

Integral and differential developments of carrier density of states in the intercalated layered crystal

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The effect of the layered crystal intercalation on the functional dependence of the carrier density of states is analyzed. The conditions of thermodynamic stability of intercalation process depending on Fermi energy and microscopic parameters are studied.

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Introduction

It is well known that density of elementary excitation of states $\rho(\omega)$ is widely used in calculating the physical quantities observed in experiments. Two approximations can be distinguished which result from utilizing $\rho(\omega)$. On the one hand, $\rho(\omega)$ is widely used in the search for the mean value of energy characteristics. The result of the integration process in the whole range of frequencies is determined by the functional dependence of $\rho(\omega)$ in the region of integration. As an example, we can take the use of $\rho(\omega)$ for calculations of the indirect interaction between adatoms on a tight-binding solid [1]. On the other hand, a number of examples can be presented when this or that physical characteristic is determined by the value of $\rho(\omega)$ at a certain energy point. For instance the critical temperature of the transition to the superconductor state according to BCS theory is determined by density of states at the Fermi energy ε_F [2]. The second example of the benefit of knowledge of $\rho(\omega)$ can be the $2\frac{1}{2}$ type Lifshitz transition. Such a transition is realized in a layered crystal due to the peculiarities of its structure [3]. The layered crystal can be represented as a set of packed «sandwiches» tied by weak Van der Waals forces. Each sandwich is a set of monatomic layers with covalent or ion–covalent bond. Small but nonzero electron overlap between layers is much better described by a strongly anisotropic three-dimensional dispersion law with different effective masses within the layer plane and normal to it ($m_{x,y}^* \ll m_z^*$) [4]. In

our paper the layered crystal will be described by a model dispersion law which is distinguished from the isotropic and anisotropic ones by a much smaller electron overlap integral t_c across the layers than within the layer plane α_c . It was first written by Fivaz [5]

$$\varepsilon(\chi, k) = \alpha_c \chi^2 + t_c (1 - \cos k), \quad (1)$$

where all the quasi-momenta $\chi = (k_x, k_y)$, $k_z \equiv k$ are written in units of the lattice constant, $\alpha_c = 1/2m_{\perp c}^*$, $m_{\perp c}^*$ is the electron effective mass within the layer plane, $t_c = 1/2m_{\parallel c}^*$, $m_{\parallel c}^*$ is the electron effective mass across the layer plane, and $\hbar = 1$. As much as the parameters α_c, t_c are determined by effective masses, they will be taken from the experimental data. In terms of the density of states, the Eq. (1) corresponds to $\rho_0(\omega)$ as follows:

$$\rho_0(\omega) = \begin{cases} \frac{2\pi}{\alpha_c} \arccos \frac{2t_c - \omega}{2t_c}, & \text{at } \omega \leq 2t_c, \\ \frac{\pi^2}{\alpha_c}, & \text{at } \omega \geq 2t_c \end{cases}. \quad (2)$$

As follows from (2), at the point $\omega = 2t_c$ the derivative $\partial\rho_0/\partial\omega$ is discontinuous, and the value $\omega = 2t_c$ corresponds to the topological $2\frac{1}{2}$ type Lifshitz transition, which characterizes the transition from the open to the closed isoenergy surface of a layered crystal.

Discrimination in chemical bonds causes a number of phenomena specific to layered crystals. One of them, i.e., intercalation, which consists in introducing the guest atom into the gaps between sandwiches, the

so-called Van der Waals gaps. We define host material as the recipient of the guest species, the intercalate as the guest species resident in the host material, and the intercalant as the guest species substance [6].

In intercalation of the transition metal dichalcogenides MX_2 (where M is atom of a metal of a transition group, $X = S, Se$) with various electron-donor species, the changes observed in the electronic properties can be satisfactorily explained by the charge transfer resulting in the gradual filling of the host lattice band without any appreciable change in its shape or its mutual position – a model known as the rigid-band approximation [7]. Firm evidence for the validity of this model is available for the cases where the intercalate is an alkali (or alkaline-earth) metal, a noble metal, or a first-row transition metal. So, by changing the carrier concentration during the intercalation process, the Fermi energy can be raised up to the topological $2\frac{1}{2}$ type Lifshitz transition. The rigid-band model satisfactorily describes effects in which the factors of importance are the integral developments of band structure and population of the band (like kinetic properties) rather than the details of the band structure. Naturally, this model can be regarded as a crude approximation.

