LATTICE MODEL OF INTERCALATION

T.S. MYSAKOVYCH, V.O. KRASNOV, I.V. STASYUK

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Institute for Condensed Matter Physics, Nat. Acad. of Sci. of Ukraine
(1, Svientsitskii Str., 29011 Lviv, Ukraine; e-mail: mysakovych@icmp.lviv.ua)

The thermodynamics of a lattice model of intercalation of ions in crystals is considered in the mean-field approximation (MFA). The pseudospin formalism is used for the description of the interaction of electrons with ions, and the possibility of the hopping of intercalated ions between different positions is taken into account. Phase diagrams are built. It is shown that the effective interaction between intercalated ions can lead to the phase separation or the appearance of a modulated phase (it depends on the filling of the electron energy band). At high values of the parameter of ion transfer, the ionic subsystem can pass to the superfluid-like state.

1. Introduction

The theoretical investigation of the intercalation of ions in crystals is an actual problem of modern physics. Metal oxides as hosts for the ion (for example, lithium ions) insertion are very promising electrode materials. It should be noted that theoretical descriptions of such processes were restricted, in most cases, to numerical *ab initio* and density-functional calculations. For example, the quantum-chemical Hartree–Fock and density-functional calculations were performed in [1–3] to investigate the lithium intercalation in a TiO_2 crystal. It was shown that Li is almost fully ionized once intercalated (Li looses its valence electron), and a reconstruction of the electron spectrum takes place at the intercalation. Thus, the ion-electron interaction can play a significant role. Another interesting feature of such crystals is a shift of the chemical potential at the intercalation into the conduction band. As a result, these crystals have metallic conductivity ([4]; for a review, see also [5]); before the intercalation, such crystals are semiconductors with wide gap. At the intercalation of lithium in TiO_2, the phase separation into Li-poor ($Li_{\sim 0.01}TiO_2$) and Li-rich ($Li_{\sim 0.5-0.6}TiO_2$) phases occurs. This two-phase behavior leads to a constant value of electrochemical potential [6, 7] (this fact is used when constructing batteries). In [8], the Monte-Carlo simulation was performed to investigate the intercalation using a Hamiltonian which included the interaction between ions only.

In our previous works [9, 10], we have formulated the pseudospin-electron model of intercalation and have taken into account the ion-electron interaction. It has been revealed that the effective attractive interaction between ions was formed, and the condition for the appearance of the phase separation has been established. The ion-electron interaction was also considered in [11] at the investigation of the thermodynamics of the $S = 1$ model of intercalation (the model was similar to the known Blume–Emery–Griffiths model), but the electron transfer, as well as the ion one, was not taken into account. It should be noted that models of the pseudospin-electron model type are widely used in the physics of strongly-correlated electron systems in recent years. The application of this model to high-temperature superconductors allows one to describe the thermodynamics of the anharmonic oxygen ion subsystem and to explain the appearance of inhomogeneous states and bistability phenomena ([12]). Such a model can also be applied to the description of hydrogen-bonded systems.

In the present paper, we deal with a more complicated model and take into account the possibility of the transfer of intercalated ions. The considered model corresponds to the hard-core boson approach. Hard-core bosons obey the Pauli spin-1/2 commutation rules. Since the original work of Mahan [13], such models were applied for the description of ionic conductors and the calculation of their conductivity. Recently, the one-particle spectrum was investigated in the one-dimensional limit [14]. A system of hard-core bosons is a particular case of the well-known Bose–Hubbard model which has been intensively investigated in the last 15 years (see, for example, [15]). The model is of great interest due to the experimental realization of optical lattices (see, for instance, [16]). This model can be directly applied to investigate such objects. The Hamiltonian of the Bose–Hubbard model includes two terms, one of which is connected with the on-site interaction U between particles, and another term is connected with the particle hopping between sites (particles in this model obey the bosonic commutation rules). In the limit $U \to \infty$, this model reduces to the hard-

core boson model. Different theoretical methods were used to study this model: mean-field theory [17], random phase approximation [18, 19], strong coupling approach [20], and quantum Monte-Carlo method [21]. Recently, a bosonic version of the dynamical mean-field theory was formulated [22]. The existence of the superfluid and Mott-insulator phases is a characteristic feature of this model.

