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I.V. Stasyuk, O.V. Velychko

INFLUENCE OF OXYGEN NONSTOICHIOMETRY ON LOCALIZATION OF APEX OXYGENS IN $YBa_2Cu_3O_{7-x}$–TYPE CRYSTALS.

ЛЬВІВ

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Вплив нестехіометрії кисню на розташування апексних киснів в кристалах типу $YBa_2Cu_3O_{7-x}$

І.В. Стасюк, О.В. Величко

Анотація. Особливості термодинаміки апексного кисню у високотемпературних надпровідниках типу $YBa_2Cu_3O_{7-x}$ під впливом вакансій кисню в ланцюгах CuO вивчаються в рамках узагальненої двопідграткової моделі Міцуї. Вплив вакансій моделюється випадковим полем з бімодальним розподілом. Термодинамічні функції моделі отримано в наближенні середнього поля для далекосяжних взаємодій при точному врахуванні внутрішньокоміркової взаємодії псевдоспінів. Система може існувати в нееквівалентних неполярних і полярній фазах, що відповідають різному впорядкуванню апексних киснів. Досліджуються умови появи фазового переходу першого роду між неполярними фазами при $x \neq 0$, який виявляється як ефект структурної бістабільності.

Influence of oxygen nonstoichiometry on localization of apex oxygens in $YBa_2Cu_3O_{7-x}$–type crystals

I.V. Stasyuk, O.V. Velychko

Abstract. The study of specific features of the apex oxygens thermodynamics in the $YBa_2Cu_3O_{7-x}$–type high–T_c superconductors affected by oxygen vacancies in CuO chains is made in the framework of the extended two–sublattice Mitsui model. The influence of vacancies is modelled by a random field with the bimodal distribution. Thermodynamic functions of the model are calculated in the mean field approximation for long–range interactions with an exact treatment of the intracell interaction of pseudospins. The system can have nonequivalent nonpolar phases and the polar one which correspond to different arrangements of apex oxygens. Conditions of appearance of the phase transition between nonpolar phases at $x \neq 0$ which is of the first order and manifests itself as a structure bistability effect are investigated.

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1. Introduction

Already in early works on the $YBa_2Cu_3O_7$ structure an anomalous behaviour of apex oxygens O(4) (namely an elongation of thermal ellipses along the c–axis) was pointed out. For present time various experimental evidences of an apex oxygen anharmonic behaviour exist but its nature is still a matter of discussion.

An indirect evidence can be obtained from works on Raman scattering in $YBa_2Cu_3O_7$, especially those concerning the change of main characteristics of O(4) modes in dependence on a concentration of the chain oxygen O(1). It should be emphasized that the frequency and the width of the O(4) mode strongly depend on oxygen content, history and preparation technique of a sample as well as on a laser excitation beam frequency. There are two main points of view on the apex oxygen mode behaviour. In the held in early works first approach the interpretation of experimental data was based on the assumption that only one apex oxygen mode A_g exists in the region 440–500 cm^{-1} which shifts to lower frequencies when the concentration of vacancies increase and has a maximum width at the intermediate values of x [1–3]. In the last years the another approach was developed basing on the recent experimental data (see for example [4,5]). In its framework the above mentioned behaviour of O(4) mode was interpreted as a superposition of three modes with concentration independent frequencies and widths while their intensities depend on x. These three modes correspond to different O(1) arrangements (in the vicinity of O(4) ions) which realize in different phases. On the Fig. 1 the characteristic regions of O(4) vibration frequencies are presented. The region 498–502 cm^{-1} corresponds to the $x \simeq 0$ (ortho–I phase), 485–490 cm^{-1} — to intermediate concentrations (ortho–II phase), 475–480 cm^{-1} — to $x \simeq 1$ (tetragonal phase).

An attempt to explain the described behaviour of the O(4) mode was made on the early stage of the investigations [6] proceeding from the assumption about the existence of a double–well asymmetric potential for the O(4) ions and the redistribution of the occupation of both possible

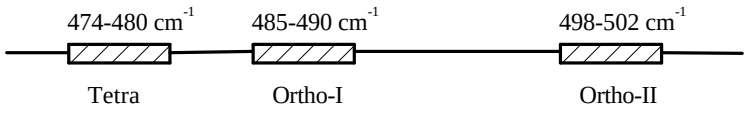

Figure 1. Characteristic frequencies of O(4) Raman active vibrations.

positions at the change of stoichiometry. Authors of the latter works [2–5] hold the similar point of view but they also consider a one–well potential for the apex oxygen with the localization of its minimum defined mainly by the occupation of the nearest O(1) positions in the CuO chains.

