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СПРОЩЕНА МОДЕЛЬ ІНТЕРКАЛЯЦІЇ ІОНІВ У НАПІВПРОВІДНИКОВІ  
КРИСТАЛИ ТИПУ  $\text{TiO}_2$

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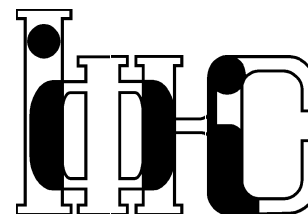
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SIMPLE MODEL OF ION INTERCALATION IN  
SEMICONDUCTING CRYSTALS OF  $\text{TiO}_2$ -TYPE

ЛЬВІВ

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### Спрощена модель інтеркаляції іонів у напівпровідникові кристали типу $\text{TiO}_2$

Т.С.Мисакович, І.В.Стасюк

**Анотація.** Запропоновано псевдоспін-електронну модель для опису інтеркаляції іонів у напівпровідникові кристали типу  $\text{TiO}_2$ . Ефективна взаємодія між псевдоспинами (іонами) формується завдяки псевдоспін-електронній взаємодії. В наближенні середнього поля виявлено можливість фазових переходів у системі, пов'язаних зі зміною концентрації інтеркальованих іонів та значним зростанням електростатичної ємності системи.

### Simple model of ion intercalation in semiconducting crystals of $\text{TiO}_2$ -type

T.S.Mysakovych, I.V.Stasyuk

**Abstract.** The pseudospin-electron model is proposed for the description of the intercalation of ions in semiconducting crystals of  $\text{TiO}_2$ -type. The effective interaction between pseudospins (ions) is formed due to pseudospin-electron interaction. The possibility of the phase transitions in the system connected with the change of the concentration of intercalated ions and significant increase of electrostatic capacity of the system is revealed in the mean field approximation.

## 1. Introduction

Titanium dioxide,  $\text{TiO}_2$ , is one of the materials which are intensively investigated as hosts for lithium insertion. It is known that such systems are semiconductors, gap is approximately 3 eV.

Using neutron diffraction powder profile analysis [1], it was found that inserted Li ions in  $\text{Li}_{0.5}\text{TiO}_2$  - anatase occupied octahedral interstices. In  $\text{LiTi}_2\text{O}_4$  - spinel lithium occupied tetrahedral sites, while in  $\text{Li}_2\text{Ti}_2\text{O}_4$  lithium filled the octahedral sites and was displaced from the tetrahedral sites [1]. In [2] using quantum chemical Hartree-Fock calculations it was established that Li lost its valence electron (electron occupying Li 2s atomic orbital) which transferred to Ti ion (calculated Li charges were  $\sim 0.8$ ). A conclusion was made that Li induced local one-electron energy level in the gap between the upper valence band and the conduction band, this level was composed mainly of Ti 4s atomic orbitals. In [3], [4] using pseudopotential plane-wave formalism the calculations indicated a distinct preference for intercalation of lithium into the octahedral sites in anatase and rutile. It was shown that effective Li-Li interaction was highly anisotropic, the computed lithium diffusion constants were anisotropic also. The calculations revealed the tendency of the valence band to narrowing and increasing of the band gap at the lithium intercalation.

