

## Electronic Spectrum of Intercalated Layered Crystals: Model Analysis

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Within the framework of the Kronig-Penny model, changes in the electron spectrum of a layered crystal caused by intercalation are analyzed. Special attention is paid to both the geometric changes of the crystal and its energy characteristics during intercalation. The extraordinary behavior of the spectrum caused by the geometric intercalation factor is observed.

**Keywords:** Layered crystals, Intercalation, Electronic spectrum.

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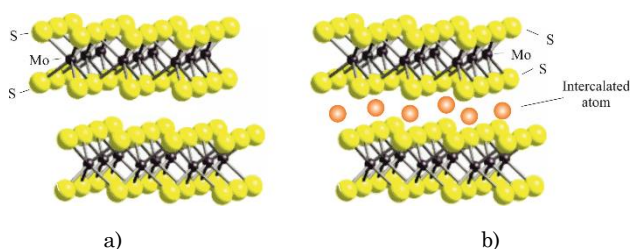
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### 1. INTRODUCTION

In nature, there are a number of so-called low-dimensional structures or layered crystals which have sharp anisotropic properties. Such structures are packs of mono-atomic planes (packets) interconnected by covalent or ionic-covalent forces, whereas the connection between the packets is realized by much weaker, van der Waals, forces. Therefore, sometimes such structures are called quasi-two-dimensional structures. Among them, the most widespread are graphite, dichalcogenides of transition metals  $MX_2$  (Mo, Ta, Ti, W, Nb, Sn, Zr, Hf, V; X = S, Se, Te), compounds  $A_3B_6$  (A = Ga, In; X = S, Se, Te), and others. As an example, in Fig. 1a the layered crystal  $MoS_2$  is shown. Here, two packets, which are sets of monoatomic planes S-Mo-S, divided by van der Waals gap. GaSe takes the same shape, but with the Se-Ga-Ga-Se-packets.

Important characteristics of the layered crystals are the packet thickness  $b$  and the distance  $a$  between the adjacent packets. For example, in  $MoS_2$  they are  $\sim 3 \text{ \AA}$  and  $\sim 6.5 \text{ \AA}$  respectively [1]. It has been experimentally established that in case of approaching the force of interaction between the layers (packets) to zero the layered crystals possess unique characteristics. Splendiani et al. [1] has found that in the case of a solitary layer  $MoS_2$  the quantum efficiency of its luminescence  $\sim 10^4$  times increased.

This phenomenon once again emphasizes the extraordinary manifestations of two-dimensionality and has a certain analogy with the unique properties previously found in well-known monocrystalline graphitic films [2].



**Fig. 1** –  $MoS_2$ -type layered crystal: (a) pure (up to intercalation) crystal and (b) intercalated crystal

Various physical characteristics offers such a unique phenomenon of the layered crystals as interca-

lation or introduction of foreign atoms or organic and inorganic molecules into the van der Waals gap of the layered crystal [3]. Intercalation, in particular, can solve such an important problem as the creation (unlike lithium-ion energy storage) of large-scale energy storage based on sodium and potassium.

It is important to note some aspects of this phenomenon. As a rule, intercalated atoms fall into each van der Waals gap of the layered crystals. However, the so-called  $n$ -stage ordering ( $n > 1$ ) occurs (especially in graphite) when the intercalated atoms fill each  $n$ -th van der Waals gap [4]. With a certain amount of intercalated atoms, the latter can form an ordered structure also in the van der Waals gap.

Depending on the nature of the intercalated atoms, on their surroundings in the van der Waals gap, they can vary interlayer distances from 0.1 nm (in  $Li^+$ -intercalated compounds) to more than 5 nm. In the case when intercalated atoms are oligomers or polymers, such intercalated structures are called nanocomposites.

The possibility of intercalation is also determined by the charge nature of the intercalated atom. Thus, in the chalcogenide intercalated compounds, the intercalated atoms are exclusively donor atoms or molecules, whereas in the graphite intercalated compounds, intercalated atoms can be both donors and acceptors.