In addition to our previous investigations [9], the aim of this work is the study of the ion transfer influence on equilibrium states of the intercalated ion subsystem. As was shown in [9, 10], the effective interaction between ions can change (depending on the electron band filling) its character from repulsion to attraction, leading to the charge-ordered modulated phases or phase separation into uniform phases with different particle concentrations, respectively. The ion hopping between local positions is unfavorable for the realization of such phases or phase transitions. In addition, the ion hopping leads to the appearance of a superfluid-type phase.

We investigate phase transitions in the intercalated ion subsystem within the framework of the lattice model with ion transfer in the regime of the fixed chemical potential of ions and electrons. The electron subsystem is described by a partially filled one energy band.

2. The Model

We consider the following model Hamiltonian:

$$H = \sum_{ij} \Omega_{ij} S_i^+ S_j^- + \sum_{ij\sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + \sum_{i\sigma} (g S_i^z n_{i\sigma} - \mu n_{i\sigma}) -$$

$$- \sum_i h S_i^z. \tag{1}$$

Here, we introduce the pseudospin variable S_i^z which takes two values, $S_i^z = 1/2$ when there is an intercalated ion at the site i and $S_i^z = -1/2$ when there is no ion, and $c_{i\sigma}^+$ and $c_{i\sigma}$ are the electron creation and annihilation operators, respectively. We take into account the possibility of ion and electron jumps between sites (the first and the second term in (1)) and the interaction of electrons with ions (g term). The last one is related to the electron band shift at the intercalation (such an effect is known, for example, for the system Li_xTiO_2 [3]); μ and h play the role of the chemical potentials of electrons and ions.

It should be noted that we do not consider the direct interaction between ions. In our previous paper [9], it was shown that the ion-electron interaction leads to the

formation of an effective interaction between ions and, even at the repulsive direct ion-ion interaction, an effective ion-ion interaction of the attractive type can be formed. This can lead to a phase transition of the first order between uniform phases with jumps of the ion and electron concentrations.

The thermodynamics of the model is investigated in the mean-field approximation

$$g n_i S_i^z \to g \langle n_i \rangle S_i^z + g n_i \langle S_i^z \rangle - g \langle n_i \rangle \langle S_i^z \rangle$$

$$\Omega S_i^+ S_j^- \to \Omega \langle S_i^+ \rangle S_j^- + \Omega S_i^+ \langle S_j^- \rangle - \Omega \langle S_i^+ \rangle \langle S_j^- \rangle. \tag{2}$$

Here, the average ion concentration $w = \langle S^z \rangle + 1/2$ is introduced; in our approximation, $\langle S^+ \rangle = \langle S^- \rangle = \langle S^x \rangle$, $\langle S^y \rangle = 0$. The average value $\langle S^x \rangle$ plays the role of order parameter for the case of the superfluid phase (this is a phase with condensate of the Bose-type) and determines the concentration of condensed particles.

Application of the MFA to strongly correlated systems in the limit of a weak one-site correlation makes it possible to satisfactorily describe their properties, when there is no correlational splitting of the electron band. This approximation is an analogy to the virtual crystal approximation which is often used for mixed systems. To go beyond the MFA, one can use more complicated approximations, for instance, the coherent potential-like approximations. In addition, in the case of the Bose–Hubbard model, the kinetic energy term is often considered within the mean-field approach. This approximation is well known to give a reasonable estimate of the critical on-site repulsion at which the Mott-insulator – superfluid phase transition occurs [15, 17].

In [23, 24], the case $\Omega = 0$ was considered. It was shown that if the chemical potential is near the band center, the double modulation phase is realized in the system, while the phase transition between uniform phases occurs in the case where the chemical potential is close to the band edges. At intermediate values of the chemical potential, the incommensurate modulated phase appears. In the present investigation, we restrict ourselves to the cases of double modulation phase and uniform phase.

The Hamiltonian of the model in the MFA is as follows:

$$H^{\mathrm{MFA}} = \sum_{i\alpha\sigma} (g\eta_\alpha - \mu) n_{i\alpha\sigma} + \sum_{i\alpha} (g n_\alpha - h) S_{i\alpha}^z +$$