The dynamics of lithium in lithiated anatase  $\text{TiO}_2$  was also investigated (see [5]). The carried out in [6] analysis of neutron diffraction data revealed two available Li-ion positions within the oxygen octahedron in lithiated anatase and the distance between the sites was 0.7-1.8 Å depending on lithium concentration. The intra-octahedron dynamics was investigated using molecular dynamics method and quasi-elastic neutron scattering [6]. It was shown that lithium diffused more easily through the Li-rich phase. It is known that at intercalation of lithium in anatase  $\text{TiO}_2$  phase separation in Li-poor and Li-rich phases occurred, Li-rich phase grew with increasing of content of lithium [6,7]. Such two-phase behaviour leads to a constant value of electrochemical potential. In [8] the structural properties of  $\text{Li}_x\text{TiO}_2$  spinel were investigated using a cluster expansion (based on pseudopotential ground state energy calculations) and a Monte Carlo simulation. Coexistence of two phases (when  $1/2 < x < 1$ )  $\text{Li}_{1/2}\text{TiO}_2$  (Li on tetrahedral sites) and  $\text{LiTiO}_2$  (Li on octahedral sites) was established. It was shown that insertion of Li first resulted in filling of the tetrahedral sites (which are energetically more favorable), when  $x=1/2$  all tetrahedral sites are filled and at  $x>1/2$  additional Li filled octahedral sites. Electronic structure calculations re-

vealed that in LiTiO<sub>2</sub> the Fermi level was situated near the bottom of the conduction band.

Using a Monte-Carlo method, intercalation of lithium in cubic-spinel Li[Ti<sub>5/3</sub>Li<sub>1/3</sub>]O<sub>4</sub> was investigated in [9]. According to their model, the Hamiltonian included interaction between Li ions, the interaction between Li ions and electrons was not taken into account. It was proposed that the potential plateau indicated the coexistence of Li-poor and Li-rich phases due to the repulsive interactions between lithium ions.

As it was noted above, the reconstruction of electron spectrum in such crystals upon intercalation takes place and this means that interaction between lithium and electrons may play an important role in such systems. In the current study we take into account the interaction of Li ions with electrons and investigate the possibility of phase transition, which is connected with lithium intercalation and phase coexistence in such systems.

## 2. The model

The Hamiltonian of the model has the following form

$$\begin{aligned}
 H = & \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}}^c c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}}^v a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} + \sum_{ij\sigma} g_{ij}^c n_{i\sigma}^c (S_j^z + \frac{1}{2}) \quad (2.1) \\
 & + \sum_{ij\sigma} g_{ij}^v n_{i\sigma}^v (S_j^z + \frac{1}{2}) - \mu \sum_{i\sigma} (n_{i\sigma}^c + n_{i\sigma}^v) \\
 & + \frac{1}{2} \sum_{ij} J_{ij} (S_i^z + \frac{1}{2}) (S_j^z + \frac{1}{2}) - h \sum_i (S_i^z + \frac{1}{2}),
 \end{aligned}$$

here the pseudospin formalism is used, the pseudospin variable  $S_i^z$  takes two values,  $S_i^z = 1/2$  when lithium ion is present in site  $i$  and  $S_i^z = -1/2$  when lithium is absent. We take into account two electron orbital states per site (conduction and valence band electrons, the first and the second terms in (2.1), as usually,  $c, a$  and  $c^+, a^+$  are electron creation and annihilation operators respectively), their interaction with lithium ions ( $g^v$  and  $g^c$  terms) and direct interaction between Li ions ( $J$ -term);  $\mu$  and  $h$  play the role of the chemical potentials of electrons and Li ions respectively.

It should be noted that models of such type are intensively investigated in the theory of the strongly correlated electron systems. For example, they are used to take into account the presence of the locally anharmonic structure elements in the high temperature superconduc-

tors [10,11]. There is a direct connection between pseudospin-electron model and Falicov-Kimball model (for example, see [12]).

We use the following approximation in the interaction terms

$$\begin{aligned}
 g n_i S_j^z & \rightarrow g \langle n_i \rangle S_j^z + g n_i \langle S_j^z \rangle - g \langle n_i \rangle \langle S_j^z \rangle \quad (2.2) \\
 J S_i^z S_j^z & \rightarrow J \langle S_i^z \rangle S_j^z + J S_i^z \langle S_j^z \rangle - J \langle S_i^z \rangle \langle S_j^z \rangle;
 \end{aligned}$$

here the pseudospin-electron and pseudospin-pseudospin interactions are taken into account in the spirit of the mean field approximation (MFA) through an internal self-consistent fields which act on electrons and pseudospins. We suppose that direct interaction between pseudospins and pseudospin-electron interaction is nonlocal and may be long-ranged; this enable us to use MFA. It should be noted that this approximation is valid in the case when the concentration of intercalated ions is not too low. In the last case one should take into account the possibility of formation of local electron states near impurities.