The intercalated layered crystals may be considered as superstructures, which are an infinite iteration of a primitive lattice on its period (in the case of a binary AB-system, this period is  $LA + LB$ , where  $LA$ ,  $LB$  are the thicknesses of the A and B materials respectively) along the structure growth axis [5]. The layered crystal structure have similar AB-superstructure, in which A and B are the packet thickness and the thickness of van der Waals gap together with the intercalated atom, respectively. However, there is a difference in this analogy. The emergence of one-dimensional quantum wells and nanoheterostructures was the result of technological success, since the 70's of the last century. Modern epitaxial technology (metal-organic vapor deposition, beam epitaxy) allow obtaining arbitrary nanoscale thicknesses of materials A and B. In the case of the layered crystals, the change of a lattice parameter along the normal to the layers is the result of intercalation, and such a change is exclusively a geometric change of the interlayer distance, since the thickness of the packet is practically unchanged.

On the other hand, such geometric factor is accompanied by changes in the energy spectrum both in quantum wells, superstructures, and in the intercalated layered crystal. Specific intercalated atoms (intercalated molecules) can substantially change the potential of the interlayer space – both to increase and decrease it, and thus, change the degree of interlayer mixing.

Such factors allow creating, in particular, the high-effective energy storage based on potassium or sodium, as opposed to the lithium-ion storage [7].

## 2. MODEL

The first descriptions of the electronic structure of quantum wells and superstructures were made [5-6] on the basis of the envelope function approximation. Further theoretical models confirmed the conclusions of such an approximation, which gave not only a qualitative understanding of the behavior of the electronic spectrum but also its agreement with experimental data.

An analogy between superstructures and intercalated layered crystals allows us to use the conclusion [5] that the dispersion law in them inevitably must be determined from the transcendental equation

$$\cos kd = f(E), \quad (1)$$

where in the case of intercalated layered crystal  $k$  is a quasi-momentum,  $d = a + b$  is a lattice parameter along the normal to the layers ( $a$  is the interlayer distance,  $b$  is the thickness of the packet).

Equation (1) is valid regardless of the potential inside the primitive cell, but the function  $f(\varepsilon)$  essential-

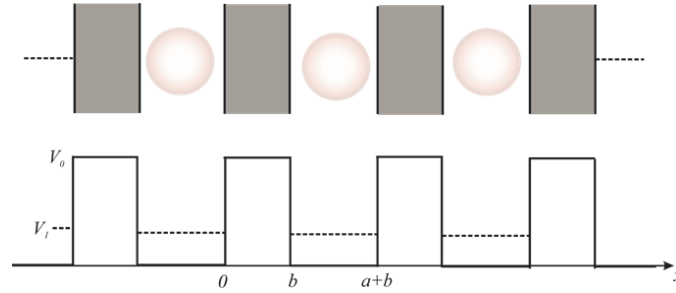


Fig. 2 – Packets with intercalated atoms (at the top) and potential of the system (at the bottom)

ly depends on the form of such a potential. As the compression of the layered crystal increases, it becomes more and more isotropic [9]. For example, an increase of the low-frequency mode  $\omega = 23 \text{ cm}^{-1}$  in GaSe at  $p = 170 \text{ kbar}$  up to  $76 \text{ cm}^{-1}$  was a confirmation of this situation [9].

In any crystal, an electronic spectrum determines its physical properties. The purpose of our work is a qualitative description of the phenomenon of intercalation. To do this, we use the one-dimensional model of the layered crystal along the normal to it within the framework of the Kronig-Penny model [10], which is shown in Fig. 2. Here the barriers of thickness  $b$ , which simulate packets are separated by the van der Waals gaps  $a$ . We assume that intercalated atoms (molecules) fill each the van der Waals gap. The inter-

ly depends on the form of such a potential.

As noted above, an important consequence of the differences between interaction forces in the layer packet and interlayer interaction in a layered crystal is the fact that external compression mainly changes the width of the van der Waals gap.

