

Density of Electron States and Relaxation Time of Intercalated Layer Crystals

N.K. TOVSTYUK^{a,*} AND YE.M. SHEREGIY^b

^aNational University "Lvivska Politechnika", 13, Bandera Str., L'viv, 79013, Ukraine

^bUniversity of Rzeszów, Centre for Microelectronics and Nanotechnology, S. Pigionia 1, 35-959 Rzeszów, Poland

The density of electron states of layered crystal intercalated by guests of different nature is calculated within the framework of virtual crystal considering filling of both octahedral and tetrahedral interstitial hollows. It is found that the shift of the gap of density of states is caused firstly by the nature of intercalant (placing of ground energy states of both intercalants) and their average concentrations. In the case when one type of intercalant gives localized level in the forbidden gap and another intercalant forms the resonance one in the conductive band the gap disappears. Relaxation time corresponding to the transitions from one to another band is calculated.

DOI: [10.12693/APhysPolA.128.225](https://doi.org/10.12693/APhysPolA.128.225)

PACS/topics: 71.20.-b, 71.55.-i, 77.22.Gm

1. Introduction

Intercalation of layer crystal by different guest atoms, particularly $3d$ -atoms, allows us to create new materials which can be very important for using in different aspects of applied physics [1]. The structures with alternating semiconducting and magneto-active layers can serve as materials on the base of those ones, can create the spintronics elements, particularly, as the medium structures or spin-gated transistors. Essential success in hybrid spintronics [2] is due to the intercalation of nanostructures. That is why complex studies of such structures provide additional opportunities to modify their magnetic properties in a wide range. Recently this direction is essentially enriched by theoretical studies of phase transitions considering both direct host-guest ion interaction and guest-guest interaction within the framework of pseudospin-electron model [3]. It is obvious that changes of electron spectrum of intercalated layer crystal influence to a certain degree the thermodynamics, kinetics and magnetic properties of the received intercalates.

In this paper the density of electron states of layered crystal intercalated by different guest atoms is calculated within the framework of virtual crystal considering filling of both octahedral O and tetrahedral T_1 or T_2 interstitial hollows (IH): first ones are placed in the centrum of van der Waals gaps, T_1 or T_2 are placed closely to the monoatomic host layers nearest to the van der Waals gap (Fig. 1).

2. Model

Intercalant in the position T_1 or T_2 interacts with 4 nearest host atoms, in the position O it interacts with 6 nearest host atoms. That is why the ground energy state of the same intercalant in tetrahedral or octahedral IH

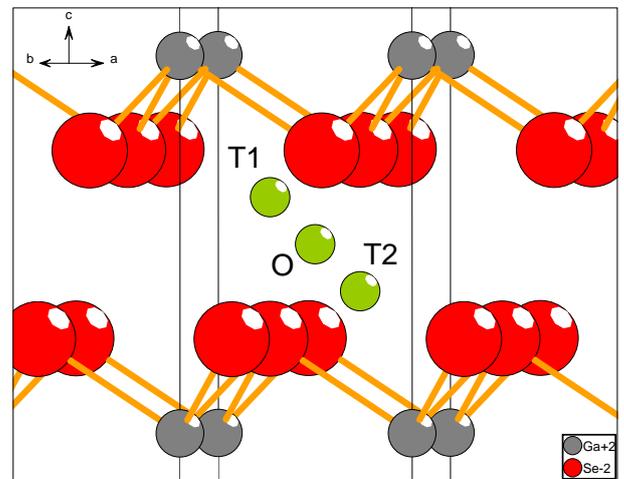


Fig. 1. Positioning of intercalant in tetrahedral (T_1 and T_2) and octahedral (O) IH of GaSe.

is different (electron state with energy ε_1 lies lower than another one with energy ε_2).

In the case when intercalant occupies positions T_1 and T_2 , electret effect can occur because ordered position of intercalant can cause the appearance of intrinsic field. It consequently leads to the asymmetry of T_1 and T_2 wells. In the case of electret effect polar state in the crystal exists. Then electrons localized on the intercalant occupy IH T_1 or T_2 with different average concentrations of p_1 and p_2 and the same ground energy state ε_2 .