Here we consider the uniform case (spatially uniform, independent on the site number electron and ion concentration):  $\langle \sum_{\sigma} n_{i\sigma} \rangle = n$ ,  $\langle S_i^z \rangle = \eta$ . The Hamiltonian of the model in the MFA can be written as:

$$\begin{aligned}
 H^{MFA} = & \sum_{\mathbf{k}\sigma} (\epsilon_{\mathbf{k}}^c - \mu + g^c \langle S^z + \frac{1}{2} \rangle) c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma} \quad (2.3) \\
 & + \sum_{\mathbf{k}\sigma} (\epsilon_{\mathbf{k}}^v - \mu + g^v \langle S^z + \frac{1}{2} \rangle) a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} \\
 & + (g^c n^c + g^v n^v - h + J \langle S^z + \frac{1}{2} \rangle) \sum_i S_i^z - g^c n^c \langle S^z \rangle N \\
 & - g^v n^v \langle S^z \rangle N - \frac{1}{2} \langle S^z \rangle^2 N J + \frac{1}{8} N J - \frac{h}{2} N,
 \end{aligned}$$

here  $N$  is the number of the lattice sites. The electron conduction and valence bands  $E_{\mathbf{k}}^c = \epsilon_{\mathbf{k}}^c + g^c (\eta + \frac{1}{2})$ ,  $E_{\mathbf{k}}^v = \epsilon_{\mathbf{k}}^v + g^v (\eta + \frac{1}{2})$  change their positions depending on the average value of pseudospin  $\eta$ . This means that bands are shifted at intercalation (the parameter  $\eta + 1/2$  determines the concentration  $n_{Li}$  of intercalated ions).

We will make the following substitution to take into account the fact that the system can possess some electrical potential at the presence of field. Instead of the chemical potentials of electrons and ions we will use the corresponding electrochemical potentials  $\mu \rightarrow \mu^* = \mu - e\varphi$ ,  $h \rightarrow h^* = h + e\varphi$  (here  $\mu^*$ ,  $h^*$  are the electrochemical potentials,  $-e$  is an electron charge). Such substitution follows from the fact that at the presence of external field the terms  $q\varphi$  (where  $q$  is a particle charge and  $\varphi$  is a potential of the field) should be included in the Hamiltonian.

The mean values of pseudospin and electron concentration obey the following equations:

$$\begin{aligned} \langle S^z \rangle &= \frac{1}{2} \tanh\left(\frac{\beta}{2}(h^* - g^c n^c - g^v n^v - J\langle S^z + \frac{1}{2} \rangle)\right) \quad (2.4) \\ n^c &= \frac{1}{N} \sum_{\mathbf{k}\sigma} \frac{1}{1 + e^{\beta(\epsilon_{\mathbf{k}}^c - \mu^* + g^c \langle S^z + \frac{1}{2} \rangle)}} \\ n^v &= \frac{1}{N} \sum_{\mathbf{k}\sigma} \frac{1}{1 + e^{\beta(\epsilon_{\mathbf{k}}^v - \mu^* + g^v \langle S^z + \frac{1}{2} \rangle)}}. \end{aligned}$$