$$+ \sum_{i\alpha, j\beta} t_{ij}^{\alpha\beta} c_{i\alpha\sigma}^+ c_{j\beta\sigma} + \sum_{\alpha\beta i} 2\Omega^{\alpha\beta} \langle S_\alpha^x \rangle S_{i\beta}^x - g \sum_{i\alpha} n_\alpha \eta_\alpha -$$
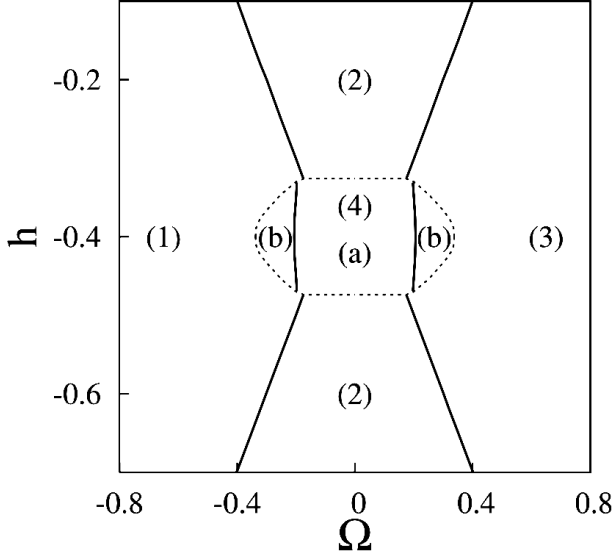
Fig. 1. Phase diagram in the $(h-\Omega)$ plane at $\mu = 0$. The parameter values are: $g = -0.4$, $W = 1$, $T = 0.03$. (1), (3) – uniform phase with $\langle S^x \rangle \neq 0$ ((1): $\langle S_1^x \rangle = \langle S_2^x \rangle$, (3): $\langle S_1^x \rangle = -\langle S_2^x \rangle$); (2)– uniform phase with $\langle S^x \rangle = 0$; (4)– modulated phase ((a): $\langle S_{1,2}^x \rangle = 0$, (b): $\langle S_{1,2}^x \rangle \neq 0$). The solid line denotes the phase transitions of the second order and the dotted line denotes the phase transition of the first order

$$-N\Omega\langle S_1^x \rangle\langle S_2^x \rangle. \tag{3}$$

Here, we consider two sublattices: $\langle \sum_\sigma n_{i\alpha\sigma} \rangle = n_\alpha$, $\langle S_{i\alpha}^z \rangle = \eta_\alpha$; $\alpha = 1,2$ is a sublattice index, i is an unit cell index, N is the number of lattice sites, $\Omega \equiv \Omega^{12} = \Omega^{21} = \sum_i \Omega_{ij}^{12}$; $\Omega^{\alpha\alpha} = t^{\alpha\alpha} = 0$.

This Hamiltonian can be diagonalized. We pass to the **k**-representation and perform the unitary transformation in the pseudospin subspace

$$H^{\mathrm{MFA}} = \sum_{\alpha\sigma\mathbf{k}} (\lambda_{\mathbf{k}\alpha} - \mu)\tilde{n}_{\mathbf{k}\alpha\sigma} - \sum_{i\alpha} \tilde{\lambda}_\alpha \sigma_{i\alpha}^z -$$

$$-g\frac{N}{2}(n_1\eta_1 + n_2\eta_2) - N\Omega\langle S_1^x \rangle\langle S_2^x \rangle \tag{4}$$

$$\lambda_{\mathbf{k}\alpha} = g\frac{\eta_1 + \eta_2}{2} + (-1)^\alpha \sqrt{(g\frac{\eta_1 - \eta_2}{2})^2 + t_{\mathbf{k}}^2}$$

$$c_{\mathbf{k}1\sigma} = \tilde{c}_{\mathbf{k}1\sigma} \cos\phi + \tilde{c}_{\mathbf{k}2\sigma} \sin\phi,$$

$$c_{\mathbf{k}2\sigma} = -\tilde{c}_{\mathbf{k}1\sigma} \sin\phi + \tilde{c}_{\mathbf{k}2\sigma} \cos\phi,$$

$$\sin 2\phi = \frac{t_{\mathbf{k}}}{\sqrt{(g\frac{\eta_1 - \eta_2}{2})^2 + t_{\mathbf{k}}^2}}$$

$$S_{i\alpha}^z = \sigma_{i\alpha}^z \cos\theta_\alpha + \sigma_{i\alpha}^x \sin\theta_\alpha,$$

$$S_{i\alpha}^x = \sigma_{i\alpha}^x \cos\theta_\alpha - \sigma_{i\alpha}^z \sin\theta_\alpha, \quad \sin\theta_\alpha = \frac{2\Omega\langle S_\beta^x \rangle}{\tilde{\lambda}_\alpha},$$

$$\tilde{\lambda}_\alpha = \sqrt{(gn_\alpha - h)^2 + (2\Omega\langle S_\beta^x \rangle)^2}, \quad \alpha \neq \beta.$$

The doubling of a unit cell leads to the splitting in the electron spectrum. Two subbands are separated by the gap $g|\eta_1 - \eta_2|$. The electron band changes its position at the intercalation.