We introduce quantum wave function $\Psi(\mathbf{r})$ as an expansion of wave functions of electron localized on host atom $\psi_n(\mathbf{r})$ and wave functions of electrons in the different IH T_1 and T_2 $\varphi_n(\mathbf{r})$ and $\chi_n(\mathbf{r})$:

$$\Psi(\mathbf{r}) = \sum_n c_n \psi_n(\mathbf{r}) + \sum_n p_1(n) a_n \chi_n(\mathbf{r}) + \sum_n p_2(n) b_n \varphi_n(\mathbf{r}). \quad (1)$$

A summation is carried out over all the cells with the probability $p_{1,2}(n) = 1$ in the case when in the n -th cell

*corresponding author; e-mail: ntovstyuk@gmail.com

in the position 1 or 2 intercalant exists, in the opposite case $p_{1,2}(n) = 0$.

In the one-electron approximation we move to the representation of second quantization on this quantum function. The received Hamiltonian is written in the approximation of virtual crystal with constant average concentrations p_1 and p_2 . Using Fourier-representation of c_n , a_n , b_n , Hamiltonian is rewritten in the quasi-momentum representation as follows [4]:

$$H = \sum_{\mathbf{k}} \varepsilon_c(\mathbf{k}) c_{\mathbf{k}}^+ c_{\mathbf{k}} + p_1^2 \sum_{\mathbf{k}} \varepsilon_1(\mathbf{k}) a_{\mathbf{k}}^+ a_{\mathbf{k}} \quad (2)$$

$$+ p_2^2 \sum_{\mathbf{k}} \varepsilon_2(\mathbf{k}) b_{\mathbf{k}}^+ b_{\mathbf{k}} + p_1 \sum_{\mathbf{k}} V_1(\mathbf{k}) c_{\mathbf{k}}^+ a_{\mathbf{k}}$$

$$+ p_2 \sum_{\mathbf{k}} V_2(\mathbf{k}) c_{\mathbf{k}}^+ b_{\mathbf{k}} + p_1 p_2 \sum_{\mathbf{k}} V_{12}(\mathbf{k}) a_{\mathbf{k}}^+ b_{\mathbf{k}} + \text{H.c.},$$

where $\varepsilon_c(\mathbf{k})$ coincides with dispersion law of the conduction band of layer crystal

$$\varepsilon_c(\mathbf{k}) = \alpha(k_x^2 + k_y^2) + t(1 - \cos(k_z d_z)), \quad (3)$$

where α is effective mass of electron within the layer plane, t — electron mixing among the nearest layers along the anisotropy axis. Here and below $\hbar = 1$. Two additional bands, created by electrons localized on the intercalant in the different IH are described as follows:

$$\varepsilon_1(\mathbf{k}) = \alpha_1(k_x^2 + k_y^2) + t_1(1 - \cos(k_z d_z)) + \varepsilon_1^0/p_1,$$

$$\varepsilon_2(\mathbf{k}) = \alpha_2(k_x^2 + k_y^2) + t_2(1 - \cos(k_z d_z)) + \varepsilon_2^0/p_2. \quad (4)$$

Two time retarded Green functions are considered for $\langle\langle c_{\mathbf{k}} | c_{\mathbf{k}}^+ \rangle\rangle$ layer lattice and for intercalant $\langle\langle a_{\mathbf{k}} | a_{\mathbf{k}}^+ \rangle\rangle$ $\langle\langle b_{\mathbf{k}} | b_{\mathbf{k}}^+ \rangle\rangle$. Motion equation for $\langle\langle c_{\mathbf{k}} | c_{\mathbf{k}}^+ \rangle\rangle$, $\langle\langle a_{\mathbf{k}} | a_{\mathbf{k}}^+ \rangle\rangle$ and $\langle\langle b_{\mathbf{k}} | b_{\mathbf{k}}^+ \rangle\rangle$ is written.

These results allow us to receive density of electron states of the intercalated layer crystal (Fig. 2).

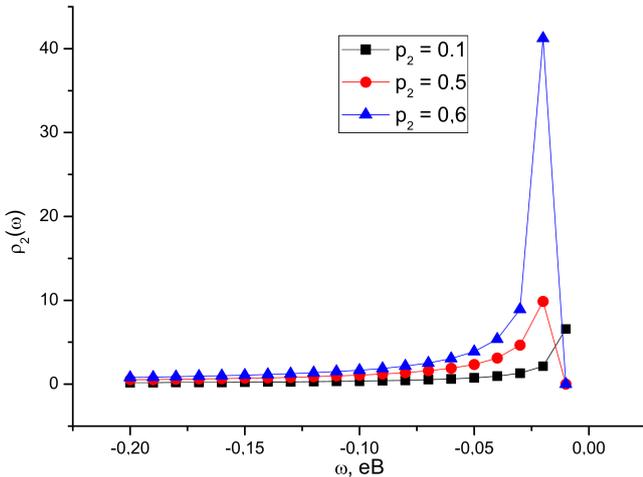


Fig. 2. Density of electron states of intercalated layer crystal with intercalant in O and T IH and chosen values of ground energies $\varepsilon_1 = -0.1$ eV, $\varepsilon_2 = -0.02$ eV.