The grand canonical potential of the system can be written as

$$\begin{aligned} \Omega &= -g^c n^c \langle S^z \rangle - g^v n^v \langle S^z \rangle - \langle S^z \rangle^2 \frac{J}{2} - \frac{h^*}{2} + \frac{J}{8} \quad (2.5) \\ &- T \ln(2 \cosh(\frac{\beta}{2}(g^c n^c + g^v n^v - h^* + \langle S^z + \frac{1}{2} \rangle J))) \\ &- T \frac{1}{N} \sum_{\mathbf{k}\sigma} \ln(1 + e^{-\beta(\epsilon_{\mathbf{k}}^c + g^c \langle S^z + \frac{1}{2} \rangle - \mu^*)}) \\ &- T \frac{1}{N} \sum_{\mathbf{k}\sigma} \ln(1 + e^{-\beta(\epsilon_{\mathbf{k}}^v + g^v \langle S^z + \frac{1}{2} \rangle - \mu^*)}). \end{aligned}$$

We take into account that at intercalation the chemical potential  $\mu$  is situated in the lower part (near the bottom) of the conduction band (see, for example, [4,8]). This means that at room temperature the valence band is fully occupied,  $n^v = 2$  (the band gap in titanium dioxide is approximately 3 eV).

### 3. The phase transition and phase separation

We have solved the set of equations (2.4) using the semielliptic density of states for the conduction band,  $\rho(\epsilon^c) = \frac{2}{\pi W^2} \sqrt{\epsilon(2W - \epsilon)}$ ,  $0 < \epsilon^c < 2W$ ,  $W$  is a half-width of the conduction band (the width of the conduction band  $2W = \Delta E^c$  in titanium dioxide is approximately 3eV, this band is created by Ti-3d states).

In Fig. 1 the dependence of the mean pseudospin value  $\eta$  and electron concentration  $n^c$  on the chemical potential of ions is shown (the regime of the fixed chemical potential of electrons and fixed potential  $\varphi$ ). We have chosen the following set of parameter values:  $g^c = -0.5$ ,  $g^v = -0.7$ ,  $J = 0.1$ ,  $W = 1.5$  (as it was noted above,  $2W \sim 3\text{eV}$ ); here we suppose repulsion interaction between lithium ions,  $J > 0$ . We have also taken into account that at intercalation the band gap increases (for example, it was

shown in [4] using density-functional calculations that the gap increase ranges from 0.1 to 0.4 eV depending on the lithium concentration). As it was noted above, the conduction band  $E_{\mathbf{k}}^c = \epsilon_{\mathbf{k}}^c + g^c(\eta + \frac{1}{2})$  and the valence band  $E_{\mathbf{k}}^v = \epsilon_{\mathbf{k}}^v + g^v(\eta + \frac{1}{2})$  change their positions at intercalation and at the chosen values of parameters ( $g^c = -0.5$ ,  $g^v = -0.7$ ) the band gap increases and at  $\eta = \frac{1}{2}$  this increase is of the order of 0.2 eV. From Fig. 1 we can see that the system undergoes the first order phase transition with jumps of the mean values of the pseudospin ( $\eta_1$  and  $\eta_2$ ) and electron concentration ( $n_1$ ,  $n_2$ ) at the change of the chemical potential of the ions  $h$ . The phase transition point (dashed line) is calculated using the Maxwell rule. In the regime of the fixed ion concentration the phase separation into two phases with different values ( $n_{Li_1} = \eta_1 + 1/2$  and  $n_{Li_2} = \eta_2 + 1/2$ ) of ion concentration takes place.

In Fig. 2 the dependence of the total charge  $Q = e(\langle S^z \rangle + 1/2 - n)$  on the chemical potential of ions is shown. The dependence of the derivative  $dQ/d\varphi$  on the chemical potential of ions is also shown in this figure (it should be noted that this derivative is connected with the electrostatic capacity  $C$  of the system). It should be noted that we don't consider here the regime when the system total charge is equal to zero (the neutrality condition). Instead of that we consider the regime of the fixed potential  $\varphi$ . If we consider the regime of the fixed total charge (for example,  $Q = 0$ ) we can find the corresponding value of the potential  $\varphi$ . From Fig. 2 we can see that sharp increase of the derivative  $dQ/d\varphi$  occurs at the phase transition point (at the change of the chemical potential of the ions). The units in the figure are the following: the case  $dQ/d\varphi = 1$  corresponds to the capacity  $C \sim 1.6 \cdot 10^{-19}\text{F}$  (it is a capacity per site). The capacity connected with the change of the ion charge only (such a capacity is in close connection with the capacity obtained in experimental studies) can also be calculated (as derivative  $d(e\langle S^z + 1/2 \rangle)/d\varphi$ ), but here we will not dwell on this question.