Using MFA, we can calculate the mean values of both the electron and ion concentrations:

$$n_\alpha = \frac{1}{N}\sum_{\mathbf{k}\sigma}\left(\frac{1 + \cos 2\phi}{2}(e^{\frac{\lambda_{\mathbf{k}\alpha} - \mu}{T}} + 1)^{-1} + \right.$$

$$\left. +\frac{1 - \cos 2\phi}{2}(e^{\frac{\lambda_{\mathbf{k}\beta} - \mu}{T}} + 1)^{-1}\right), \tag{5}$$

$$\eta_\alpha = \frac{h - gn_\alpha}{2\tilde{\lambda}_\alpha}\tanh(\frac{\beta\tilde{\lambda}_\alpha}{2}), \langle S_\alpha^x \rangle = -\frac{2\Omega\langle S_\beta^x \rangle}{2\tilde{\lambda}_\alpha}\tanh(\frac{\beta\tilde{\lambda}_\alpha}{2}).$$

To find the thermodynamically stable states, we have to calculate also the grand canonical potential

$$\frac{\Phi}{\frac{N}{2}} = -\frac{T}{N}\sum_{\mathbf{k}\sigma}\ln((e^{\frac{\mu - \lambda_{\mathbf{k}1}}{T}} + 1)^{-1})(e^{\frac{\mu - \lambda_{\mathbf{k}1}}{T}} + 1)^{-1})) -$$

$$-T\ln(4\cosh(\frac{\beta\tilde{\lambda}_1}{2})\cosh(\frac{\beta\tilde{\lambda}_2}{2})) - g(n_1\eta_1 + n_2\eta_2) -$$

$$-2\Omega\langle S_1^x \rangle\langle S_2^x \rangle. \tag{6}$$

The absolute minima of the Φ-function determine the equilibrium states.

3. Results

The semielliptic density of states, $\rho(\epsilon) = \frac{2}{\pi W^2}\sqrt{W^2 - \epsilon^2}$, $-W < \epsilon < W$, where W is a half width of the electron band, was used (W is chosen as the energy unit; in our calculations, we put $W = 1$). Using this density of states, we perform the summation over **k** in the equations of self-consistency (5) and in the expression for the grand canonical potential (6).

As noted above, the stable states are obtained using the condition of minimum of the function Φ. In Figs. 1
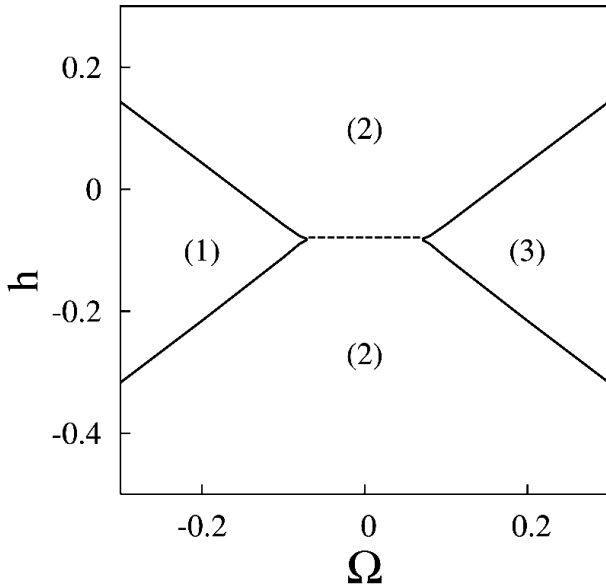
Fig. 2. Phase diagram in the $(h - \Omega)$ plane at $\mu = -0.7$. The parameter values are: $g = -0.4$, $W = 1$, $T = 0.03$. The notations are the same as in Fig. 1. The solid line denotes the phase transition of the second order and the dashed line denotes the phase transition of the first order

Fig. 3. Phase diagram in the $(h-\mu)$ plane at $\Omega = 0$. The parameter values are: $g = -0.4$, $W = 1$, $T = 0.03$. The notations are the same as in Figs. 1 and 2

Fig. 4. Phase diagram in the $(h - \mu)$ plane at $\Omega = 0.25$. The parameter values are: $g = -0.4$, $W = 1$, $T = 0.03$. The notations are the same as in Figs. 1 and 2

and 2, the $(h - \Omega)$ phase diagrams are shown for the cases $\mu = 0$ (at the center of the band) and $\mu = -0.7W$ (near the lower band edge).

