PSEUDOSPIN–ELECTRON MODEL OF INTERCALATION

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The pseudospin–electron model with two orbital electron states per site is considered in this work. This model can be employed for the description of the intercalation of ions in crystals. The pseudospin formalism is used for describing the interaction of electrons with ions. The thermodynamics of the model is studied in the mean field approximation. The possibility of the phase transitions connected with the change of the concentration of intercalated ions and significant increase of electrostatic capacity of the system is analyzed.

Key words: intercalation, pseudospin–electron model, phase transition, capacity.

I. INTRODUCTION

Transition metal oxides are intensively studied as hosts for lithium insertion, they are promising electrode materials and can be used in batteries. One of such materials is titanium dioxide, TiO_2. Such systems are semiconductors, the gap being approximately 3 eV. These materials have been the subject of intensive experimental and theoretical investigations in recent years.

The crystal structures of three lithium titanates ($Li_{0.5}TiO_2$ — anatase, $LiTi_2O_4$ — spinel, obtained by heating $Li_{0.5}TiO_2$ — anatase, and $Li_2Ti_2O_4$) were investigated by neutron diffraction powder profile analysis [1]. It was found that inserted Li ions in $Li_{0.5}TiO_2$ occupied octahedral interstices. In $LiTi_2O_4$, spinel lithium occupied tetrahedral sites, while in $Li_2Ti_2O_4$ lithium filled the octahedral sites and was displaced from the tetrahedral sites [1]. In [2] quantum chemical Hartree–Fock calculations were done to study lithium intercalation in rutile and anatase. Equilibrium geometries and atomic charges were calculated. It was established that Li lost its valence electron (electron occupying Li $2s$ atomic orbital) which transferred to Ti ion (calculated Li charges were ~ 0.8). Li-induced local one-electron energy level was found in the gap between the upper valence band and the conduction band, this level was composed mainly of Ti $4s$ atomic orbitals. A conclusion was made that lithium can be intercalated with larger probability in the anatase structure than in rutile. Using pseudopotential plane-wave formalism the calculations indicated a distinct preference for intercalation of lithium into the octahedral sites in anatase [3]. There was shown that fast diffusion of lithium along c axes and slow diffusion in the ab plane took place. In [4] density-functional calculations were performed to investigate lithium intercalation into rutile. It was shown that effective Li–Li interaction was highly anisotropic, the computed lithium diffusion constants were anisotropic also. The calculations revealed a tendency of the valence band at narrowing and increasing the band gap at the lithium intercalation.

The dynamics of lithium in lithiated anatase TiO_2 was also tackled (see [5]). The analysis of neutron diffraction data revealed two available Li-ion positions within the oxygen octahedron in lithiated anatase [6], these sites were never occupied at the same time (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]. The hopping of lithium between different octahedra was investigated too. It was shown that lithium diffused more easily through the Li-rich phase (activation energy for Li-rich phase was less than activation energy for Li-poor phase). At intercalation of lithium in anatase TiO_2 phase separation in Li-poor ($Li_{\sim 0.01}TiO_2$) and Li-rich ($Li_{\sim 0.5-0.6}TiO_2$) phases occurred, Li-rich phase grew with the 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 Li_xTiO_2 spinel were investigated using a cluster expansion (based on pseudopotential ground state energy calculations) and a Monte Carlo simulation. The coexistence of two phases (when $1/2 < x < 1$) $Li_{\frac{1}{2}}TiO_2$ (Li on tetrahedral sites) and $LiTiO_2$ (Li on octahedral sites) was established. The insertion of Li first resulted in the 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 occur. It was shown that Li is fully ionized once intercalated. Electronic structure calculations revealed that in $LiTiO_2$ the Fermi level was situated near the bottom of the conduction band; in the valence region the energy states are represented by three sets of bands: the s-bands (dominated by O-$2s$ states), the p-bands (dominated by the O-$2p$ states) and the d-bands (dominated by the Ti-$3d$ states).

The intercalation of lithium in cubic-spinel $Li[Ti_{5/3}Li_{1/3}]O_4$ was investigated in [9] with the help of the Monte Carlo method. According to their model, the Hamiltonian included interaction between Li ions. They did not take into account the interaction between Li ions and electrons. 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.

The reconstruction of the electron spectrum in such crystals upon intercalation means that the interaction between lithium and conduction and valence electrons may play an important role in such systems. In the cur-

rent 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.

