

phys. stat. sol. (b) **159**, K73 (1990)

Subject classification: 71.70

Institute of Material Sciences,
Academy of Sciences of the Ukrainian SSR, Chernovtsy¹⁾

Change in the Electronic Subsystem Energy by Intercalation of Layered Crystals

By

M.F. OMEL'YAN, B.A. LUKIYANETS, and K.D. TOVSTYUK

The present report deals with a theoretical study of the change in the electronic subsystem energy, occurring by intercalation of layered crystals (LC). The interest in such a study is evident in view of the technical application of the intercalation phenomena in high-capacity energy storages based on intercalated LC.

Below we will solve the problem of stability of the intercalated LC electronic subsystem.

Let us consider an intercalated LC whose electronic subsystem is described by the Hamiltonian

$$H = \sum_{\vec{k}} \varepsilon_{\vec{k}} a_{\vec{k}}^{\dagger} a_{\vec{k}} + E_0 a_0^{\dagger} a_0 + \sum_{\vec{k}} V(\vec{k}) a_{\vec{k}}^{\dagger} a_0 + \text{h.c.}, \quad (1)$$

which may be regarded as a rather simplified spinless Anderson Hamiltonian.

In (1), the first term is the electronic Hamiltonian of the crystal matrix ($\varepsilon_{\vec{k}}$ is the electron dispersion relation; $a_{\vec{k}}^{\dagger}$ is the creation operator of an electron in the state $|\vec{k}\rangle$); the second term represents the energy of an electron of an intercalated atom; and the third term is the intercalant-LC electronic mixing.

As known, within the scope of a single-impurity model of the Anderson model type, the change in the LC electronic subsystem energy at intercalation of an atom is [1]

$$\Delta W = 2 \left(\int_{-\infty}^{\varepsilon_F^0} E \rho(E) dE - \int_{-\infty}^{\varepsilon_F^0} E \rho_0(E) dE \right), \quad (2)$$

where ε_F^0 , $\rho_0(E)$, ε_F , $\rho(E)$ are, respectively, the Fermi level and density of states of the LC before and after the introduction of the intercalated atom in it.

At $T = 0$ K ΔW coincides with the change of the free energy.

On condition that the carrier concentration remains unchanged,

$$\Delta W = 2 \int_{-\infty}^{\varepsilon_F} (E - \varepsilon_F) \Delta \rho(E) dE, \quad (3)$$

where

$$\Delta \rho(E) = \rho(E) - \rho_0(E) = \frac{1}{\pi} \text{Im} \left\{ \frac{\partial E}{\partial} \ln |1 - V_{\vec{k}} G_q \bar{G}_0| \right\}. \quad (4)$$

¹⁾ Zhovtneva 5, SU-274001 Chernovtsy, USSR.

In (4)

$$\bar{G}_0 = \frac{\Omega}{N} \int \frac{d^3 k}{(2\pi)^3} G_0(k, E) = \frac{\Omega}{N} \int \frac{d^3 k}{(2\pi)^3} \frac{1}{E - \varepsilon_{\vec{k}} + i\eta} \quad (5)$$

and

$$G_q = \frac{1}{E - E_0 + i\eta} \quad (6)$$

Separating out real and imaginary parts in \bar{G}_0 , G_q , we represent \bar{G}_0 , G_q as $\bar{G}_0 = (a - ib)$, $G_q = (c - id)$ with

$$\begin{aligned} a &= \frac{\Omega}{N} P \int \frac{d^3 k}{(2\pi)^3} \frac{1}{E - \varepsilon_{\vec{k}}} , & b &= \frac{\Omega}{N} \pi \int \frac{d^3 k}{(2\pi)^3} \sigma(E - \varepsilon_{\vec{k}}) , \\ c &= P \frac{1}{E - E_0} , & d &= \pi \sigma(E - E_0) . \end{aligned} \quad (7)$$