EXAFS experiment data for $YBa_2Cu_3O_{7-x}$ crystals also have something in common with the above considerations. According to the works [7–9] the anharmonic behaviour of apex oxygen may be described by a double–well potential (ϕ^4 or double parabola) which best matches the experimental data.

Recent polarized X–ray absorption measurements on photodoped oxygen deficient $YBa_2Cu_3O_{7-x}$ [10] also support conception of the double–well potential. Nevertheless a different interpretation of EXAFS data one can find in the recent work [11]. It was suggested that two possible positions of O(4) are caused by the influence of vacancies and each position corresponds to a one–well potential. A vacancy shifts its nearest O(4) neighbours towards CuO chains and diagonal neighbours towards CuO_2 planes making well known distance 0.1Å between these positions. Such interpretation is consistent with the result of works [12,13] where on the basis of the full potential LAPW method is shown that the apex oxygen has a one–minimum potential. A position of the minimum depends on temperature. Unfortunately a possible dependence of the minimum position on the oxygen stoichiometry was not investigated.

Next a range of works should be mentioned where hysteresis phenomena in the $YBa_2Cu_3O_{7-x}$ were observed during the temperature cycling. For instance it was observed the hysteresis of ultrasonic absorption (in the temperature range 100-350 K [14]) and velocity (50-230 K [14] and a double loop 60-280 K [15]). The distinction between the superconducting sample ($x = 0.05$) and the dielectric one ($x = 0.7$) lies mainly in a shift of the hysteresis temperature range [14]. The hysteresis loops of thermal conductivity for two superconducting samples $x < 0.05$ (90-210 K) and $x = 0.1$ (90-320 K) are also differed by a similar temperature shift [16]. It was reported about a specific heat hysteresis of the superconducting sample ($T_c \simeq 92$ K, 190-230 K) [17]. As a possible origin of the hysteresis a process of ordering of O(1) oxygens in the CuO chains (a variety of transitions between phases Ortho–I, –II, etc.) is considered in the mentioned works. It seems that the apex oxygen rearrangement between two possible positions is a more resonable explanation of these phenomena [18,19].

There is a number of theoretical approaches utilizing conception of two possible positions of apex oxygens. Historically the first one was a one–sublattice pseudospin–electron model concerning an interaction be-

tween electrons and highly anharmonic O(4) vibrations described in the pseudospin formalism [20–24]. An obvious two–sublattice nature of the system demands to a two–sublattice generalization of the model [25]. A pseudospin part of such model corresponds to the Mitsui–type model [26]. In the framework of these models the peculiarities of the electron spectrum are investigated, calculations of the transverse dielectric susceptibility are made and the role of the anharmonic subsystems in the superconductive state appearance is studied. In the work [26] the issue of the possible manifestation of ferroelectric type anomalies and the appearance of a ferroelectric phase at certain conditions is considered for the two–sublattice model.

A different approach was used in the works [18,19] where anharmonic vibrations of apex oxygens in one sublattice were considered in framework of a scalar one component $\phi^3 + \phi^4$ model. The abrupt changes in positions of apex oxygen ions at the change of temperature with a possible metastability phenomena were predicted. On the basis of the obtained results authors proposed a mechanism of the possible structure bistability in the system.

It should be also emphasized that a direct application of the one sublattice $\phi^3 + \phi^4$ model to the $YBa_2Cu_3O_{7-x}$ structure–like compounds is not sufficiently justified. In the framework of this model an ordered state of the anharmonic ions is always polar therefore the jump of the position occupations corresponds to a phase transition between two different polar phases [18]. But in the two–sublattice crystal structure the dipole moments are as a rule compensated. For this reason a picture of possible phase transitions in the system should be more complicated than in the one–sublattice case.

The present paper is aimed for the investigation of a possible redistribution of apex oxygen ion localizations taking into account the real crystal structure and presence of oxygen vacancies in the O(1) positions of nonstoichiometric compounds. On the basis of the mentioned data we consider that any apex oxygen can occupy two possible equilibrium positions in the cell. Investigation is made in the framework of two–sublattice pseudospin Mitsui model with taking into account the influence of a caused by vacancies random field. Thermodynamical functions of the model are calculated and equilibrium states are explored at various values of the model parameters, temperature and the vacancy concentration. Phase diagrams are built and a special attention is payed to the bistability phenomenon manifesting as the first order phase transitions between nonpolar phases with different pseudospins arrangements (what corresponds to different occupations of two oxygen positions). Conditions of realization of the bistability effects in the investigated model are considered.