II. THE MODEL

The Hamiltonian of the model is defined as

$$
H = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}}^c c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}}^v a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} + \sum_{ij\sigma} g_{ij}^c n_{i\sigma}^c \left(S_j^z + \frac{1}{2} \right) + \sum_{ij\sigma} g_{ij}^v n_{i\sigma}^v \left(S_j^z + \frac{1}{2} \right) - \mu \sum_{i\sigma} (n_{i\sigma}^c + n_{i\sigma}^v) \tag{1}
$$
$$
+ \frac{1}{2} \sum_{ij} J_{ij} \left(S_i^z + \frac{1}{2} \right) \left(S_j^z + \frac{1}{2} \right) - h \sum_i \left(S_i^z + \frac{1}{2} \right).
$$

The pseudospin variable S_i^z takes two values, $S_i^z = 1/2$ when lithium ion is present in the 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 (1), as usual, 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); μ and h play the role of the chemical potentials of electrons and Li ions, respectively.

The models of such a type were formulated a short time ago and 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 superconductors [10, 11]. There is a direct connection between the pseudospin–electron model and Falicov–Kimball model (for example, see [12]).

To investigate the thermodynamics of the model we use the following approximation in the interaction terms

$$
gn_i S_j^z \rightarrow g\langle n_i \rangle S_j^z + gn_i \langle S_j^z \rangle - g\langle n_i \rangle \langle S_j^z \rangle \tag{2}
$$
$$
JS_i^z S_j^z \rightarrow J\langle S_i^z \rangle S_j^z + JS_i^z \langle S_j^z \rangle - J\langle S_i^z \rangle \langle S_j^z \rangle;
$$

here the pseudospin–electron and pseudospin–pseudospin interactions are taken into account in the spirit of the mean field approximation (MFA) through internal self-consistent fields which act on electrons and pseudospins. We suppose that direct interaction between pseudospins and pseudospin–electron interaction is non-local and may be long-ranged; this enables 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 into account the possibility of formation of local electron states near impurities.

We will 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 has the following form:

$$
H^{MFA} = \sum_{\mathbf{k}\sigma} (\epsilon_{\mathbf{k}}^c - \mu + g^c\langle S^z + \frac{1}{2}\rangle) c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma} (\epsilon_{\mathbf{k}}^v - \mu + g^v\langle S^z + \frac{1}{2}\rangle) a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma}
$$
$$
+ (g^c n^c + g^v n^v - h + J\langle S^z + \frac{1}{2}\rangle) \sum_i S_i^z - g^c n^c \langle S^z \rangle N - g^v n^v \langle S^z \rangle N - \frac{1}{2}\langle S^z \rangle^2 NJ + \frac{1}{8}NJ - \frac{h}{2}N, \tag{3}
$$

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 the pseudospin η. 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 the field. Instead of the chemical potentials of electrons and ions we wil use the corresonding electrochemical potentials $\mu \rightarrow \mu^* = \mu - e\varphi$, $h \rightarrow h^* = h + e\varphi$ (here μ^*, 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 φ is a potential of the field) should be included in the Hamiltonian.

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

$$\langle S^z \rangle = \frac{1}{2} \tanh\left(\frac{\beta}{2} \left(h^* - g^c n^c - g^v n^v - J \langle S^z + \frac{1}{2} \rangle \right) \right),$$

$$n^c = \frac{1}{N} \sum_{\mathbf{k}\sigma} \frac{1}{1 + e^{\beta(\epsilon_{\mathbf{k}}^c - \mu^* + g^c \langle S^z + \frac{1}{2} \rangle)}}, \qquad (4)$$

$$n^v = \frac{1}{N} \sum_{\mathbf{k}\sigma} \frac{1}{1 + e^{\beta(\epsilon_{\mathbf{k}}^v - \mu^* + g^v \langle S^z + \frac{1}{2} \rangle)}}.$$

The grand canonical potential of the system can be written as

$$\Omega = -g^c n^c \langle S^z \rangle - g^v n^v \langle S^z \rangle - \langle S^z \rangle^2 \frac{J}{2} - \frac{h^*}{2} + \frac{J}{8} \qquad (5)$$

$$-T \ln \left(2 \cosh \left(\frac{\beta}{2} (g^c n^c + g^a n^a - h^* + \left\langle S^z + \frac{1}{2} \right\rangle J) \right) \right)$$

$$-T \frac{1}{N} \sum_{\mathbf{k}\sigma} \ln(1 + e^{-\beta(\epsilon_{\mathbf{k}}^c + g^c \langle S^z + \frac{1}{2} \rangle - \mu^*)})$$

$$-T \frac{1}{N} \sum_{\mathbf{k}\sigma} \ln(1 + e^{-\beta(\epsilon_{\mathbf{k}}^v + g^v \langle S^z + \frac{1}{2} \rangle - \mu^*)}).$$

We take into account that at intercalation the chemical potential μ 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).

