frac{N\delta}{2A\theta}\left(\frac{I_0(2\delta)I_1(\delta)}{(\mathrm{I}_0(\delta))^3}-\frac{I_1(2\delta)}{(\mathrm{I}_0(\delta))^2}\right)\right) \qquad (6)$$

Expressions from the well known dependences of the energies and statistical sum (1) (see for example [6,7]) are considered for the electron gas energy and specific heat. Using (1) we found them to be:

$$\mathrm{U} = N\theta\left(1+\delta\left(1-\frac{I_1(\delta)}{I_0(\delta)}\right)\right)$$
$$C = Nk\left(1+\delta^2\left(\frac{I_2(\delta)}{I_0(\delta)}-\left(\frac{I_1(\delta)}{I_0(\delta)}\right)^2\right)\right) \qquad (7)$$

We analyzed the temperature dependences of the thermodynamic functions (6) and (7) and compared them with the well known parabolic dependence [5-7] for an electron gas, using *GaSe* parameters. Comparing these investigations in the temperature range 250-550 K we conclude that: a) the electron gas energy shows similar values for both dependences – the largest relative divergence of the energies is 2.1 %, which occurs at 550 K; b) the specific heat differs slightly more in this temperature range and shows a relative divergence within the range 1.7 % for 250 K and 5.1 % for 550 K; c) the thermodynamic potentials differ significantly – almost over the whole temperature range we observe about 30 % higher absolute values of *Ω* for the parabolic spectrum (typical of isotropic semiconductors) – this difference is explained by the chemical bonding in layered semiconductors; but both functions show nearly the same increase with increasing temperature: d) the entropy shows anomalously small differences for both models; the relative divergence decreases from $1.1{\cdot}10^{-4}$ % at 250 K to $3.7{\cdot}10^{-5}$ % at 550 K.

This enables us to conclude that the dependences of the thermodynamic functions on temperature are quite similar for both models as long as we deal with a quasi-classical gas.

Intercalation – *i.e.* introducing of other ions and molecules into interlayer space – is typical of layered semiconductor technology and is widely used in material science of such crystals [8-10]. Intercalation makes it possible to introduce a new generation of energy storage devices.

It has been shown that in many cases intercalation increases the interlayer distance without introducing new chemical bonding between the matrix and the intercalated molecules. For example, in [11] it is shown that strong intercalation of organic molecules into TiS_2 and PbI_2 increases the interlayer distances to 54 Å and 66.56 Å. In [12] intercalation is suggested to affect the electron spectrum by decreasing γ in (4). A change of γ can also be noticed by submitting the samples to pressure [13]. Using (6) and (7), we found the dependence of the thermodynamic functions of a quasi-classical electron gas on this parameter. The γ dependences of the electron energy and specific heat are shown in Fig. 1 and Fig. 2.

The non monotonic character of these functions can be seen from Fig. 1 and Fig. 2. They show transitions from closed to open energy surfaces, which are known as Lifshitz transitions in layered crystals [14-16]. As we see from Fig. 1, the open energy surfaces are more strongly affected by changing γ than the closed ones. This is in good agreement with the results of [13], where optical and structural examinations together with band investigations were carried out for samples of *GaSe* under pressure. It is shown in [13] that the bands with small dispersion along the [001] direction are much more affected by pressure than the bands for which energy is strongly dependent on k_Z.

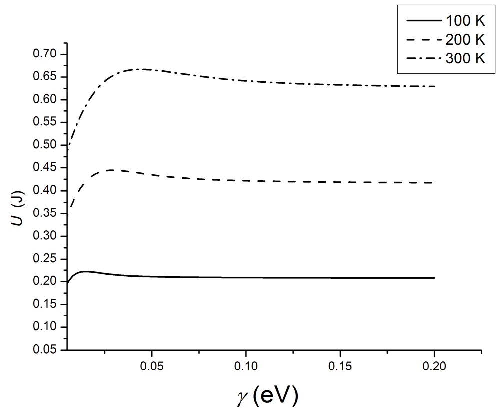

Fig. 1 Electron gas energy as a function of γ for different temperatures.

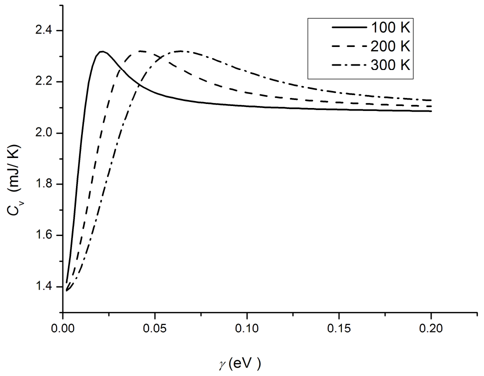

Fig. 2 Specific heat as a function of γ for different temperatures.