Let us make some estimation of the capacity of the system. It is known that for the localized noninteracting particles  $C \sim e^2/T$  and for band noninteracting electrons  $C \sim e^2 \rho(E_F) \sim e^2/2W$  (here  $\rho(E_F)$  is density of states at the Fermi level), which is of the order of  $10^{-19}\text{F}$ . Our results obtained in the case of the presence of ion-electron interaction considered above agree with such an estimate. If we consider the "surface" capacity per 1 mm<sup>2</sup>, we will obtain the value  $C \sim 10^{-7}\text{F}$  (here we suppose that density of "active centres" is of the order of  $10^{12}$  per 1 mm<sup>2</sup>). The "volume" capacity is then of the order of  $10^{-1}\text{F}$ . Of course, such an enormously huge capacity is unattainable in real systems due to different reasons (our estimation works in the ideal case, when all "active

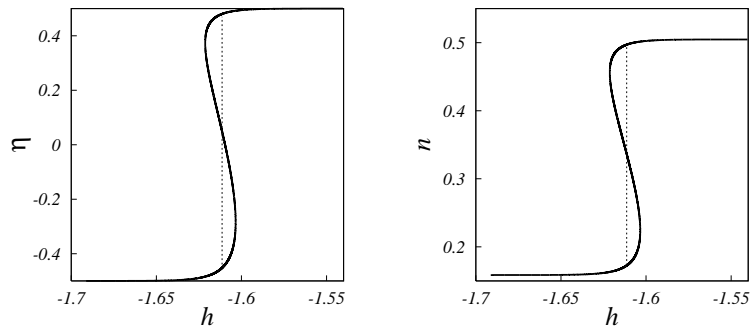


Figure 1. The dependence of the mean pseudospin value ( $\eta + 1/2 = n_{Li}$ ) and electron concentration on the chemical potential of the ions. The parameter values are:  $g^c = -0.5, g^v = -0.7, J = 0.1, W = 1.5, \varphi = 0.1, \mu = 0.5, T = 0.01$ .

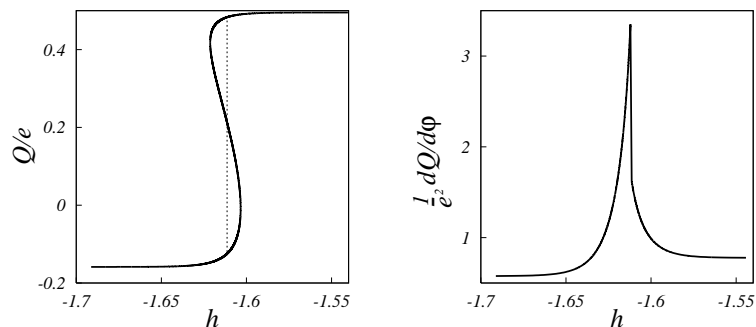


Figure 2. The dependence of the charge  $Q$  and derivative  $dQ/d\varphi$  on the chemical potential of the ions. The parameter values are:  $g^c = -0.5, g^v = -0.7, J = 0.1, W = 1.5, \varphi = 0.1, \mu = 0.5, T = 0.01$ .

centres” are uniformly distributed over the whole crystal). Nevertheless, the increase of capacity due to the above mentioned “volume effect” takes place in such systems.