As is shown in [8], intercalation of $TlGaS_2$ (space group cc , with lattice constants $a = b = 10,31 \text{ \AA}$, $c = 15,16 \text{ \AA}$ and the thickness of Van der Waals gap is $3,64 \text{ \AA}$ [9]) by Li increases the degree of anisotropy of electro-, photo-, and x-ray-conductivity anisotropy via the diminution of interlayer mixing. In this case an intercalated crystal has a more expressed «two-dimensionality». However, this effect is most conveniently achieved by the intercalation of organic molecules, in particular, the long-chain amines and related macromolecules. For example, in a solid such as $2H-TaS_2$ (trigonal structure with lattice constants $a = 3,36 \text{ \AA}$, $c = 5,89 \text{ \AA}$ and a thickness of Van der Waals gap of nearly 3 \AA [10]) intercalated with n-octadecylamine, the layers can be separated by a bilayer of octadecylamine molecules with a dimension approaching 60 \AA where the thickness of the single layer is $\sim 6 \text{ \AA}$. Since the interaction between the layers is now considerably weakened, this also makes the crystal more close to «two-dimensional» [11]. All these facts confirm that the rigid-band model is not capable of describing the phenomena concerned with the change of lattice parameters and thus with the energy parameters such as electron overlap.

That is why it seems interesting to study i) the boundaries of the rigid-band model applicability, ii) the effect of the host–guest interaction on the shape of the density of states, particularly, in the topological $2\frac{1}{2}$ type Lifshitz transition, iii) the change

of free energy of the electron subsystem depending on intercalant and carrier concentration at different microscopic parameters.

The goal of this paper is to analyze $\rho(\omega)$ in the intercalated layer due to the insertion of foreign atoms within the framework of a model with the following peculiarities. Intercalants locate only in the Van der Waals gap. The guest–guest interaction causes splitting of the intercalant energy level ε_0 into a band with a dispersion law similar to (1). We restrict ourselves to the virtual crystal model, i.e., when N_0 impurities occupy each cell equiprobably with the equal probability $p = N_0/N$, where N is total number of cells.

Electron density of states in intercalated layered crystal

The carrier density of states in the intercalated layered crystal will be calculated below as a function of the intercalant concentration in a wide region of energy, and, particularly in certain energy regions like the band bottom and energy corresponding to the $2\frac{1}{2}$ type Lifshitz transition. Two different descriptions of such a problem exist: i) change of the chemical potential at unaltered dispersion law or, in other words, unaltered energy states (the rigid-band model), ii) change of the dispersion law caused by intercalation at unaltered chemical potential. In fact, the importance of choice (i) or (ii) depends on the concrete problem, namely, chemical bonds and the degree of anisotropy, i.e., the energy characteristics of the host and degree of host–guest interaction.

The case of an interacting host–guest system at unaltered chemical potential will be considered. Let us construct the Hamiltonian of the electron subsystem of the host with N_0 foreign atoms intercalated into it. We will use operational functions

$$\hat{\Psi}(\mathbf{r}) = \sum_{\mathbf{n}} \hat{c}_{\mathbf{n}} \psi_{\mathbf{n}}(\mathbf{r}) + \sum_{\mathbf{n}} p(\mathbf{n}) \hat{a}_{\mathbf{n}} \varphi_{\mathbf{n}}(\mathbf{r}), \quad (3)$$

where the summation is over all cells; $\psi_{\mathbf{n}}(\mathbf{r})$ is a wave function of electron on the site of layered crystal with weighting coefficient $\hat{c}_{\mathbf{n}}$, $\varphi_{\mathbf{n}}(\mathbf{r})$ is a wave function of an electron on the site of the intercalant with weighting coefficient $p(\mathbf{n}) \hat{a}_{\mathbf{n}}$: $p(\mathbf{n})$ is the probability

$$p(\mathbf{n}) = \begin{cases} 1, & \text{if the intercalant is in the } \mathbf{n}\text{-th cell} \\ 0, & \text{otherwise} \end{cases}. \quad (4)$$