2. Hamiltonian of the model and vacancy random field

The Hamiltonian of two–sublattice pseudospin model under consideration is as follows

$$\begin{aligned} H &= -\sum_i h_i(S^z_{1i} - S^z_{2i}) - \frac{1}{2}\sum_i\sum_j j_{11}(i,j)(S^z_{1i}S^z_{1j} + S^z_{2i}S^z_{2j}) \\ &\quad -\sum_i\sum_j j_{12}(i,j)S^z_{1i}S^z_{2j} - Ed\sum_i(S^z_{1i} + S^z_{2i}). \end{aligned} \tag{1}$$

Here $S^z_{\alpha i} = \pm\frac{1}{2}$ values of pseudospin z–component corresponds to two possible positions of anharmonic O(4) ion from α sublattice ($\alpha = 1, 2$) in the i–th unit cell. The first term in (1) describes an asymmetry of a double–well potential for O(4) ions; in the pseudospin representation it has a meaning of interaction with some internal field acting on pseudospins of different sublattices of opposite directions. Two next terms describe interactions between pseudospins located in the same and in the different sublattices. The last term describes an interaction of pseudospins with an external field E (here the effective dipole moment d connected with hopping of O(4) ion between its equilibrium positions is introduced; vector $\vec{d}$ is parallel to c axis of crystal).

In the present model the field h_i is random and depends on a unit cell index. It consists of two parts

$$h_i = h + \Delta h_i, \tag{2}$$

where h is an asymmetry parameter in the case of fully oxygenated sample of $YBa_2Cu_3O_{7-x}$ crystal ($x = 0$), Δh_i is an additional term arising due to influence of vacancies. As was mentioned above a caused by vacancies random field has a complicated structure. In the present paper a simple bimodal approximation for the field h_i is used. Namely in the case without vacancies it is equal to h ($h > 0$; both O(4) oxygens are closer to plains CuO_2 — Fig. 2a) and near a vacancy it is equal to h_{vac} ($h_{vac} < 0$; both O(4) oxygens are closer to chains — Fig. 2b).

The random field probability distribution looks like

$$P(h_i) = c\delta(h_i - h) + (1-c)\delta(h_i - h_{vac}) = \sum_{n=1}^{2} p_n\delta(h_i - h_n), \tag{3}$$

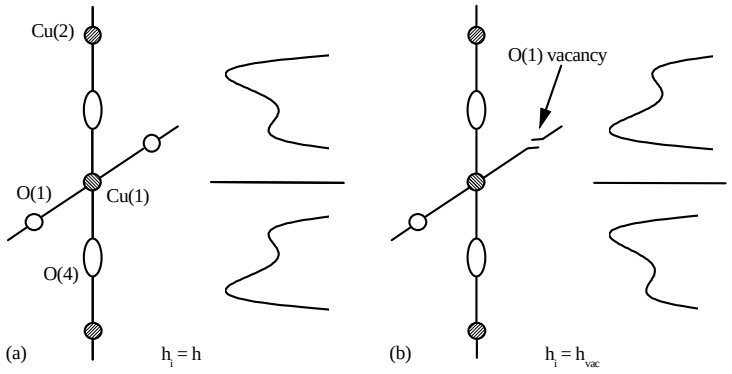

Figure 2. Shape of an O(4) potential well near fully occupied O(1) chains (a) and near an O(1) vacancy (b).

where $p_1 = c$, $p_2 = 1 - c$ and $1 - c = x$ is the concentration of O(1) vacancies. The correlations between random fields on different cells are not included. For this reason such distribution function can be applied in the case of $YBa_2Cu_3O_{7-x}$ at sufficiently small values of x (ortho–I phase, $x < 0.15$), when the ordering processes of vacancies have not yet take place and its distribution is random.

Hence a simple configurational averaging procedure

$$\overline{A(\dots h_i \dots)} = \prod_i \sum_{n_i} p_{n_i} A(\dots h_{n_i} \dots) \tag{4}$$

for calculation of thermodynamic quantities will be used below.

3. Thermodynamic functions in cluster mean field approximation

Phase transitions in the Mitsui model may be analyzed in the mean field approximation (MFA) [27]. As follows from the corresponding phase diagram, with the change of temperature the system can have none, one (of the first or the second order), two of the second order, and even three (in small region) phase transitions depending on the values of parameters. Thus even ordinary Mitsui model exhibits a complicated behaviour.