In the case $\mu = 0$ and at small values of the ion hopping parameter Ω, the system undergoes the phase transition of the first order from the uniform to modulated phase (in the modulated phase, $n_1 \neq n_2, \eta_1 \neq \eta_2$) at a change of the chemical potential of ions (dotted line in Fig. 1). In the case $\mu = -0.7W$ and at small values of Ω, the phase transition of the first order between two uniform phases with jumps of the average ion and electron concentrations (and the phase separation in the regime of the fixed concentration, see [9, 10, 23, 24] for more details) takes place (dashed line in Fig. 2).

It is easy to see that, at high values of the parameter of ion transfer Ω, the only possible phases are the uniform phases with $\langle S^x \rangle \neq 0$ and $\langle S^x \rangle = 0$. The phase with $\langle S^x \rangle \neq 0$ appears due to the presence of the ion hopping between sites; this phase is an analog to a superfluid phase in the systems of hard-core bosons and can correspond to the state with a high mobility of intercalated ions. In the case $\Omega < 0$, one finds $\langle S_1^x \rangle = \langle S_2^x \rangle$, while, in the case $\Omega > 0$, one finds $\langle S_1^x \rangle = -\langle S_2^x \rangle$.

In Figs. 3 and 4, the $(h-\mu)$ phase diagrams are shown for the cases $\Omega = 0$ and $\Omega = 0.25$. The dotted line denotes the first order phase transition between the uni-
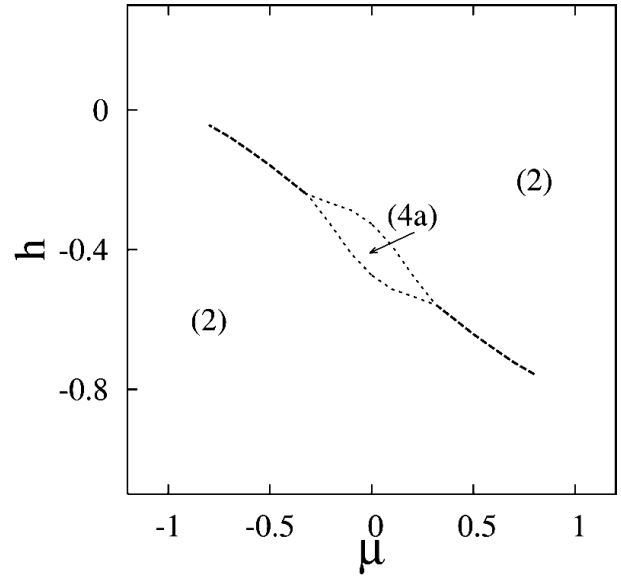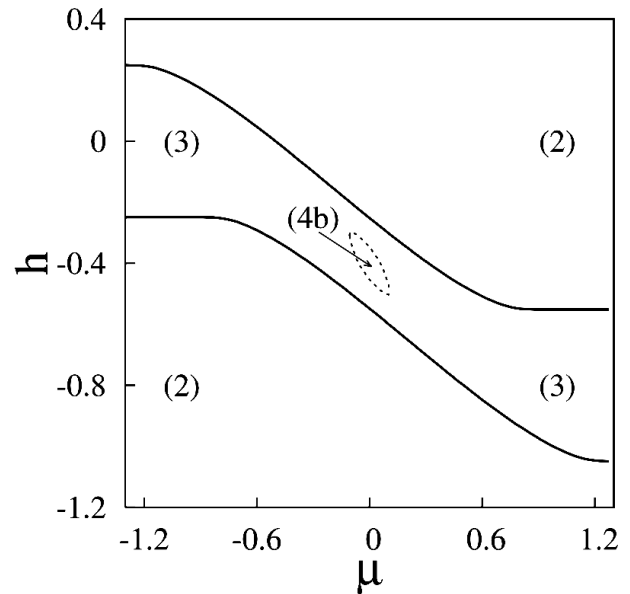
form and modulated phases, and the dashed line denotes the first-order phase transition between uniform phases.