In the case of a one-electron description, in the second-quantization representation on the unary Hamiltonian and operational functions (3) Hamiltonian will have the form

$$\begin{aligned} \mathcal{H} = & \sum_{\mathbf{n}, \mathbf{n}'} t(\mathbf{n}, \mathbf{n}') c_{\mathbf{n}}^+ c_{\mathbf{n}'} + \sum_{\mathbf{n}, \mathbf{n}'} p(\mathbf{n}) p(\mathbf{n}') t_i(\mathbf{n}, \mathbf{n}') a_{\mathbf{n}}^+ a_{\mathbf{n}'} + \\ & + \sum_{\mathbf{n}} p(\mathbf{n}) \varepsilon_0 a_{\mathbf{n}}^+ a_{\mathbf{n}} + \left[\sum_{\mathbf{n}} p(\mathbf{n}) V_0 a_{\mathbf{n}}^+ c_{\mathbf{n}} + \text{h. c.} \right] + \\ & + \left[\sum_{\mathbf{n}, \mathbf{n}'} p(\mathbf{n}) V(\mathbf{n}, \mathbf{n}') a_{\mathbf{n}}^+ c_{\mathbf{n}'} + \text{h. c.} \right]. \end{aligned} \quad (5)$$

Here, the first term describes electron mixing on the host sites in \mathbf{n}, \mathbf{n}' cells ($c_{\mathbf{n}}, c_{\mathbf{n}'}^+$ are Fermi operators of annihilation and creation, respectively); the second and the third ones are an analogous mixing in the guest subsystem (ε_0 is the energy level of the intercalant, $a_{\mathbf{n}}, a_{\mathbf{n}'}^+$ are Fermi operators of annihilation and creation of the intercalant, respectively). The remaining terms describe an electron host–guest mixing in the same and in the nearest cells, respectively. Electron overlap in the guest subsystem $t_i(\mathbf{n}, \mathbf{n}')$ and electron host–guest overlap $V(\mathbf{n}, \mathbf{n}')$ satisfies the condition of translational invariance, i.e., $t_i(\mathbf{n}, \mathbf{n}') = t_i(\mathbf{n} - \mathbf{n}')$, $V(\mathbf{n}, \mathbf{n}') = V(\mathbf{n} - \mathbf{n}')$.

In the virtual crystal approximation in the momentum representation equation (5) takes the following form

$$\begin{aligned} \mathcal{H} = & \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) c_{\mathbf{k}}^+ c_{\mathbf{k}} + p^2 \sum_{\mathbf{k}} \tilde{\varepsilon}_i(\mathbf{k}) a_{\mathbf{k}}^+ a_{\mathbf{k}} + \\ & + p \sum_{\mathbf{k}} \varepsilon_0 a_{\mathbf{k}}^+ a_{\mathbf{k}} + p \sum_{\mathbf{k}} V(\mathbf{k}) c_{\mathbf{k}}^+ a_{\mathbf{k}} + \text{h. c.}, \end{aligned} \quad (6)$$

where $\varepsilon(\mathbf{k})$ is the dispersion law of the host subsystem (1), $c_{\mathbf{k}}^+, c_{\mathbf{k}}$ are Fermi operators of creation and annihilation in the host subsystem, respectively, $a_{\mathbf{k}}^+, a_{\mathbf{k}}$ are Fermi operators of creation and annihilation in the guest subsystem,

$$\tilde{\varepsilon}_i(\mathbf{k}) = \alpha_i \chi^2 + t_i (1 - \cos k) \quad (7)$$

is the dispersion law of the guest subsystem, α_i, t_i are the electron overlap integrals of the nearest guest atoms within and normal to the layer, respectively. The second and the third terms in (6) can be combined into one. Then the Hamiltonian (6) will have the form

$$\begin{aligned} \mathcal{H} = & \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) c_{\mathbf{k}}^+ c_{\mathbf{k}} + p^2 \sum_{\mathbf{k}} \varepsilon_i(\mathbf{k}) a_{\mathbf{k}}^+ a_{\mathbf{k}} + \\ & + p \sum_{\mathbf{k}} V(\mathbf{k}) c_{\mathbf{k}}^+ a_{\mathbf{k}} + \text{h. c.} \end{aligned} \quad (8)$$

with the dispersion law $\varepsilon_i(\mathbf{k}) = \tilde{\varepsilon}_i(\mathbf{k}) + \varepsilon_0/p$, measured from ε_0/p , and the Fourier transform of $V_0 + V(\mathbf{n}, \mathbf{n}')$ is equal to $V(\mathbf{k})$. The change of inter-

calant concentration p governs the value of the constants before the second and third terms in (8), i.e., $p^2 \alpha_i, p^2 t_i, pV(\mathbf{k})$.