It is well known that standard MFA gives good results for systems, where a some physical quantity on a site has a large number of identical

interactions, and fails if some interactions become peculiar (e.g. much stronger). In the apex oxygen subsystem an interaction between nearest neighbours from different sublattices is presumed to be significant due to the charge transfer and direct correlations through the common Cu atom [28]. For this reason one should treat this interaction $j_{12}(i,i)$ separately and consider as a basic one a cell formed by nearest pseudospins from different sublattices with the same site index. To do this the basis of four states of the pair of pseudospins in the cell $|S^z_{1i} S^z_{2i}\rangle$ is introduced

$$|1\rangle = |++\rangle, \quad |2\rangle = |+-\rangle, \quad |3\rangle = |-+\rangle, \quad |4\rangle = |--\rangle. \tag{5}$$

As the next step pseudospin variables are expressed in terms of Hubbard operators acting in the space of these states

$$\begin{aligned} S^z_{1i} &= \frac{1}{2}\left(X_i^{11} + X_i^{22} - X_i^{33} - X_i^{44}\right) \equiv \sum_p \alpha_{1p} X_i^{pp}, \\ S^z_{2i} &= \frac{1}{2}\left(X_i^{11} - X_i^{22} + X_i^{33} - X_i^{44}\right) \equiv \sum_p \alpha_{2p} X_i^{pp}. \end{aligned} \tag{6}$$

Now the Hamiltonian (1) looks like

$$H = -\sum_i \sum_p \varepsilon_{ip} X_i^{pp} - \frac{1}{2} \sum_{i \neq j} \sum_{pq} V_{pq}(i,j) X_i^{pp} X_j^{qq} \tag{7}$$

where

$$\begin{aligned} \varepsilon_{ip} &= (\alpha_{1p} - \alpha_{2p}) h_i + \alpha_{1p}\alpha_{2p} j_{12}(i,i), \\ V_{pq}(i,j) &= j_{11}(i,j)\alpha_{1p}\alpha_{1q} + j_{12}(i,j)\alpha_{1p}\alpha_{2q} + \\ &\quad j_{21}(i,j)\alpha_{2p}\alpha_{1q} + j_{22}(i,j)\alpha_{2p}\alpha_{2q}. \end{aligned}$$

Now one can treat intracell interactions exactly and intercell interactions in the MFA (this procedure may be considered as cluster MFA with cluster consisting of two pseudospins). It should be noted that here in the MFA decoupling scheme a full average values (a configurational and thermodynamic averaged variables) are used in the spirit of the work [29]:

$$\begin{aligned} \hat{A}_i \hat{B}_j &= \left(\overline{\langle A \rangle} + (\hat{A}_i - \overline{\langle A \rangle})\right)\left(\overline{\langle B \rangle} + (\hat{B}_j - \overline{\langle B \rangle})\right) \simeq \\ &\quad \overline{\langle A \rangle}\hat{B}_j + \overline{\langle B \rangle}\hat{A}_i - \overline{\langle A \rangle}\,\overline{\langle B \rangle}; \end{aligned}$$

the notation $\langle \dots \rangle$ is used for the thermodynamic averaging procedure. For convenience the Hamiltonian is expressed in dimensionless quantities by normalization of all relevant terms on $j_{12}(0) + j_{11}(0)$. Then the

Hamiltonian in the MFA is as follows

$$H_{MFA} = \frac{1}{2}N\sum_{pq}\tilde{V}_{pq}(0)\overline{\langle X^{pp}\rangle}\,\overline{\langle X^{qq}\rangle} - \sum_{i}\sum_{q}\lambda_{iq}X_i^{qq} \tag{8}$$

where nonvanishing elements of $\tilde{V}_{pq}(0)$ are

$$\begin{aligned}\tilde{V}_{11}(0) = \tilde{V}_{44}(0) = \tfrac{1}{2},\ \tilde{V}_{14}(0) = \tilde{V}_{41}(0) = -\tfrac{1}{2},\\ \tilde{V}_{23}(0) = \tilde{V}_{32}(0) = \tfrac{1}{2}a,\ \tilde{V}_{22}(0) = \tilde{V}_{33}(0) = -\tfrac{1}{2}a;\end{aligned} \tag{9}$$

and $\lambda_{iq} = \tilde{\varepsilon}_{iq} + \sum_p \tilde{V}_{pq}(0)\overline{\langle X^{pp}\rangle}$:

$$\begin{aligned}\lambda_{i1} &= \frac{1}{4}j + Ed + \eta, \qquad \lambda_{i4} = \frac{1}{4}j - Ed - \eta,\\ \lambda_{i2} &= -\frac{1}{4}j + h_i - a\xi, \quad \lambda_{i3} = -\frac{1}{4}j - h_i + a\xi,\end{aligned} \tag{10}$$

where

$$\begin{aligned}\eta = \tfrac{1}{2}(\langle S_1^z\rangle + \langle S_2^z\rangle),\ \xi = \tfrac{1}{2}(\langle S_1^z\rangle - \langle S_2^z\rangle),\\ a = \frac{j_{12}(0) - j_{11}(0)}{j_{12}(0) + j_{11}(0)},\ j = \frac{j_{12}(i,i)}{j_{12}(0) + j_{11}(0)}.\end{aligned} \tag{11}$$

The MFA Hamiltonian consists of a static part and an effective single site part where λ_{iq} are its eigenvalues. The parameters η, ξ and a are introduced, where η is the order parameter describing the ferroelectric like state with nonzero total dipole (pseudospin) moment appearing due to decompensation ($\langle S_1^z\rangle \neq -\langle S_2^z\rangle$) of sublattice dipole momenta.