The next four diagrams which are shown in Figs. 5–8 are the $(T - h)$ phase diagrams. In Fig. 5, the first-order phase transition curve between two uniform phases with jumps of the ion and electron concentrations is shown.
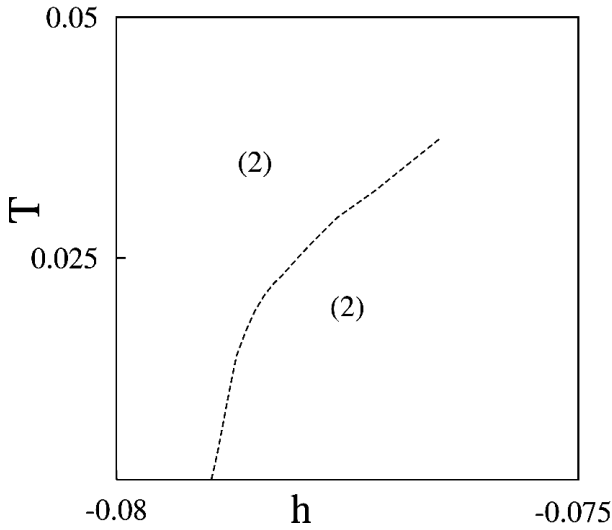
Fig. 5. Phase diagram in the $(T - h)$ plane at $\Omega = 0$. The parameter values are: $g = -0.4$, $W = 1$, $\mu = -0.7$. The notations are the same as in Figs. 1 and 2
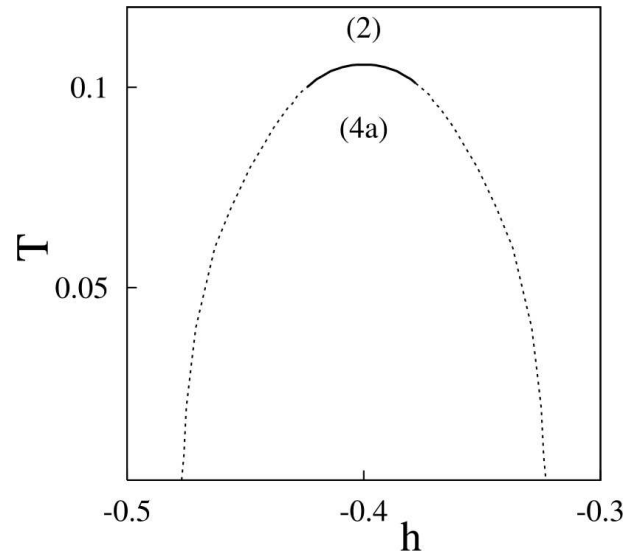

Fig. 7. Phase diagram in the $(T - h)$ plane at $\Omega = 0$. The parameter values are: $g = -0.4$, $W = 1$, $\mu = 0$. The notations are the same as in Figs. 1 and 2
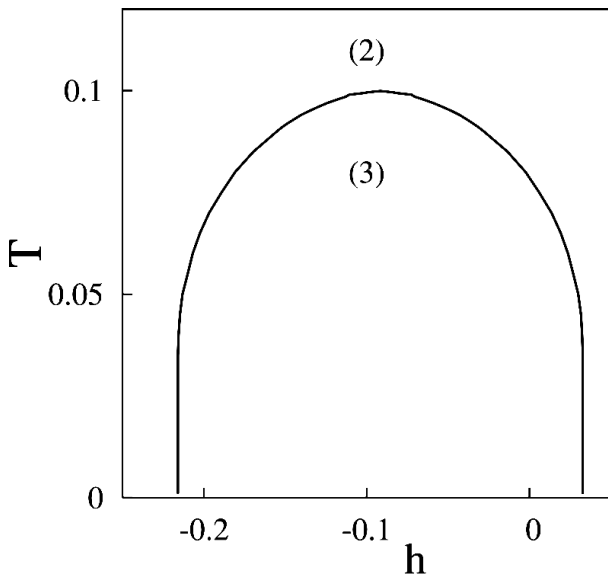