Let us use method of two-time retarded Green's function and calculate the carrier density of states. For the system described by Eq. (5) the Green's functions for the intercalate and host subsystem are [12]

$$\langle\langle a_k | a_k^+ \rangle\rangle = \frac{\omega - \varepsilon(\mathbf{k})}{[\omega - \varepsilon(\mathbf{k})][\omega - p^2 \varepsilon_i(\mathbf{k})] - p^2 V^2(\mathbf{k})} \quad (9)$$

and

$$\langle\langle c_k^+ | c_k^+ \rangle\rangle = \frac{p^2 \varepsilon_i(\mathbf{k})}{[\omega - \varepsilon(\mathbf{k})][\omega - p^2 \varepsilon_i(\mathbf{k})] - p^2 V^2(\mathbf{k})}, \quad (10)$$

respectively. The density of states $\rho_m(\omega)$ is defined from the corresponding Green's function $\langle\langle a_m | a_m^+ \rangle\rangle$ by [13]

$$\rho_m(\omega) = -\frac{1}{\pi} \lim_{\varepsilon \rightarrow 0} \text{Im} \langle\langle a_m^+ | a_m^+ \rangle\rangle_{|\omega + i\varepsilon}. \quad (11)$$

Then, we obtain

$$\begin{aligned} \rho_c(\omega) = & \frac{1}{2(2\pi)^2} \int_{k_1}^{k_2} \frac{\omega - p^2 \varepsilon_i(q_1)}{|2bK(q_1) + c(cq_1 + d)|} dk - \\ & - \frac{1}{2(2\pi)^2} \int_{k_3}^{k_4} \frac{\omega - p^2 \varepsilon_i(q_2)}{|2bK(q_2) + c(cq_2 + d)|} dk, \end{aligned} \quad (12)$$

$$\begin{aligned} \rho_i(\omega) = & \frac{1}{2(2\pi)^2} \int_{k_1}^{k_2} \frac{\omega - \varepsilon(q_1)}{|2bK(q_1) + c(cq_1 + d)|} dk - \\ & - \frac{1}{2(2\pi)^2} \int_{k_3}^{k_4} \frac{\omega - \varepsilon(q_2)}{|2bK(q_2) + c(cq_2 + d)|} dk \end{aligned} \quad (13)$$

where the notation $b = \frac{\alpha_c + p^2 \alpha_i}{2}$, $c = \frac{\alpha_c - p^2 \alpha_i}{2}$, $d = \frac{(t - p^2 t_i)(1 - \cos z) - p\varepsilon_0}{2}$ is used, and $K(q_i)$ with $q_i \equiv \chi_i^2$ is

$$K(q_i) = \frac{1}{2} \sqrt{[\varepsilon(\mathbf{k}) - p^2 \varepsilon_i(\mathbf{k})]^2 + 4p^2 |V(\mathbf{k})|^2}. \quad (14)$$

The regions of integration k_i are determined by the condition $(2\pi)^2 \geq q_i \geq 0$, and $V(\mathbf{k}) \equiv V$ (the Fourier transform of $V_0 + V(\mathbf{n}, \mathbf{n}')$) will be chosen to be constant.

The total carrier density of states of the intercalated layered crystal is of the form $\rho(\omega) = \rho_c(\omega) + \rho_i(\omega)$. Remember that the goal of this paper is to find out the

dependence and the tendency of $\rho(\omega)$ to change in the region of the topological $2\frac{1}{2}$ type Lifshitz transition. To this end it is necessary to know the change of the behavior of the densities of states of the host $\rho_c(\omega)$ and guest $\rho_i(\omega)$ with increasing p and varying microscopic parameters V and t_i . The results of calculations of $\rho_c(\omega)$ and $\rho_i(\omega)$ performed according to (12), (13) for different p, V are given in Figs. 1 and 2, respectively.