III. THE PHASE TRANSITION AND PHASE SEPARATION

We have solved the set of equations (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 3 eV, this band is created by Ti-3d states).

In Fig. 1 the dependence of the mean pseudospin value η 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 φ). We have chosen the following set of parameter values:

$g^c = -0.5, g^v = -0.7, J = 0.1, W = 1.5$ (as was noted above, $2W \sim 3$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 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 (η_1 and η_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). We do not consider here the regime when the system total charge equals zero (the neutrality condition). Instead of that we consider the regime of the fixed potential φ. If we consider the regime of the fixed total charge (for example, $Q = 0$) we can find the corresponding value of the potential φ. From Fig. 2 we can see that a 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 $C \sim 1.6 \cdot 10^{-19}$ 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.
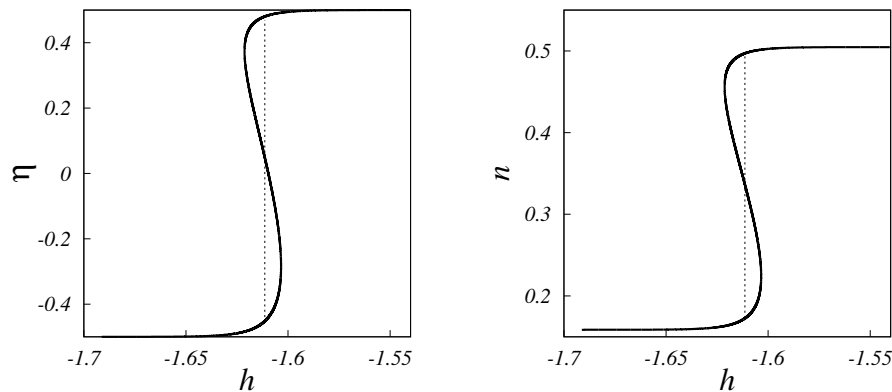

Fig. 1. Dependence of the mean pseudospin value ($\eta + 1/2 = n_{Li}$) and electron concentration on the chemical potential of the ions. The parameter values are: $g^c = -0.5, g^v = -0.7, J = 0.1, W = 1.5, \varphi = 0.1, \mu = 0.5, T = 0.01$.
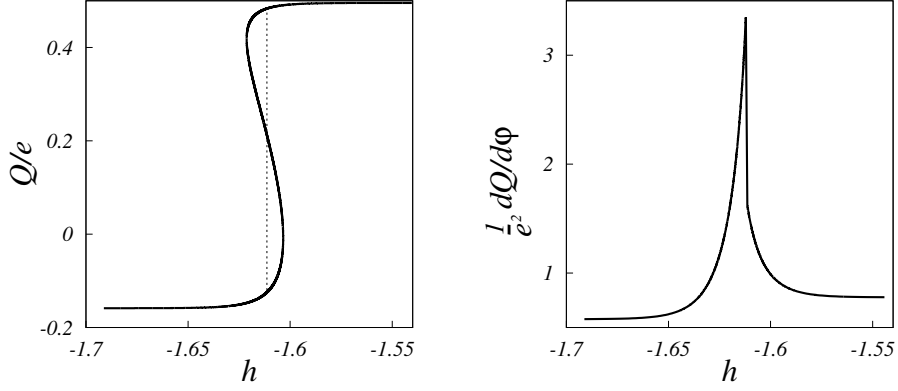
Fig. 2. Dependence of the charge Q and derivative $dQ/d\varphi$ on the chemical potential of the ions. The parameter values are: $g^c = -0.5, g^v = -0.7, J = 0.1, W = 1.5, \varphi = 0.1, \mu = 0.5, T = 0.01$.
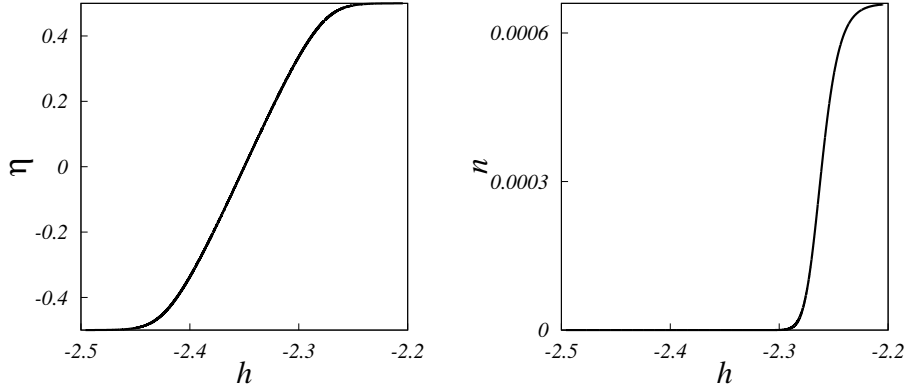