3. Thermodynamic functions for a Fermi gas in a layered structure

To find the thermodynamic functions for an electron gas at low temperature with energy dependence on the quasi-momentum (4), the statistical weight, thermodynamic potential and energy can be expressed as [5]:

$$G(\varepsilon)=\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} Z(\beta)\, e^{\beta\varepsilon}\frac{d\beta}{\beta},$$

$$-\Omega=\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\frac{\beta\pi\theta}{\sin(\beta\pi\theta)}\cdot\frac{\exp\{\beta\mu\}}{\beta^2}Z(\beta)d\beta, \qquad (8)$$

$$U=\Omega+\theta S-\mu\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} \text{ with } \beta=\frac{1}{\theta}$$

Using (1) we found the thermodynamic potential [17]:

$$-\Omega=\frac{A}{2}\begin{cases}\begin{cases}\left[(\mu-\gamma)^2+\frac{(\pi\theta)^2}{3}+\frac{\gamma^2}{2}\right]x_0+\\ \frac{3}{2}(\mu-\gamma)\sqrt{\mu(2\gamma\text{-}\mu)}\text{, if}\mu\le 2\gamma\end{cases}\\ \left\{\left[(\mu-\gamma)^2+\frac{(\pi\theta)^2}{3}+\frac{\gamma^2}{2}\right]\pi\text{, if}\mu\ge 2\gamma\right.\end{cases} \qquad (9)$$

and the entropy:

$$S=\frac{1}{3}Ak\pi^2\theta\cdot\begin{cases}x_0\text{, for }\mu\le 2\gamma\\ \pi\text{, for }\mu\le 2\lambda\end{cases}. \qquad (10)$$

The electron energy looks as:

$$U=\left(\frac{A}{2}\right)\begin{cases}\left[\begin{matrix}\frac{\gamma^2}{2}(L(\mu)-2x_0)+\frac{(\pi\theta)^2}{3}L(\mu)\text{-}\\ (\mu-\gamma)^2\left(\frac{\mu}{2K(\mu)}+x_0\right)+\\ (\mu-\gamma)\left(2\mu x_0-\frac{3K(\mu)}{2}\right)+\frac{3}{2}\mu K(\mu)\end{matrix}\right]\text{, if}\mu\le 2\gamma;\\ \left[\begin{matrix}-(\mu-\gamma)^2+\frac{(\pi\theta)^2}{3}-\frac{\gamma^2}{2}+\\ 2\mu(\mu-\lambda)\end{matrix}\right]\pi\text{, if}\mu\ge 2\gamma,\end{cases} \qquad (11)$$

where $L(\mu)=\left(\frac{\mu}{K(\mu)}+x_0\right), K(\mu)=\sqrt{\mu(2\gamma-\mu)}$

and the specific heat:

$$C_2=\frac{A\pi^2\theta k}{3}\cdot\begin{cases}L\text{, if}\mu\le 2\gamma;\\ \pi\text{, if}\mu\ge 2\gamma\end{cases} \qquad (12)$$

Having examined the temperature dependences of the thermodynamic functions (9)-(12) in the range 4 K < T < 100 K and having compared them with the well known functions for weakly anisotropic crystals in [5-7] we came to the following conclusions: 1) the absolute values of the thermodynamic potential, entropy, energy and heat capacity for isotropic crystals are larger for isotropic crystals than for anisotropic crystals, both for closed and open energy surfaces; 2) the thermodynamic potential and energy of electron gas depend stronger on the temperature for closed energy surfaces than for open ones, while their derivatives (entropy and specific heat) exhibit stronger changes for open surfaces than for closed ones.

As it is seen in (9)-(12) the transition from closed to open energy surfaces depends on the correlation between γ and μ.: when μ. increases we move from closed to open energy surfaces and from a semiconductor to a conductor. The dependences of the thermodynamic functions on μ are shown in Figs. 3-6.

As it follows from Fig. 3, for some combinations of parameters in layered crystals, a small region ($\Omega(\mu) > 0$) of negative volume expansion coefficient appears. This agrees with the results of [18], where a negative value of the linear expansion coefficient is shown. The authors of [18,19] explain this phenomenon by bending waves, which are typical of phonon spectra of layered crystals. But in [20] no bending wave was found for *GaSe*. For some closed energy surfaces, atypical correlations are observed between the electron energy for isotropic crystals (usually larger) and the electron energy for layered crystals (usually smaller). They can be explained by comparing the densities of states [21], which show an area of electron frequencies where the density is larger for strongly anisotropic crystals than for isotropic crystals. The results of [21] could explain in a satisfactory way the anomalous increase of the absorption coefficient for some frequencies, as reported for *GaSe* [21], In_6S_7 [22], and *BiTeI* [23].

Fig. 5 shows the independence of the entropy with respect to μ (or the electron concentration) in the case of open energy surfaces. This observation agrees with [24], where a two-dimensional electron gas was considered. Fig. 6 shows the typical dependence of specific heat on μ, which is known as Lifshitz transition [14-16].

Conclusions

The comparison of the thermodynamic values for isotropic and strongly anisotropic (layered) crystals showed the following characteristics.

For a quasi-classical gas:

– The temperature dependences are very similar in the two cases – in layered crystals a parabolic energy dependence on the quasi-momentum can be used as long as the investigator cares about the temperature dependence and is sure that there is no physical effect on γ(due to intercalation or pressure).