As calculations showed, at a small guest concentration p [12] its increase leads to the appearance of a «tail» of the states density in the forbidden band and to a certain undershoot in the $\rho_c(\omega)$ dependence. There is also the region of energy where the dependence $\rho_c(\omega)$ is quite similar to $\rho_0(\omega)$ for the pure crystal ($\rho_c(\omega) \rightarrow A_0 + \rho_0(\omega)$). This means that the rigid-band model is quite good for the description of $\rho_c(\omega)$ in this case. The higher is p the greater is A_0 and the shape of $\rho_c(\omega)$ is not similar to that of $\rho_0(\omega)$, and the rigid-band model becomes unacceptable. An increase of the guest concentration or of the host–guest interaction V_0 smoothes the behavior of $\rho_c(\omega)$ in the region of the Lifshitz transition and shifts it in the direction of higher energies. The behavior of $\rho_i(\omega)$ as a function of p

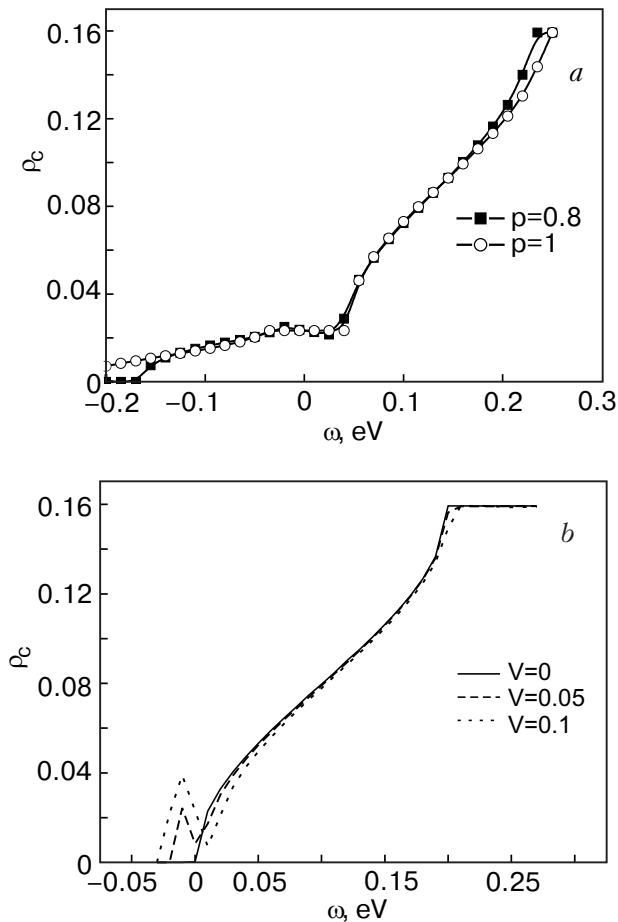


Fig. 1. Spectral dependence of electron density of states $\rho_c(\omega)$ at $\varepsilon_0 = -0.2$ eV, $\alpha_0 = 0.5$ eV, $V = 0.1$ eV: different p (a), at $p = 0.2$ and different V (b).

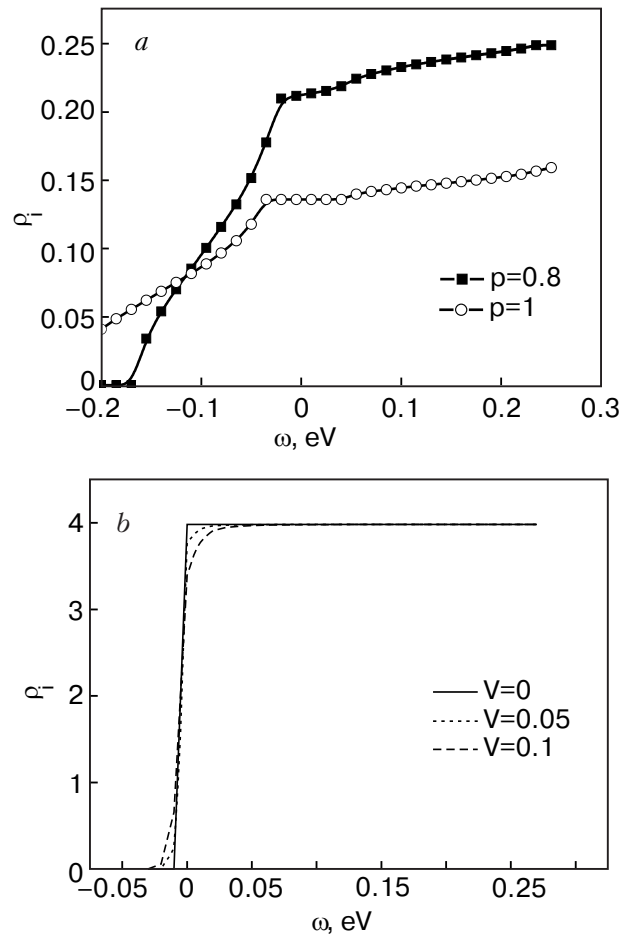


Fig. 2. Spectral dependence of electron density of states $\rho_i(\omega)$ at $\varepsilon_0 = -0.2$ eV, $\alpha_0 = 0.5$ eV, $V = 0.1$ eV: different p (a), at $p = 0.2$ and different V (b).