It is obvious that configurationally unaveraged variables η_i and ξ_i in the particular cell i can take on two possible values according to a value of the random field h_i in the cell. They can be expressed by means of selfconsistency equations

$$\begin{aligned}\eta_n &= \frac{1}{2}\left[\exp(\beta\lambda_{n1}) - \exp(\beta\lambda_{n4})\right]\left[\sum_{k=1}^{4}\exp(\beta\lambda_{nk})\right]^{-1},\\ \xi_n &= \frac{1}{2}\left[\exp(\beta\lambda_{n2}) - \exp(\beta\lambda_{n3})\right]\left[\sum_{k=1}^{4}\exp(\beta\lambda_{nk})\right]^{-1},\end{aligned} \tag{12}$$

where $n = 1, 2$. After the configurational averaging equations (12) give a set of simultaneous equations for variables η and ξ

$$\begin{cases}\eta = \sum_n p_n\eta_n\\ \xi = \sum_n p_n\xi_n.\end{cases} \tag{13}$$

Equations (12) can be recast as

$$\begin{aligned}\eta_n &= \frac{1}{4}\frac{\left(1 + \tanh(\frac{\beta}{4}j)\right)\left(\tanh(\frac{\beta}{2}k_{n1}) + \tanh(\frac{\beta}{2}k_{n2})\right)}{1 + \tanh(\frac{\beta}{4}j)\tanh(\frac{\beta}{2}k_{n1})\tanh(\frac{\beta}{2}k_{n2})}\\ \xi_n &= \frac{1}{4}\frac{\left(1 - \tanh(\frac{\beta}{4}j)\right)\left(\tanh(\frac{\beta}{2}k_{n1}) - \tanh(\frac{\beta}{2}k_{n2})\right)}{1 + \tanh(\frac{\beta}{4}j)\tanh(\frac{\beta}{2}k_{n1})\tanh(\frac{\beta}{2}k_{n2})},\end{aligned} \tag{14}$$

where $k_{n1} = \eta + h_n - a\xi, \quad k_{n2} = \eta - h_n + a\xi$. In the case $j = 0$ equations (14) pass into well-known equations of the Mitsui model in the ordinary MFA [27]. In further calculations the equations are used in the form (12) because it is more convenient for numerical calculations.

As a rule the set of simultaneous equations (13) has several solutions. It is necessary to take those of them, which corresponds to the minimum value of the free energy F of the system

$$F = \eta^2 - a\xi^2 - \frac{1}{\beta}\sum_n p_n \ln\left\{\sum_{k=1}^{4}\exp(\beta\lambda_{nk})\right\}. \tag{15}$$

The free energy can be expressed also in the following equivalent form

$$\begin{aligned}F &= \eta^2 - a\xi^2 - \frac{1}{\beta}\sum_n p_n \ln\left\{4\left[\cosh(\frac{\beta}{4}j)\cosh(\frac{\beta}{2}k_{n1})\cosh(\frac{\beta}{2}k_{n2})\right.\right.\\ &\left.\left. + \sinh(\frac{\beta}{4}j)\sinh(\frac{\beta}{2}k_{n1})\sinh(\frac{\beta}{2}k_{n2})\right]\right\}.\end{aligned}$$

Proceeding from the expression for the free energy one can derive the static dielectric susceptibility

$$\begin{aligned}\chi &= -\frac{\partial^2 F}{\partial E^2}_{|E=0} =\\ &= \beta d^2\left\{\left(\exp(\beta\lambda_1) + \exp(\beta\lambda_4)\right)\sum_n p_n\left(\sum_{k=1}^{4}\exp(\beta\lambda_{nk})\right)^{-1}\right.\\ &\left. - \left(\exp(\beta\lambda_1) - \exp(\beta\lambda_4)\right)^2\sum_n p_n\left(\sum_{k=1}^{4}\exp(\beta\lambda_{nk})\right)^{-2}\right\},\end{aligned} \tag{16}$$

which describes the ionic (connected with the redistribution of O(4) ions) part of dielectric response of the system under consideration in the c axis direction.

With use of obtained from the equation set (13) η and ξ values one can investigate possible ordered phases of the system and phase transitions between them which depend on temperature, concentration c, fields h and h_{vac} etc. and plot appropriate phase diagrams.