We represent the argument of the logarithm in (4) as $r \exp(i\phi)$, where $r^2 = [1 - V_{\vec{k}}(ac - bd)]^2 - V_{\vec{k}}^2(bc + ad)^2$ and $\phi = \arctg(bc + ad)V_{\vec{k}}/(1 - V_{\vec{k}}(ac - bd))$. In this case we get

$$\Delta\rho(E) = \frac{1}{\pi} \frac{\partial}{\partial E} \phi . \quad (8)$$

After substitution of (8) into (3) and integration by parts we obtain

$$\Delta W = - \frac{2}{\pi} \int_{-\infty}^E F \phi \, dE . \quad (9)$$

In the integration over \vec{k} in (7), we make use of the integration with the density of states in the LC band in the form

$$R(E) = \begin{cases} R_0 & \text{at } E \in [0, p] \\ 0 & \text{at } E \in [p, \infty) \end{cases} , \quad (10)$$

i.e. equal to a constant throughout the entire band p (p is the band width). Such a widely used approximation is most justified just in LC. Indeed, due to a weak interlayer mixing, the electron dispersion relation may be represented as

$$\varepsilon_{\vec{k}} = \frac{\hbar^2 k_{\perp}^2}{2m_{\perp}} + \beta(1 - \cos k_z d_z) , \quad (11)$$

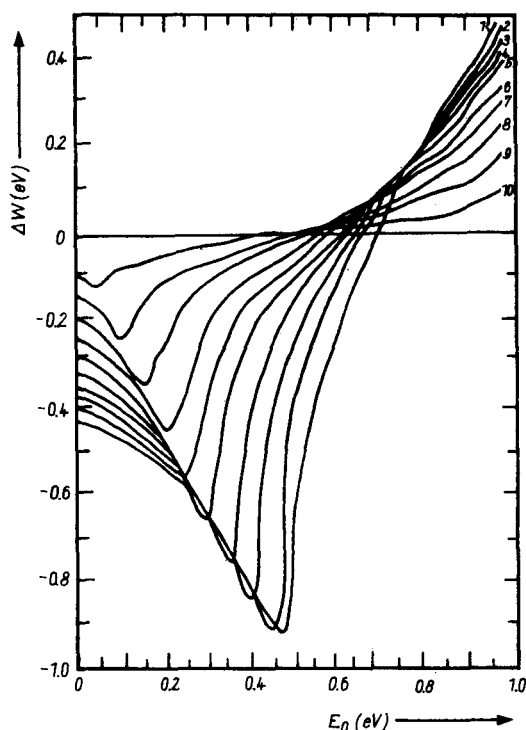


Fig. 1. Family of ΔW as a function of electron level position of the intercalant, E_0 , higher than the bottom of the band at fixed \tilde{V} . $\tilde{V} =$ (1) 0.1, (2) 0.09, (3) 0.08, (4) 0.07, (5) 0.06, (6) 0.05, (7) 0.04, (8) 0.03, (9) 0.02, (10) 0.01 eV

where m_{\perp}^* is the effective mass of electrons in the plane of layers, d_z is the lattice constant along the normal to the layers, and β is the electron interlayer mixing. Corresponding to such a dispersion relation the density of states is constant throughout the entire band, except a 2β -wide energy region at the band bottom. With such an assumption,

$$a = - \frac{\Omega R_0}{(2\pi)^3 N} \ln \left| \frac{p-E}{E} \right|.$$

Calculations of ΔW we conducted numerically by the Simpson method. In view of a specificity of the numerical computer calculation, we substituted the δ -function in the argument $\arctg x$ in ϕ by a Lorentzian curve whose halfwidth Δ tended to zero. Calculations were terminated at a stage where a further decrease of Δ did not change substantially the results of preceding calculations.

An analysis of the family of ΔW versus $\tilde{V}^2 (\tilde{V}^2 = V^2(R_0\Omega)/(2\pi)^3 N)$ as a function of the position of the electronic level of an intercalated atom E_0 from the band bottom and higher was conducted and its results are presented in Fig. 1. It demonstrates for every of such curves existence of some critical values of the level position; E_{oc} ; on passing it, ΔW reverses its sign. It should be noted that E_{oc} is different for different curves characterized by the parameter \tilde{V} , namely, the greater \tilde{V} the higher is the E_{oc} value. It corresponds to two important physical conclusions:

1. The electronic subsystem of the intercalated LC may be more stable than the non-intercalated one or vice versa depending on the intercalants, characterized by

the level E_0 in its isolated state.

2. The region of the electronic subsystem stability of the intercalated LC is the smaller the less is the electronic mixing of the intercalant-LC as well as the density of states in the band.

References

/1/ T.L. EINSTEIN and J.R. SCHRIEFFER, Phys. Rev. B 7, 3629 (1973).

(Received June 28, 1989; in revised form February 13, 1990)