or V_0 turns out to be opposite. The Lifshitz transition becomes more precise and it shifts in the direction of smaller energies. Only an increase of the guest–guest interaction up to the case when $t_i \rightarrow \alpha_i$ leads to the elimination of the Lifshitz transition.

The calculated density of states will be used for analyzing its integral development in the thermodynamic stability of the electron subsystem of the intercalated layered crystal and of the intercalate.

Thermodynamic stability

Let us consider the change of free energy for many-impurity problems at different guest concentrations and ε_0 at various i) Fermi levels, ii) electron concentrations n . The Fermi level will be the parameter which can be changed in a different way, particularly, by different impurities in the same crystal or by changing crystal energy parameters.

In our problem the ion–ion interaction was not considered. That is why the change of free energy is studied at low temperatures. Let us consider the limit case

of $T = 0$ (at higher temperatures the Fermi distribution should be taken into account). In the case $T = 0$, the free energy of the electron subsystem coincides with its internal energy $F = E$ [14].

At a small intercalant concentration the change of free energy (ΔF) of the electron subsystem of the intercalated layered crystal is similar to the interaction between adatoms (or foreign atoms) on a tight-binding solid [1]. According to that paper [1] the chemical potential changes incidentally upon the introduction of adatoms (in our case it is intercalant). Then the energy change is determined by the change of the density of states $\Delta\rho(\omega)$ caused by adatomic (or intercalant) states, i.e.,

$$\Delta F = \int_{-\infty}^{\varepsilon_F} [\rho_c(\omega) + \rho_i(\omega)] \omega d\omega - \int_0^{\varepsilon_F} \rho_0(\omega) d\omega - N_0 \varepsilon_0, \quad (15)$$

where $\rho_c(\omega)$, $\rho_i(\omega)$, $\rho_0(\omega)$, are, respectively, the electron densities of states of the host renormalized by interaction with the guest, of the guest renormalized by interaction with the host, and of the pure host; N_0 is the number of the guest species, ε_0 is a guest energy level, and ε_F is Fermi level.

We calculate ΔF as a function of:

- a) ε_F and on ε_0 at various p (N_0/N), (N is the number of crystal sites),
- b) electron concentration n and ε_0 , at various p (N_0/N).

The results of the many-impurity problem are obtained in the case of $p\varepsilon_0 \leq \varepsilon_F \leq 2t$ for localized ($\varepsilon_0 < 0$) and $-p\varepsilon_0 \leq \varepsilon_F \leq 2t$ for resonance ($\varepsilon_0 > 0$) levels, and $\alpha_c = 1$, $t = 0.1$, $\alpha_i = 0.1$, $t_i = 0.01$ (all energy parameters are given in eV).

Numerical calculations show:

- i) At $p < p_{cr}$ (p_{cr} is an intercalate concentration defined by $\Delta F(\varepsilon_F) = 0$), the dependence $\Delta F(\varepsilon_F)$ is broken into two regions with $\Delta F > 0$ and $\Delta F < 0$ (Fig. 3), within which ΔF in fact does not change both for localized ($\varepsilon_0 < 0$) and resonance ($\varepsilon_0 > 0$) levels. The higher is p , the larger is the interval between such constant values. Here, the region of ε_F where the sign of ΔF changes remains the same. For $\varepsilon_0 < 0$, the thermodynamic equilibrium state ($\Delta F < 0$) occurs at $\varepsilon_F > \varepsilon_{cr}^l$, $\varepsilon_{cr}^l < 0$, whereas for $\varepsilon_0 > 0$ it takes place at $\varepsilon_F < \varepsilon_{cr}^r$, $\varepsilon_{cr}^r > 0$ ($\varepsilon_{cr}^{l,r}$ are Fermi energies wherein $\Delta F = 0$ for localized and resonance levels, respectively). The Fermi level, wherein $\Delta F(\varepsilon_F) = 0$ is sensitive to the position of guest energy level, ε_0 , namely $\varepsilon_{cr}^r > \varepsilon_{cr}^l$. The higher is $|\varepsilon_0|$, the higher is the value of p_{cr} and still more stable is the thermodynamic state of the system both for localized and resonance levels.