Fig. 3. Dependence of the mean pseudospin value $(\eta + 1/2 = n_{Li})$ and electron concentration on the chemical potential of ions. The parameter values are: $g^c = -0.5, g^v = -0.7, J = 0.1, W = 1.5, \varphi = 1.0, \mu = 0.5, T = 0.01$.
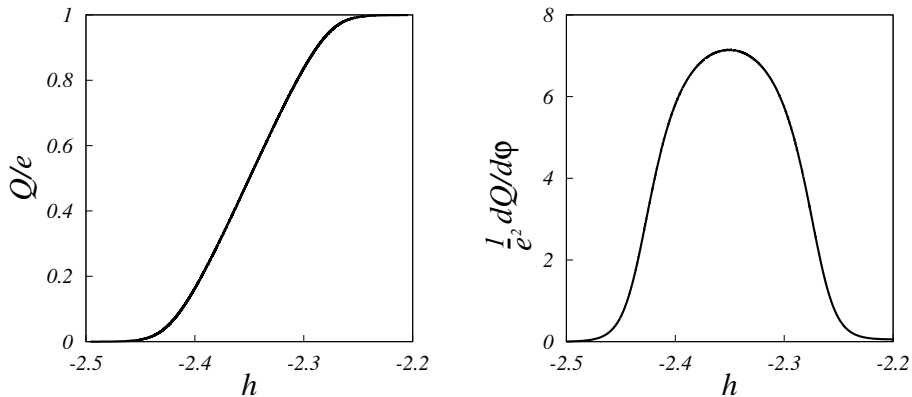

Fig. 4. Dependence of the charge Q and derivative $dQ/d\varphi$ on the chemical potential of ions. The parameter values are: $g^c = -0.5, g^v = -0.7, J = 0.1, W = 1.5, \varphi = 1.0, \mu = 0.5, T = 0.01$.

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 $C \sim e^2\rho(E_{\mathrm{F}}) \sim e^2/2W$ (here $\rho(E_{\mathrm{F}})$ is density of states at the Fermi level), which is of the order of 10^{-19} 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^2, we will obtain the value $C \sim 10^{-7}$ F (here we suppose that the density of "active centres" is of the order of 10^{12} per 1 mm^2). The "volume" capacity is then of the order of 10^{-1} 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 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 $n_{\mathrm{Li}} = \eta + 1/2$), the system cannot 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 a sharp increase of the derivative $dQ/d\varphi$ does not take place, this dependence is smooth enough. Nevertheless an increase of system capacity takes place in the same value region of the chemical potential of ions.

IV. CONCLUSIONS

In this work the pseudospin–electron model of ion intercalation in crystals is formulated. 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 the 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 phases was revealed [6, 7].

The obtained results can be considered as the first step to the description of the 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 other regimes (for example, that of the fixed (e. g. zero) total charge) and a more detailed description of phase separation also remain unsolved. A possibility of the formation of local states on lithium was not considered in our work either.

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ПСЕВДОСПІН-ЕЛЕКТРОННА МОДЕЛЬ ІНТЕРКАЛЯЦІЇ

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Розглянуто псевдоспін-електронну модель із двома орбітальними станами на вузлі. Цю модель можна застосувати для опису інтеркаляції йонів у кристали. Використано псевдоспіновий формалізм для опису взаємодії електронів з йонами. Досліджено термодинаміку моделі в наближенні середнього поля. Проаналізовано можливість фазових переходів, пов'язаних зі зміною концентрації інтеркальованих йонів та значним зростанням електростатичної ємности системи.