In Figs. 3, 4 the dependences of the  $\eta, n, Q, dQ/d\varphi$  values on the chemical potential of ions are shown in the case when the system does not undergo phase transition (this can be realized by the appropriate change

of the values of the model parameters). Unlike the previously considered case (when phase transition takes place and there is a “plateau” in the dependence of the chemical potential of the ions  $h$  on their concentration  $n_{Li} = \eta + 1/2$ ), the system can’t effectively work now as battery because the chemical potential of the ions changes continuously with the change of the ion concentration. We can see that in this case the sharp increase of derivative  $dQ/d\varphi$  does not take place, this dependence is smooth enough. Nevertheless the increase of system capacity takes place in the some value region of the chemical potential of ions.

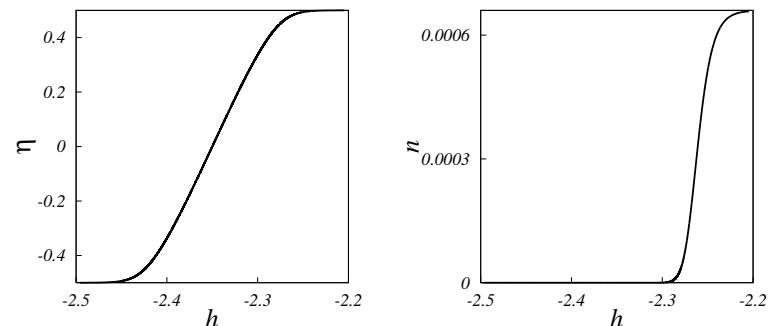


Figure 3. The dependence of the mean pseudospin value ( $\eta + 1/2 = n_{Li}$ ) and electron concentration on the chemical potential of the ions. The parameter values are:  $g^c = -0.5, g^v = -0.7, J = 0.1, W = 1.5, \varphi = 1.0, \mu = 0.5, T = 0.01$ .

## 4. Conclusions

The pseudospin-electron model of ion intercalation in crystals is considered in this study. The thermodynamics of the model is investigated in the mean-field approximation. It is shown that even at repulsion interaction between lithium ions the first order phase transition (and separation into phases with different values of ion concentration) takes place. This effect is connected with the effective interaction between ions which is formed due to the pseudospin-electron interaction (the interaction of lithium ions with electron subsystem). It is found that the total capacity of the system increases near phase transition point. In general our results are in accordance with experimental data where the coexistence of two

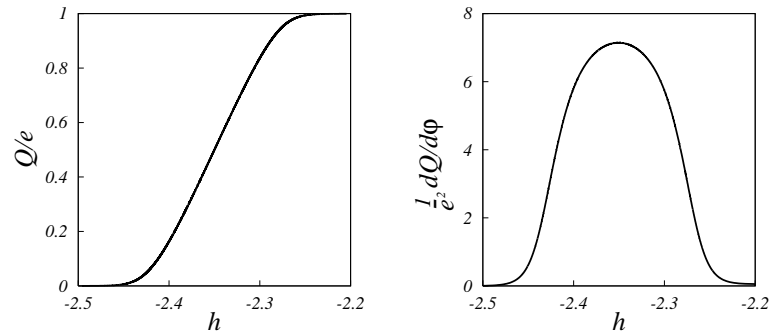


Figure 4. The dependence of the charge  $Q$  and derivative  $dQ/d\varphi$  on the chemical potential of the ions. The parameter values are:  $g^c = -0.5$ ,  $g^v = -0.7$ ,  $J = 0.1$ ,  $W = 1.5$ ,  $\varphi = 1.0$ ,  $\mu = 0.5$ ,  $T = 0.01$ .

phases was revealed [6,7].

The obtained results can be considered as the first step to the description of the  $\text{Li}^+$  ion intercalation in semiconducting crystals. It should be noted that the ion transfer was not taken into account in our model. This is the task for future investigations. The problems of considering of another regimes (for example, the regime of the fixed (e.g. zero) total charge) and more detail description of phase separation also remain unsolved. The possibility of formation of local states on lithium was not considered in our work too.

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