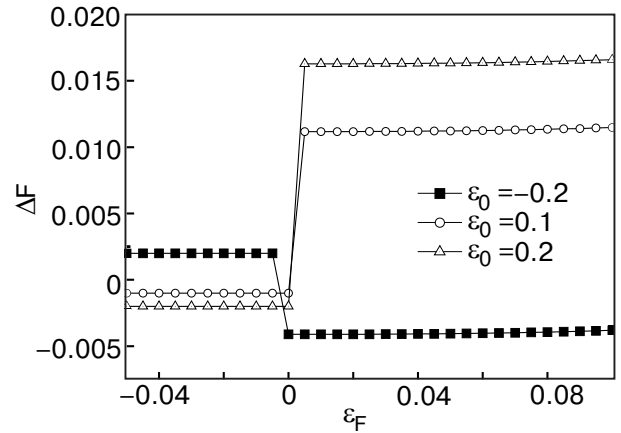


Fig. 3. The difference of free energy of intercalated layered crystal $\Delta F(\varepsilon_F)$ at different energy level of the guest and $V = 0.01$ eV.

As the guest concentration increases to $p > p_{cr}$, the dependence of $\Delta F(\varepsilon_F)$ for localized levels is changed (Fig. 4). Namely, in the vicinity of p_{cr} a minimum of $\Delta F(\varepsilon_F)$ takes place. Moreover, at $p > p_{cr}$, $\Delta F \geq 0$. For resonance levels, the higher is the guest concentration p ($p > p_{cr}$), the smoother is $\Delta F(\varepsilon_F)$ and, what is more, the thermodynamic equilibrium region over Fermi level is widened, and the difference between the maximum and minimum values of $\Delta F(\varepsilon_F)$ increases.

ii) In the case of different values of electron concentrations, the Fermi level may be determined from the following equation

$$n = \int_{-\infty}^{\varepsilon_F} [\rho_c(\omega) + \rho_i(\omega)] d\omega. \quad (16)$$

At small p ($p < p_{cr}$), the $\Delta F(n)$ behavior is similar to $\Delta F(\varepsilon_F)$ both for localized and resonance levels. The higher is p , the narrower is the region of thermody-

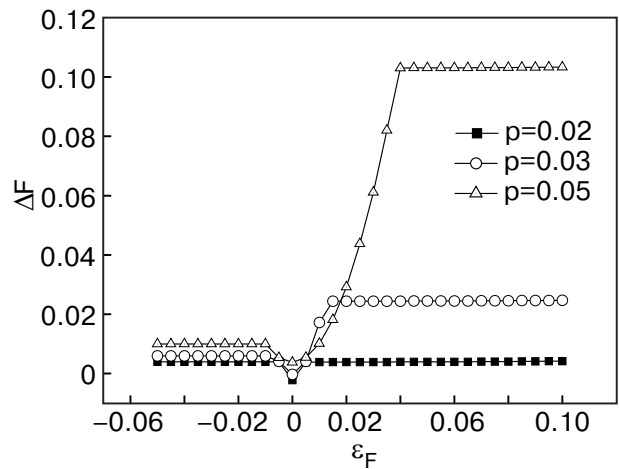


Fig. 4. The difference of free energy of intercalated layered crystal $\Delta F(\varepsilon_F)$ at different guest concentration.

dynamic equilibrium and the smaller is its stability (ΔF value). The Fermi level corresponding to the minimum of ΔF remains the same. As would be expected, an integral characteristic like the change of free energy does not vary in the region of the Lifshitz transition.

Experimental results

The measurements of the change of Gibbs energy [15] were carried out by the e.m.f. method and its temperature dependence. The position of the Fermi level (Fig. 5, curve 1) was determined by electrochemical analog of Mott–Shottky method, and free carrier concentration (Fig. 5, curve 2) was determined from galvanomagnetic measurements (Hall effect).