In the [8] the baric dependences of deformation coefficients in graphite and  $A_3B_6$ -type layered crystals are presented. For axial, along with normal to the layers (along  $OZ$ ), compression and hydrostatic compression  $p$  the deformation tensors have the following forms:

$$u_{zz} = -\frac{C_{11} + C_{12}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} p \quad (2)$$

and

$$u_{zz} = -\frac{C_{11} + C_{12} - 2C_{13}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} p, \quad (3)$$

respectively. Here  $C_{ij}$  are elastic constants:  $C_{11}, C_{12}$  describe the connection inside of the packets, and  $C_{33}, C_{13}$  describe mainly interlayer bond. Since  $C_{11}, C_{12} \gg C_{33}, C_{13}$ , then from Eq. (2), Eq.(3) it follows that in both cases the values of the coefficients  $u_{zz}$  coincide and equal  $u_{zz} = -\frac{1}{C_{13}^2} p$ .

The components of the deformation tensor in the plane of the layers are much smaller in comparison with  $u_{zz}$ . Thus, the greatest effect of any mechanical action on the layered crystal is related with the change in

calation is accompanied by a change in the crystal size. Since such changes, as noted, practically does not change the thickness of the layers (i.e.  $b$ ), then in the calculations below we choose characteristic for a series of layered crystals constant  $b = 0.8 \text{ nm}$ .

It is known that the solution of the stationary Schrödinger equation, namely

$$\frac{d^2\psi(x)}{dx^2} + (E - V(x))\psi(x) = 0 \quad (4)$$

for a crystalline system, is the Bloch function:

$$\psi(x) = u(x) \exp(jkx) \quad (5)$$

In Eq. (5)  $u(x)$  is the Bloch factor.

After substituting Eq. (5) into Eq.(4), for the Bloch factor we obtain the following homogeneous differential equation with constant coefficients

$$\frac{d^2 u_i}{dx^2} + 2jk \frac{du_i}{dx} - (k^2 - \beta_i^2) u_i = 0 \quad (6)$$

Its solutions have the following form [11]:

$$u_i(x) = A_i \exp(s_{1i}x) + B_i \exp(s_{2i}x),$$

where,  $s_{1i} = -j(k - \beta_i)$ ,  $s_{2i} = -j(k + \beta_i)$  are the roots of the characteristic Eq.(6).

Thus,

$$u_i(x) = A_i \exp(j(\beta_i - k)x) + B_i \exp(-j(\beta_i + k)x) \quad (7)$$

Here  $i=1$  corresponds to the interval  $x \in [0, a]$  of

the potential well, in which  $\beta_1 \equiv \alpha = \sqrt{\frac{2m(E - V_1)}{\hbar^2}}$  ( $V_1$

is the level of the bottom of the well; the case of  $V_1 = 0$  will be considered as the bottom of the well of the non-intercalated layered crystal), and  $i=2$  is the barrier interval in which

$$\beta_2 \equiv \beta = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}.$$

The unknown quantities in Eq.(7) can be obtained from the conditions of continuity and smoothness of the envelope at the boundary of the barrier-well and from its periodicity with the period  $d = a + b$ . In the obtained system of linear equations, the values of  $A_1, B_1, A_2, B_2$  will be non-trivial only in case when the determinant formed from the coefficients of  $A_1, B_1, A_2, B_2$  is equal zero. The expansion of such a determinant leads to the equation

$$\cos k(a+b) = -\frac{\alpha^2 + \beta^2}{2\alpha\beta} \sin \alpha a \cdot \sin \beta b + \cos \alpha a \cdot \cos \beta b \quad (8)$$

Thus, this equation coincides with Eq.(1) in which in the case of Kronig-Penny model the  $f(E)$  is of the concrete form.