4. Numerical calculations

The ordinary Mitsui model has two phases (see for example Fig. 3a): polar (when average pseudospin projections from different sublattices are antiparallel but mutually noncompensated) and nonpolar (when they are mutually compensated). A new feature of the considered here model with random field h_i is a possible existence of nonequivalent nonpolar phases (average projections of pseudospins in different sublattices are opposite but directed in different ways: $|\uparrow\downarrow\rangle$ or $|\downarrow\uparrow\rangle$ what corresponds to opposite signs of the average ξ and different arrangements of apex oxygens). At variation of the model parameter values the system can have various phase transitions between nonpolar phases and the polar one or, under a certain conditions, directly between nonpolar phases. It can be demonstrated on the "critical temperature Θ_c — internal field h" phase diagram.

The phase diagram of the ordinary Mitsui model is symmetrical with respect to the change of the sign of the h field (Fig. 3a). A phase transition between phases is mainly of the first order except a small region on the top of the diagram where it is of the second order. For the system with the bimodal random field the phase diagram becomes asymmetric and at low temperatures two nonpolar phases with the polar one between them can occure (Fig. 3b). For a strong enough negative value

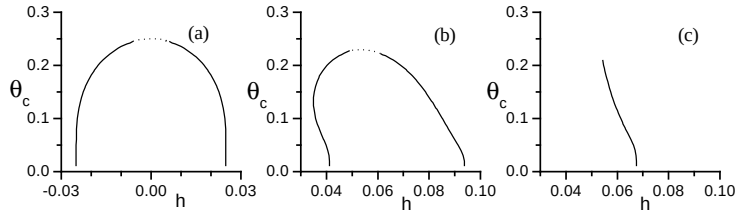

Figure 3. The transition temperature Θ_c as a function of the field h: a) $c = 0$, $j = 0$; b) $c = 0.85$, $j = 0$; c) $c = 0.85$, $j = -0.05$. Values of other parameters are $a = -0.9$, $h_{vac} = -0.4$. Solid line corresponds to the first order phase transition, dashed line — to a second order one.

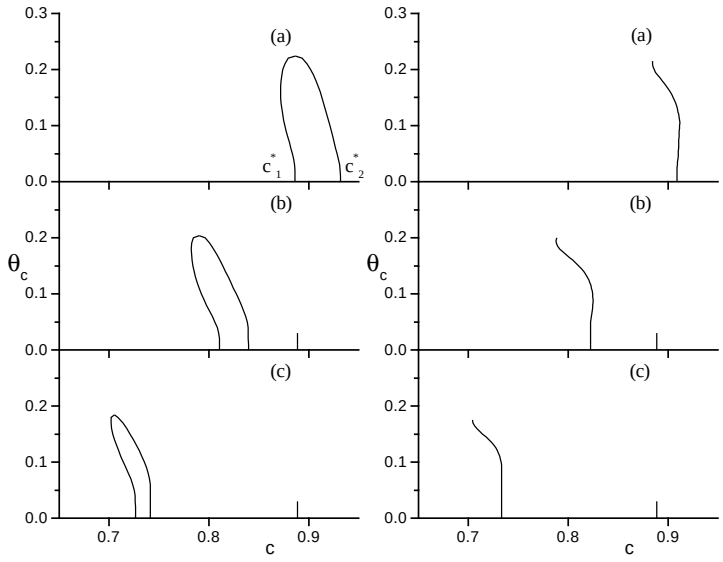

Figure 4. The transition temperature Θ_c as a function of the concentration c at various values of parameters a (on the left panel $j = -0.03$; on the right panel $j = -0.05$) and h (a) $h = 0.04$; b) $h = 0.08$; c) $h = 0.12$). Values of other parameters are $a = -0.9$, $h_{vac} = -0.4$.

of the intracell interaction parameter j the polar phase disappeares and the direct phase transition between nonpolar phases is possible (Fig. 3c). This is a specific feature of the Mitsui model with the random field taking values of different signs. The polar phase differs from the nonpolar one qualitatively because they correspond to different symmetry of the system. They are separated by a first or second order phase transition line on the phase diagram. Nonpolar phases are of identical symmetry and differ only quantitatively. Thus only first order phase transition ending at the critical point, where this difference vanishes, are possible between them and not the average ξ but its deviation $\Delta\xi = \xi - \xi_c$ from the value at the critical point has the meaning of a Landau order parameter.