The thermodynamic Gibbs potential in the host–guest system is as follows [16]:

$$\Delta G = n_e F E = \Delta S + W + \Delta \mu_F + L \frac{\partial C}{\partial x} + A_0, \quad (17)$$

where F is the Faraday number, n_e is the number of redox-electrons, E is the electromotive force, $\Delta S = kT \ln(x/x - 1)$ is the configuration entropy component, and x is the number of the introduced guest relative to one formula unit of the host (similar to the theoretical p). The other terms describe the enthalpy component. Among them W describes the interaction between guest component, i.e., the effect of intercalant concentration on the ion–ion interaction in the guest subsystem, $\Delta \mu_F$ is the change of Fermi level position of electrons or holes, L is a coefficient, linear to the potential Lennard-Jones function, $\partial C/\partial x$ is the change of lattice units, A_0 is a constant which describes the host–guest interaction which is usually taken to be independent of x [16]. As is seen in Fig. 5, the region of chemical potential minimum corresponds to small intercalant concentrations ($x = p$ is near 0,2). It is this value of concentration at which the

entropy component is already insignificant (entropy component is much higher than the enthalpy one at small and large x : $x \rightarrow 0$, $x \rightarrow 1$), and the ion–ion interaction (W) can still be neglected. Thus, the behavior $\Delta \mu(x)$ describes the change of the thermodynamic Gibbs potential $\Delta G(x)$, which at low temperatures coincides with the change of free energy [14].

Comparing the obtained theoretical results (see Fig. 4) with the experimental ones for intercalated $\text{Li}_x\text{Bi}_2\text{Te}_3$ [15] one can see (Fig. 5) that at small guest concentration ($p = x < 0,15$) Li intercalation shifts the Fermi level down to the middle of the forbidden band. As a result, the carrier concentration decreases, meaning a decrease of the thermodynamic Gibbs potential, caused by the electron subsystem contribution. As is seen in Fig. 4, the increase of intercalant concentration at a certain Fermi level leads to a decrease of the change of free energy down to a negative value, i.e., stabilization of the system under study.

The fact of the Fermi energy decrease suggests that lithium in the Van der Waals gap did not release its electrons, preserving its identity to a certain extent. In terms of the calculation, the degree of guest identity is given by the value of V : the weaker is the host–guest binding, represented by the parameter V , the higher is the guest identity.

Conclusions

The analysis of a functional dependence of carrier density of states in an intercalated layered crystal is carried out by two-time retarded Green’s functions considering host–guest and guest–guest interactions within the framework of virtual crystal model, i.e., intercalants equiprobably occupy each cell ($p \leq 1$). It is shown that the concentration increase p causes the appearance of a certain «tail» of the density of states in the forbidden band. Its shape depends on the nature of the guest, i.e., the intercalant energy level ϵ_0 . Either an increase of p and of the host–guest interaction smoothes the Lifshitz transition, shifting it in the direction of higher energies in the $\rho_c(\omega)$ dependence and makes it more clear, thus shifting the transition point in the direction of smaller energies in the $\rho_i(\omega)$ dependence. The Lifshitz transition in the $\rho_i(\omega)$ dependence disappears only if the anisotropy of the chemical bonds in the intercalate subsystem decreases. Based on the calculated density of states, the change of the free energy of electron subsystem is found. The theoretical results obtained indicate the tendency towards thermodynamic advantages or disadvantages caused by the electron host–guest subsystem, depending on the guest and carrier concentrations in the intercalation process.

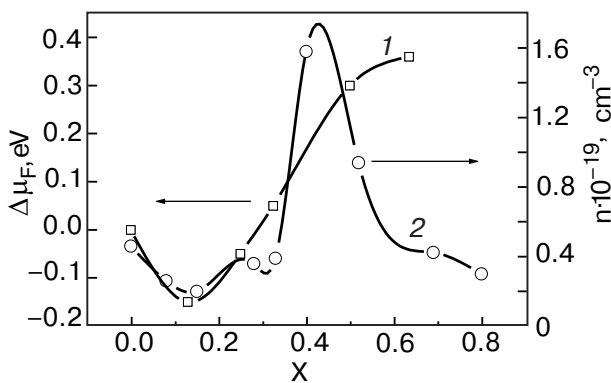


Fig. 5. Dependence of the difference of Fermi energy (1), free carriers concentration (2) on guest loading x in $\text{Li}_x\text{Bi}_2\text{Te}_3$ [15].

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