– A decrease of γleads to opening of energy surfaces, which can be noticed on the electron energy and specific heat.

– The energy of a quasi–two-dimensional system depends stronger on γ than the energy of a three-dimensional system.

For a Fermi gas:

– The absolute values of the thermodynamic potential, entropy, energy and heat capacity are larger for

isotropic crystals than for anisotropic crystals, both for closed and open energy surfaces.
– The thermodynamic potential and energy of electron gas depend stronger on the temperature for closed energy surfaces than for open ones, while their derivatives (entropy and specific heat) exhibit stronger changes for open surfaces than for closed ones.
– For particular combinations of parameters the thermodynamic potential of layered crystals shows a region of negative volume restriction coefficient.
– The energy of electron gas in layered crystals can, for some combinations of parameters, be larger than the energy of an isotropic electron gas.
– The entropy of a quasi–two-dimensional gas does not depend on the electron concentration.
– The specific heat shows a phase transition from open to closed energy surfaces, known as a Lifshitz phase transition.

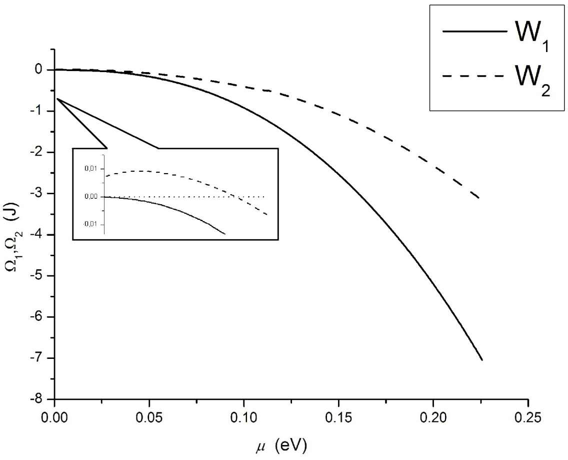

Fig. 3 Dependence of the thermodynamic potential on μ for T = 11.6 K; Ω_1 – isotropic crystals; Ω_2 – layered crystals.

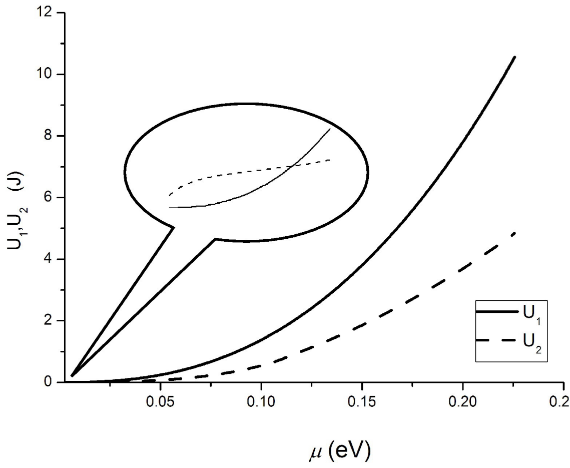

Fig. 4 Dependence of the electron energy on μ for T = 11.6 K; U_1 – isotropic crystals; U_2 – layered crystals.

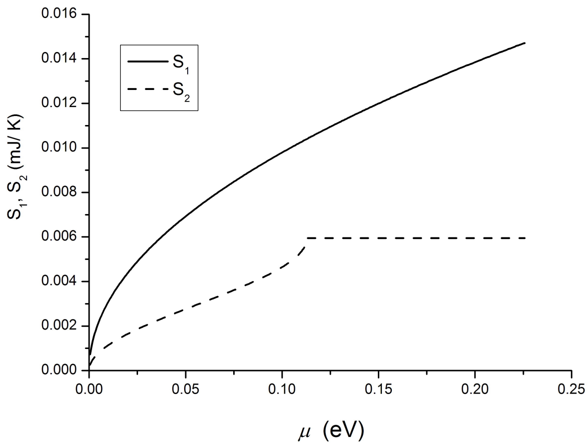

Fig. 5 Dependence of the entropy on μ for T = 11.6 K; S_1 – isotropic crystals; S_2 – layered crystals.

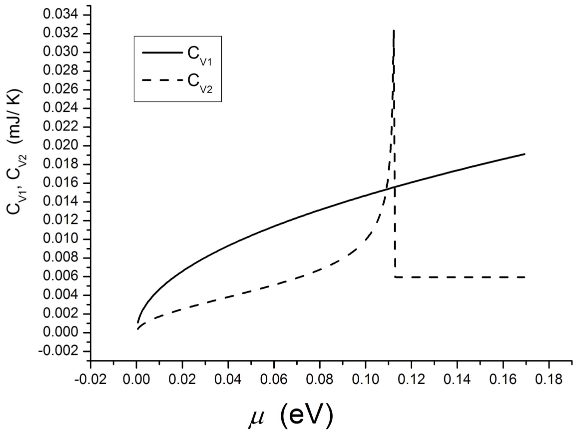

Fig. 6 Dependence of the specific heat on μ for T = 11.6 K; C_{v1} – isotropic crystals; C_{v2} – layered crystals.

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