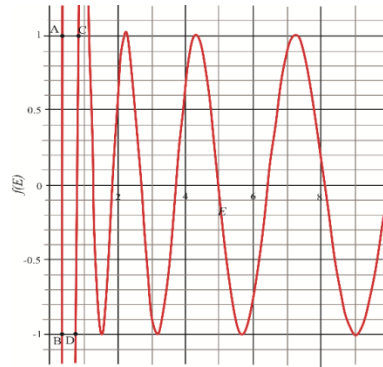
### 3. ANALYSIS OF ELECTRONIC STATES IN THE INTERCALATED LAYERED CRYSTALS

Let us consider the solution of Eq. (8) with an emphasis on the parameters, which are important in the process of intercalation. The introducing of foreign atoms (molecules) into the van der Waals gap changes its size,  $a$ , and practically does not change the size of the packets,  $b$ . On the other hand, foreign atoms, depending on their nature, can change the value of the potential of the well,  $V_1$ , namely both raise and lower it. The size of the interlayer distance,  $a$ , is a flexible parameter in the model consideration of the formulated problem.

As stated above, we use the one-dimensional model Kronig-Penny. It should be noted that a similar model,

in addition to the work quoted above [5], was used to study MQW structures [12], which are widely used as materials in the lighting industry, solar cells etc. MQW structures are a periodic set of pairs of materials with different electrical characteristics. Using the Kronig-Penny model for their description, the authors in [5] analyzed the energy spectrum at different potentials of the barrier and of its thickness.

The transcendental Eq.(8) was solved by using the Maple, Mathematica and Fortran software packages as a search for the graphic intersections of the left and right sides of this equation. Since the cosine is bounded by the interval  $[-1, 1]$ , its intersection with  $f(E)$  is possible only in such interval. In Fig.3 such intersections are presented, for example, for the parameters  $a = 1.0$  nm,  $b = 0.8$  nm,  $V_0 = 1.0$  eV,  $V_1 = 0.2$  eV. For the ground state the intersection  $f(E)$  with 1 (A) corresponds to the bottom of the zone, and the intersection  $f(E)$  with  $-1$  (B) – to its top, and the energy distance between adjacent intersections  $f(E)$  with  $-1$  (B – D) is the band gap between the zones of the ground and the first excited states. Similar contents have other intersections for the higher excited states.



**Fig. 3** – Dependence and graphical solution of Eq. (8). Its nontrivial solutions are possible in interval  $[-1, 1]$

The values of such intersections were obtained for each  $V_1 = -0.2, -0.1, 0.0, 0.1, 0.2, 0.3$  eV when the widths of the van der Waals gap were  $a = 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$ , i.e., it was taken into account both geometric factor and the energy factor induced by intercalation.

The obtained two band gaps, i.e. those between the ground and the first excited zones,  $E_{g1}$ , and between two lowest excited zones,  $E_{g2}$ , as a function of the width of the well  $a$  and of the potential  $V_1$  in it, are presented in Fig. 4. Their analysis shows that:

- For the whole set of the values  $a$ ,  $E_{g1}$  is monotonically decreasing function with the growth of the van der Waals gap  $V_1$ . A similar behavior of  $E_{g2}$  for all values  $a$  (except for  $a = 0.4$  nm, where  $E_{g2}$  increases insignificantly) is observed;