Fig. 6. Phase diagram in the $(T - h)$ plane at $\Omega = 0.2$. The parameter values are: $g = -0.4$, $W = 1$, $\mu = -0.7$. The notations are the same as in Figs. 1 and 2
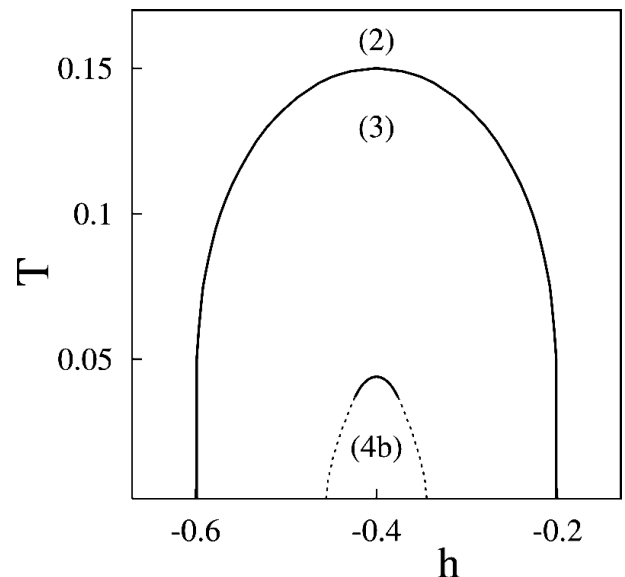

Fig. 8. Phase diagram in the $(T - h)$ plane at $\Omega = 0.3$. The parameter values are: $g = -0.4$, $W = 1$, $\mu = 0$. The notations are the same as in Figs. 1 and 2

This curve ends at the critical point at some value of temperature T_{cr}. At high values of Ω, this phase transition disappears (see Figs. 2 and 6). The existence of such phase transitions (in the regime of a fixed concentration, it corresponds to the phase separation into phases with different concentrations of ions) is in accordance with experimental data for intercalated crystals, where the appearance of poor and rich ion concentration phases

was observed (see, for example, [6]). The presence of a modulated phase in intercalated crystals is also indicated in experiments (for review, see [5]).

The phase transition from the uniform to modulated phase can be of the second or the first order; this is illustrated in Figs. 7 and 8 for the cases $\Omega = 0$ and $\Omega = 0.3$. We should draw attention to the fact that, as the temperature increases, the first-order transition

will transform into the second-order one and then will disappear (as it is shown in Figs. 7 and 8).

4. Conclusions

In this work, a pseudospin-electron model of ion intercalation in crystals has been formulated. The model can be applied for the description of the thermodynamics of such a process in materials with electron bands, where the band filling has metallic or semimetallic character (in particular, compounds of transition metals such as TiO_2 or other similar systems with narrow conduction bands). The thermodynamics of the model has been investigated in the mean-field approximation. The effective interaction between intercalated ions is formed due to their interaction with the electron subsystem. Such an interaction is attractive or repulsive depending on the filling of the electron band (in the first case, the chemical potential of electrons should be close to the band edge; the second case is realized near the half filling). The appearance of a modulated phase or phase transitions of the first order with jumps of the ion and electron concentrations (in the regime of the fixed concentrations, it corresponds to the phase separation) has been established.

An increase of the ion transfer parameter leads to the disappearance of both the modulated phase and the phase transition with jumps of the ion and electron concentrations. In addition, the new phase with $\langle S^x \rangle \neq 0$ appears due to the ion hopping between sites; this phase is an analog to the superfluid phase in the systems of hard-core bosons or the superionic phase in crystalline ionic conductors (the phase with a high mobility of ions). Such a phase can exist at intermediate values of the chemical potential of intercalated ions, and the transition to this phase is of the second order. To investigate this phase in detail, we should examine the behavior of the conductivity and other characteristics of the system. This is the task for future investigations.

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ҐРАТКОВА МОДЕЛЬ ІНТЕРКАЛЯЦІЇ

Т.С. Мисакович, В.О. Краснов, І.В. Стасюк

Р е з ю м е

Досліджено термодинаміку ґраткової моделі інтеркаляції іонів у кристали в наближенні середнього поля. Для опису взаємодії електронів з іонами використано псевдоспіновий формалізм та враховано можливість перескоку іонів між вузлами ґратки. Побудовано фазові діаграми. Показано, що ефективна взаємодія між інтеркальованими іонами може приводити до розділення фаз або до появи модульованої фази (залежно від заповнення електронної енергетичної зони). При достатньо значній інтенсивності іонного переносу підсистема іонів може перейти у стан, подібний до надплинного.