3. Results and discussion

In the case of occupying O and T IH it is found that additional gap appears in the forbidden gap (Fig. 2); its shift is caused firstly by the nature of intercalant (positioning of ground energy states of electron localized on the intercalant in O and T IH) and their average concentrations. In the case when one type of intercalant gives localized level in the forbidden gap and another intercalant forms the resonance one in the conductive band the gap disappears. It is shown that if electron mixing between three zones is absent, intercalant system behaves independently of the layer crystal system. In the case when electret effect appears we consider positioning of the same intercalant in two wells T_1 and T_2 of different depth and thus only concentrations p_1 and p_2 are different. Our calculations showed that if $p_1 = 0.98$ and p_2 changes from 0.2 up to 0.7 (Fig. 3) the width of additional gap changes in monotonic way. The shift of the additional gap depends strongly on the value of the intercalant ground energy state (ε_2), i.e. where does it lies below or above the bottom of the conduction band.

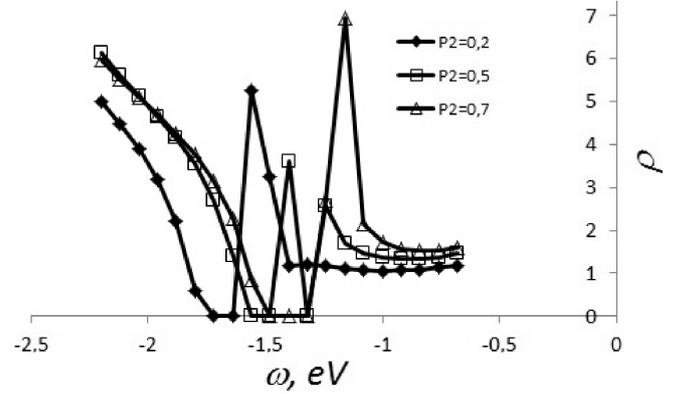


Fig. 3. Density of electron states of intercalated layer crystal with intercalant in T_1 and T_2 IH, $p_1 = 0.98$, different p_2 and corresponded ground energies $\varepsilon_1 = \varepsilon_2 = -0.1$ eV.

Relaxation time is calculated in the both cases. We found that in the case of electret effect it is an order higher than in the case of occupying symmetry different IH.

4. Conclusions

Density of electron states of the intercalated layer crystal considering different type of intercalant (atoms, ions, molecules) and possibility of occupying different interstitial hollows are studied. It is found that the shift of the additional gap in the density of electron states primarily depends on the intercalant nature, i.e. mutual positioning of ε_1 and ε_2 and their average concentrations p_1 and p_2 . Additional gap can disappear if electron localized on the one type of intercalant gives resonance level in the conduction band ($\varepsilon_1 > 0$), and an electron localized

in the another well gives localized level ($\varepsilon_2 < 0$). The proposed model allows to describe electron energy structure of layer crystal with intercalant component which possesses large dipole moment. Ordered distribution of dipoles in the van der Waals gap in respect of the sandwiches of layer crystal causes the appearance of additional intrinsic field which shifts energy levels of intercalant. In the case of random dipole distribution such field disappears and thus the value of energy shift disappears. Considering polar state of the crystal we assume that the same type of intercalant appears in two wells formed by T_1 and T_2 IH. The depth of these wells is different. Thus only concentrations p_1 and p_2 are different. Our calculations showed that the width of additional gap

in the density of electron states changes in monotonic way depending on the change of average concentration in one of T IH.

References

- [1] M. Elhabiri, A.-M. Abrecht-Gary, *Coord. Chem. Rev.* **252**, 1079 (2008).
- [2] B.P. Zakharchenya, *Phys.-Usp.* **175**, 625 (2005).
- [3] I.V. Stasyuk, Yu.I. Dublanych, *Phys. Rev. B* **72**, 224209 (2005).
- [4] N.K. Tovstyuk, *Visnyk Lviv Univ. Ser. Phys.* **48**, 109 (2013).