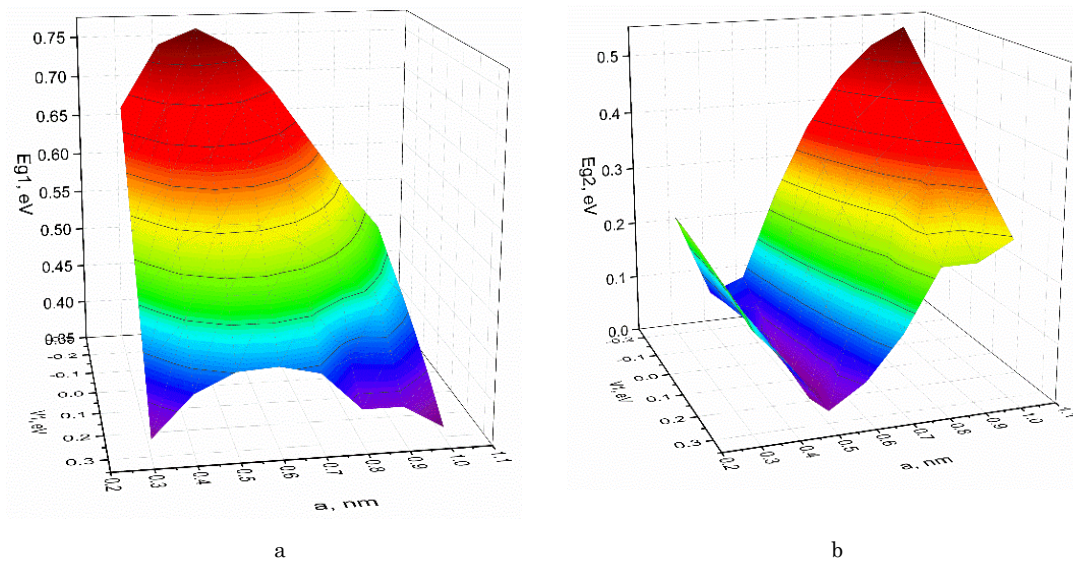
- For all fixed values of  $V_1$ , with the growth of the width  $a$  of the van der Waals gap,  $E_{g1}$  at first increases (up to  $a \approx 0.5$  nm), and then decreases;  $E_{g2}$ , on the

contrary, at first decreases, reaches its minimum at the values  $a$  where  $E_{g1}$  reaches a maximum, and then increases;

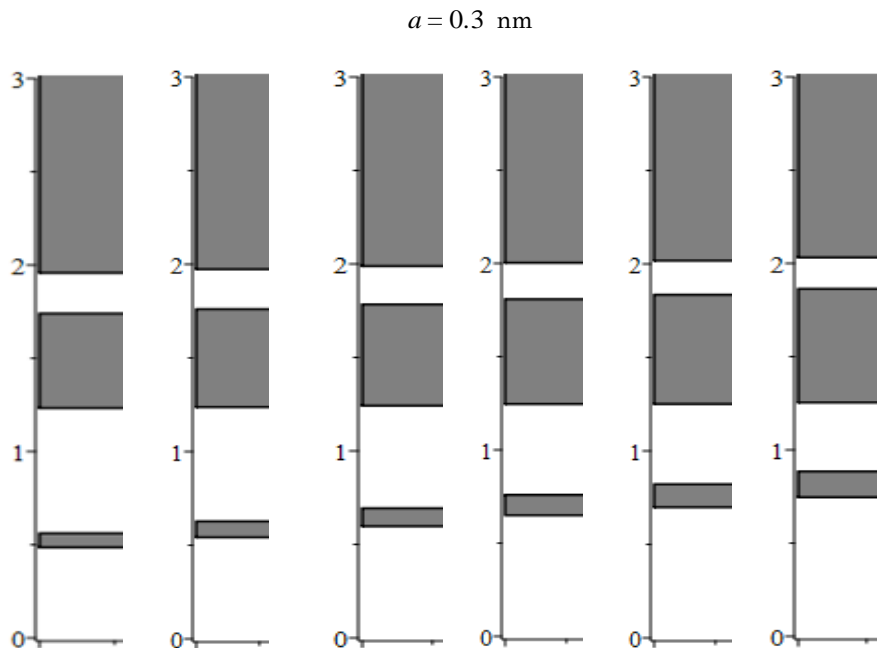
- For any value of the parameters  $a, V_1$  the width of the allowed zone of the ground state is less than the width of the allowed zone of the excited state. This fact is clear from the point of view of the tunneling effect, according to which the tunneling of the electron from the ground state (and hence its blurring) is less than the tunneling from the higher states. It turns out that the growth of the bandgap width  $E_{g1}$  is only in the case of those van der Waals gap widths  $a$  when the ground and first excited states are subbarri-

er. For those  $a$  in which the first excited state becomes over-barrier,  $E_{g1}$  decreases with the increase of  $a$ .