Depending on values of the system parameters the phase diagram can undergo qualitative changes. The region of existence of the polar phase narrows not only when j becomes negative but also at $a \to -1$ and finally as it has mentioned above a line of a first order phase transition between nonpolar phases appears instead (Fig. 4). Depending on values of fields h and h_{vac} one (Fig. 4a) or two (Fig. 4b,c) regions of polar

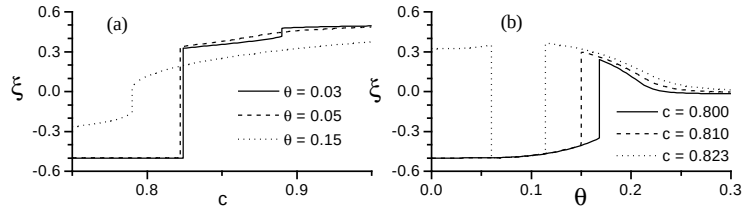

Figure 5. Dependence of ξ on the concentration c at various temperatures Θ (a) and on the temperature Θ at various concentrations c (b) in the phase transition region. Values of other parameters are $j = -0.05$, $a = -0.9$, $h = 0.08$, $h_{vac} = -0.4$.

phases (or lines of the first order phase transition) can exist. A case, when at temperature $\Theta = 0$ two nonpolar phases exist and the average ξ is equal $-\frac{1}{2}$ ($c < c^*$) or $\frac{1}{2}$ ($c > c^*$), is shown on the Fig. 4a. Increase of the field h value leads to appearance between them an intermediate nonpolar phase with $\xi = c - \frac{1}{2}$. Analysis of the phase diagram at $\Theta = 0$ and numerical calculation indicate that increase of h at the fixed value of h_{vac} extends the distance between phase transition regions (Fig. 4b,c).

As mentioned before the average ξ corresponds to arrangement of apex oxygens further from or closer to CuO chains. Plots of $\xi(c)$ at various temperatures Θ (Fig. 5a) demonstrate a smooth behaviour except the regions of phase transitions. Plots of $\xi(\Theta)$ at various concentrations c (Fig. 5a) confirm this assertion. Thus there is a region of the chain oxygen concentration where change of concentration or temperature causes a sharp rearrangement of apex oxygens. In this region the dielectric susceptibility χ of the system also has peaks or abrupt jumps (Fig. 6). It is obvious that the increasing of temperature reduces jumps of ξ and χ.

It should be stressed that the regions of c and h values, where phase transitions are possible at a certain temperature, are narrow (Fig. 7). A subsequent increase of an absolute value of the parameter a strengthens the acting on pseudospins mean field. As a result a concentration region, where the phase transition exists, narrows what is ilustrated on the Fig. 8a at $j = 0$ and $a < -1$ ($j_{12} < 0$). Increase of the parameter j absolute value has a similar but slightly different influence on the shape of the phase diagram (Fig. 8b); in the real system the phase instability region should be wider due to a hysteresis phenomena.

A similar bistable behaviour was obtained in the works [18,19] where

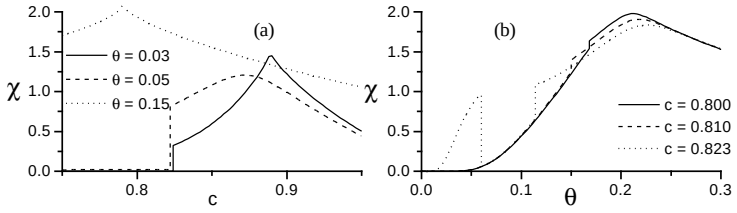

Figure 6. Dependence of the dielectric susceptibility χ on the concentration c at various temperatures Θ (a) and on the temperature Θ at various concentrationc c (b) in the phase transition region. Values of other parameters are $j = -0.05$, $a = -0.9$, $h = 0.08$, $h_{vac} = -0.4$.

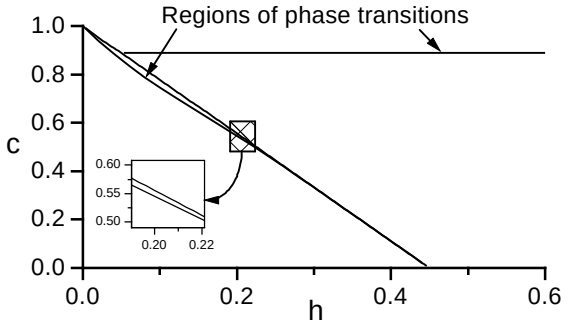

Figure 7. Region where a first order phase transition between nonpolar phases is possible (most of subregions are of a line width in the picture scale). Values of other parameters are $j = -0.05$, $a = -0.9$, $h_{vac} = -0.4$.

the apex oxygen subsystem was studied in the framework of a scalar one–component $\phi^3 + \phi^4$ model. In spite of succesfull explanation of some $YBa_2Cu_3O_{7-x}$ properties (a step–like behaviour and abrupt jumps of the transition temperature T_c into the superconducting state at variation of the chain oxygen contents, temperature hysteresis phenomena) the model has an obvious shortcoming originated from its one sublattice nature. For this reason in terms of pseudospin representation only polar phases and phase transitions between them are possible (i.e. $\langle S^z \rangle \neq 0$ always due to presence of the asymmetry field h). As one could see the considered in present paper two–sublattice model is more realistic and describes a wider variety of phases and phase transitions.

