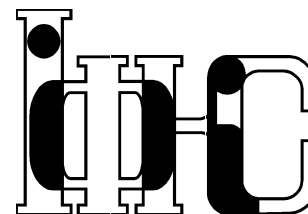


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PSEUDOSPIN-ELECTRON MODEL OF INTERCALATION

ЛЬВІВ

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Псевдоспін-електронна модель інтеркаляції

Т.С.Мисакович, І.В.Стасюк

Анотація. В даній роботі розглядається псевдоспін-електронна модель з двома орбітальними станами на вузлі. Ця модель може бути застосованою для опису інтеркаляції іонів в кристали. Використано псевдоспіновий формалізм для опису взаємодії електронів з іонами. Досліджено термодинаміку моделі в наближенні середнього поля. Проаналізовано можливість виникнення в системі фазового розширення.

Pseudospin-electron model of intercalation

T.S.Mysakovych, I.V.Stasyuk

Abstract. 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. Pseudospin formalism is used for the description of interaction of electrons with ions. The thermodynamics of the model is investigated in the mean field approximation. The possibility of the appearance of phase separation in the system is analyzed.

1. Introduction

Transition metal oxides are intensively investigated 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, gap is approximately 3 eV. These materials are the subject of intensive experimental and theoretical investigations in the last years.

The crystal structures of three lithium titanates ($\text{Li}_{0.5}\text{TiO}_2$ - anatase, LiTi_2O_4 - spinel, obtained by heating $\text{Li}_{0.5}\text{TiO}_2$ - anatase, and $\text{Li}_2\text{Ti}_2\text{O}_4$) were investigated by neutron diffraction powder profile analysis [1]. It was found that inserted Li ions in $\text{Li}_{0.5}\text{TiO}_2$ occupied octahedral interstices. In LiTi_2O_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] 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 calculations of [3] indicated a distinct preference for intercalation of lithium into the octahedral sites in anatase. 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. Their 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 TiO_2 was also investigated (see [5]). 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 also. 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 TiO₂ phase separation in Li-poor (Li_{~0.01}TiO₂) and Li-rich (Li_{~0.5-0.6}TiO₂) phases occurred, Li-rich phase grew with increasing of content of lithium [6,7]. Such two-phase behaviour leads to a constant electrochemical potential. In [8] the structural properties of Li_xTiO₂ 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) Li_{1/2}TiO₂ (Li on tetrahedral sites) and LiTiO₂ (Li on octahedral sites) was established. 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. It was shown that Li is fully ionized once intercalated. Electronic structure calculations revealed that in LiTiO₂ 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).

Intercalation of lithium in cubic-spinel Li[Ti_{5/3}Li_{1/3}]O₄ was investigated in [9] with the help of a Monte Carlo method. According to their model, the Hamiltonian included interaction between Li ions. They did not take into account 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 electron spectrum in such crystals upon intercalation means that interaction between lithium and conduction and valence 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 appearance of phase separation in such systems.

2. The model

The Hamiltonian of the model is defined as

$$H = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}}^c c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}}^v a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} + \sum_{ij\sigma} g_{ij}^c n_{i\sigma}^c (S_j^z + \frac{1}{2}) \quad (2.1)$$

$$+ \sum_{ij\sigma} g_{ij}^v n_{i\sigma}^v (S_j^z + \frac{1}{2}) - \mu \sum_{i\sigma} (n_{i\sigma}^c + n_{i\sigma}^v)$$

$$+ \frac{1}{2} \sum_{ij} J_{ij} (S_i^z + \frac{1}{2})(S_j^z + \frac{1}{2}) - h \sum_i (S_i^z + \frac{1}{2}).$$

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); μ and h play the role of the chemical potentials of electrons and Li ions respectively.

Models of such type were formulated in recent time 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].

To investigate the thermodynamics of the model we use the following approximation:

$$g n_i S_j^z \rightarrow g \langle n_i \rangle S_j^z + g n_i \langle S_j^z \rangle - g \langle n_i \rangle \langle S_j^z \rangle \quad (2.2)$$

$$J S_i^z S_j^z \rightarrow J \langle S_i^z \rangle S_j^z + J S_i^z \langle S_j^z \rangle - J \langle S_i^z \rangle \langle S_j^z \rangle,$$

where 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.

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:

$$H^{MFA} = \sum_{\mathbf{k}\sigma} (\epsilon_{\mathbf{k}}^c - \mu + g^c \langle S^z + \frac{1}{2} \rangle) c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma} \quad (2.3)$$

$$+ \sum_{\mathbf{k}\sigma} (\epsilon_{\mathbf{k}}^v - \mu + g^v \langle S^z + \frac{1}{2} \rangle) a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma}$$

$$+ (g^c n^c + g^v n^v - h + J \langle S^z + \frac{1}{2} \rangle) \sum_i S_i^z - g^c n^c \langle S^z \rangle N$$

$$- g^v n^v \langle S^z \rangle N - \frac{1}{2} \langle S^z \rangle^2 N J + \frac{1}{8} N J - \frac{h}{2} N,$$

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 η . This means that bands are shifted at intercalation. The mean values of pseudospin and electron concentration obey the following equations:

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

In addition to the equation (2.4) we should take into account the following condition

$$n^c = 2 - n^v + \langle S^z + \frac{1}{2} \rangle. \quad (2.5)$$

This condition ensures the neutrality of the system. We suppose that lithium is fully ionized and the number of electrons in the conduction band is equal to the number of holes in the valency band (the first term in the right side of the equation (2.5)) plus the number of lithium ions (the second term in the right side of the equation (2.5)). We take into account that at intercalation the chemical potential is situated in the conduction band (see, for example, [4,8]). This means that at room temperatures valency 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) taking into account the condition (2.5). We have used 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. In Fig. 1a the dependence of the mean pseudospin value η on the chemical potential of ions is shown (the regime of the fixed chemical potential). We have chosen the following set of parameters: $g^c = -0.4$, $g^v = -0.8$, $J = 0.2$, $W = 1.5$; here we suppose repulsion interaction between lithium ions, $J > 0$. We have also taken into account that at intercalation the band gap increases (see, for example, [4]). 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 ($g^c = -0.4$, $g^v = -0.8$) the band gap increases. From Fig. 1a 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) 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 (η_1 and η_2) of ion concentration takes place. At the increase of temperature the possibility of phase separation disappears, this is illustrated in Fig. 1b.

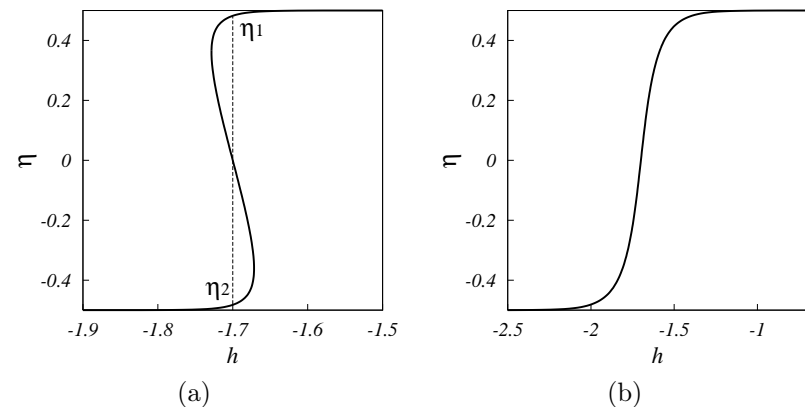


Figure 1. The dependence of the mean pseudospin value on the chemical potential of the ions. The parameter values are: $g^c = -0.4$, $g^v = -0.8$, $J = 0.2$, $W = 1.5$. a) $T = 0.024$ b) $T = 0.1$.

Now we will illustrate some interesting effect which takes place when we consider the regime $n = \eta + 1/2 = const$. We will demonstrate the possibility of phase separation into two charged phases, when the neutrality condition $n = \eta + \frac{1}{2}$ is fulfilled for the whole crystal only and $n_i \neq \eta_i + \frac{1}{2}$. This means that two phases (n_1, η_1) and (n_2, η_2) are charged. To obtain phase separation we consider the following equations:

$$n = \alpha n_1 + (1 - \alpha)n_2; \quad \eta = \alpha \eta_1 + (1 - \alpha)\eta_2; \quad n = \eta + \frac{1}{2}, \quad (3.1)$$

where n_1, n_2, η_1, η_2 are mean values of electron concentrations and pseudospins of two coexisting phases. To solve the system 3.1 we at first did not take into account the neutrality condition and found values of

n_1, n_2, η_1, η_2 for two coexisting phases (when we do not take into account the condition (2.5)). These values depend on the chemical potential of electrons μ and ions h , so we have $n_i(\mu, h), \eta_i(\mu, h)$. Then we take into account the neutrality condition and we can find $n_i^*(\mu^*, h^*), \eta_i^*(\mu^*, h^*)$, which ensures the fulfillment of the condition $n^* = \eta^* + 1/2 = const$, so we can build phase separation regions. They are shown in Fig. 2; rectangular density of states was used for simplification of calculations. It can be seen from Fig. 2 that at the increase of temperature the phase separation region narrows. However, it should be noted that such phase

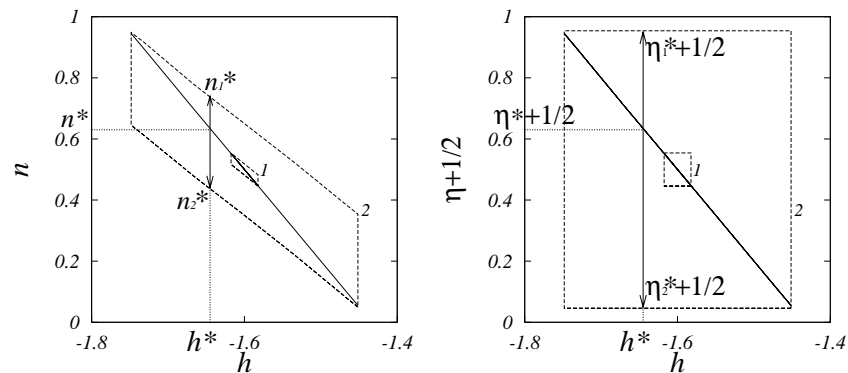


Figure 2. The phase separation regions (dashed lines) in the regime $n = \eta + 1/2 = const$ are shown for two temperatures, 1: $T = 0.0166$, 2: $T = 0.01$. The parameter values are: $g^c = -0.5, g^v = -0.7, J = 0.1, W = 1.5$.

separation into charged phases should be considered more carefully, introducing the electrochemical potential, so obtained above results have only illustrative character.

4. 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. The effective interaction between ions is formed due to pseudospin-electron interaction. The appearance of phase separation is established. 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. Introducing of electrochemical potential is also the task for such study.

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