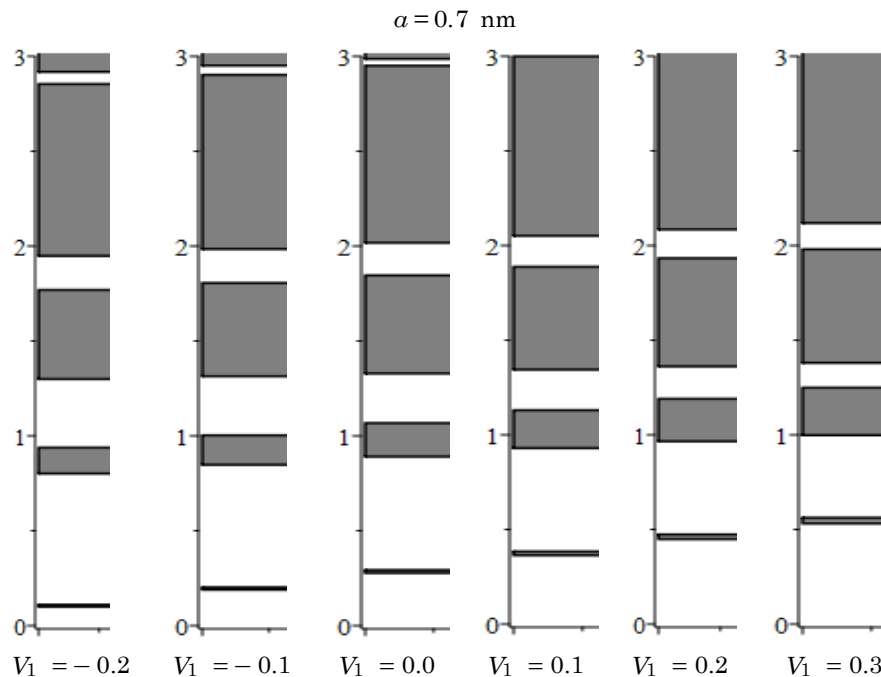
Fig. 5 shows the dependence of electronic states on the potential  $V_1$  of the well with the width of the package  $b = 0.8$  nm and with the value of its potential  $V_0 = 1.0$  eV for two values of the width of the well:  $a = 0.3$  nm and  $a = 0.7$  nm. In the case of  $a = 0.3$  nm, the first excited state is an over-barrier for all  $V_1$ ; whereas in the case of  $a = 0.7$  nm, there is its transition from a subbarrier to an over-barrier state.



**Fig. 4** – Dependences of the band gap  $E_{g1}$  (a) and  $E_{g2}$  (b) on the width of the well  $a$  and on the potential  $V_1$  in it (width  $b = 0.8$  nm, and potential  $V_0 = 1.0$  eV)







**Fig. 5** – Dependence of electronic states on potential  $V_1$  of a well in the Kronig-Penny model with a packet width  $b = 0.8$  nm and with its potential  $V_0 = 1.0$  eV for the case of width of well  $a = 0.3$  nm and  $a = 0.7$  nm. Dark areas are the widths of allowed bands

#### 4. CONCLUSIONS

We considered the phenomenon of intercalation as a simultaneous manifestation of both the geometric change of the layered crystal and the variation of the van der Waals gap potential caused by the intercalated atom. The both factors depend on the characteristics of the intercalated atom – its size, charge state, interaction with the crystalline matrix. The obtained results have established the monotonically decreasing nature

of the widths of the band-gaps with the increase in the van der Waals gap potential  $V_1$  at arbitrary values of its thickness  $a$ . In contrast, the dependence of the widths of such band-gaps with different fixed  $V_1$  on  $a$  is of nonmonotonic character. We will note that mechanical compression can be an additional factor of the change in  $a$ , and therefore it can cause the unusual behavior of the gaps.

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