Another question is how to take into account the influence of oxygen

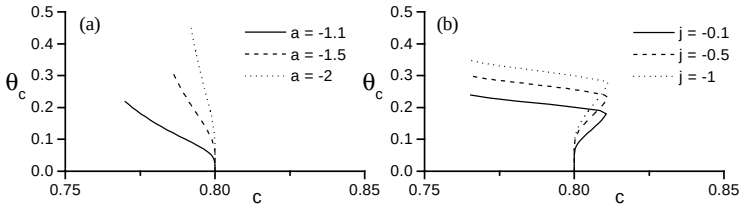

Figure 8. The transition temperature Θ_c as a function of the concentration c at various values of parameters a at $j = 0$ (a) and j at $a = -1.1$ (b). Values of other parameters are $h = 0.1$, $h_{vac} = -0.4$.

vacancies on the shape of an apex oxygen potential well. In the work [18] two types of the potential well which correspond to different values of x were considered but x–depending probability of their occurencies was calculated in rather sophisticated percolation approach. In the work [19] unlike [18] only one x–depending shape of the potential well was considered i.e. a set of existing different shapes at specified x was substituted by one "averaged" shape. The adopted here random field approach seems to be more appropriate for description of the influence of oxygen vacancies.

A certain shortcoming of our model is a "frozeness" of the chain oxygen subsystem. In this case the configurational averaging over the distribution of random field is performed. It is well known that oxygens O(1) in $YBa_2Cu_3O_{7-x}$ are movable enough and form phases with various arrangements (tetra, ortho–I, –II etc.). One can consider the model in which the chain oxygen ions subsystem is in statistical equilibrium and these ions interact one with another [1]. In this case the intermediate phase (Fig. 4b,c) may correspond to a phase separation region. This conclusion can be drawn on the basis of the results of the pseudospin–fermion model investigation [31].

In the framework of the investigated here model an influence of the applied to a sample external pressure on the O(4) oxygens arrangement can be considered. It is natural to suppose that value of the asymmetry field h can be changed by applying of pressure p. The (T, h) phase diagram where the phase transition with a jump of ξ parameter takes place is shown on the Fig. 3c. It should be noted that at variation of the

[1] Such approach without consideration of the interaction with anharmonic O(4) ions (pseudospins) is used usually at the description of vacancy ordering phenomena in $YBa_2Cu_3O_{7-x}$ (see for example [30])

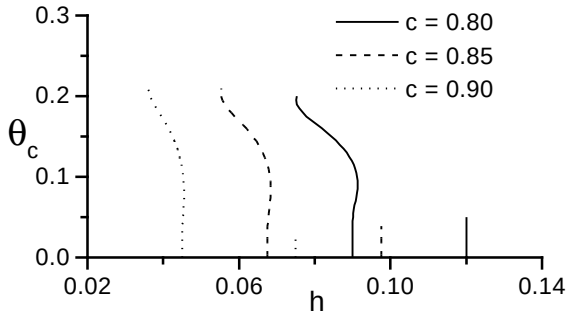

Figure 9. The transition temperature Θ_c as a function of the field h at the field $h_{vac} = h + \Delta h$, $\Delta h = -0.48$ and different values of the concentration. Values of other parameters are $j = -0.05$, $a = -0.9$.

concentration c one can pass through two regions of phase transitions while at variation of the field h there is only one such region (see Fig. 7). The change of the h field value (at the fixed h_{vac}, j and a) leads to a shift of vacancy concentration region where a bistability in apex oxygen subsystem is possible. Alternatively, utilizing the fact that a distance between apex oxygens and CuO chains practically does not depend on pressure (see for example [32]) one may assume that the vacancy induced change of the asymmetry field Δh ($\Delta h = h_{vac} - h$) does not depend on pressure too. Phase diagrams obtained in this case are presented on the Fig. 9.

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Стасюк Ігор Васильович
Величко Олег Володимирович

Вплив нестехіометрії кисню на розташування апексних киснів в кристалах типу $YBa_2Cu_3O_{7-x}$

Роботу отримано 30 вересня 1998р.

Затверджено до друку Вченою радою ІФКС НАН України

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