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A Cluster Variation Method Approach to the Problem of Low-Temperature Statistics of a Class of Ising Models

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We Study the low-temperature thermodynamical and statistical properties of the ASYNNNI model, used to describe oxygen ordering in $YBa_2Cu_3O_{6+2c}$. Analyzing the excited states we show that this model undergoes a second order phase transition at absolute zero temperature. From the divergence of the relative energy fluctuations, in the limit $T \to 0$, we deduce that for $T \approx 0$ the deviation of the chemical potential μ from its ground state value is linearly related to the partial derivative of the fraction of threefold coordinated Cu(1) ions n with respect to oxygen concentlation c. We use the cluster variation method (CVM) to determine the numerical value of the coefficient of this relation and find that it is equal to $-1/2$, independently of the values of the interaction parameters. This establishes a full equivalence between the ASYNNNI model and the one-dimensional Ising model, where the role of the nearest-neighbor interaction of the latter is played by the V_2 interaction in the former. We comment on the general applicability of low levels of the CVM approximation to systems equivalent to the one-dimensional Ising model.

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1. Introduction

The superconducting properties of the $YBa_2Cu_3O_{6+2c}$ high-T_c superconductor depend not only on oxygen content c but also on the degree of oxygen ordering in different structural phases. To understand this phenomenon and to analyze the oxygen ordering in the basal plane the two-dimensional asymmetric next-nearest-neighbor Ising (ASYNNNI) model was proposed.[1,2)] The thermodynamic and statistical properties of this model have been extensively studied within the last several years. All significant structural characteristics of the material have by now successfully been explained in terms of the ASYNNNI model. In particular, the only three structural phases, unmistakably confirmed in experiments, *i.e.* tetragonal, orthorhombic I (OI), and orthorhombic II (OII), are included in the model as ground states.

The Hamiltonian of the ASYNNNI model has the form:

$$H = V_1 \sum_{NN} \sigma_i \sigma_j + V_2 \sum_{NNN}{}' \sigma_i \sigma_j + V_3 \sum_{NNN}{}'' \sigma_i \sigma_j - \frac{\mu}{2} \sum_i \sigma_i, \tag{1}$$

where σ_i denotes the Ising spin variable of the lattice site i and takes the value $+1$ (-1) if the lattice site i is occupied (not occupied) by an oxygen atom. Summation is over the nearest-neighbor (*NN*) and next-nearest-neighbor (*NNN*) oxygen sites, $\sum'$ denotes that the summation is over all *NNN* oxygen sites with a Cu ion in between while $\sum''$ represents a sum over *NNN* sites without an intervening Cu ion. Finally, μ denotes oxygen chemical potential. The interaction parameters V_1 (*NN*) and V_3 (*NNN*) are assumed to be positive (repulsive) while the copper mediated O–O interaction V_2 is negative (attractive). This choice of parameters ensures stability of the main orthorhombic phases[1)] and is consistent with the result of first-principles calculations. The thermodynamics of the ASYNNNI model has been studied by a number of different techniques, such as the cluster variation method,[3–11)] Monte Carlo simulations,[12–17)] and transfer matrix renormalization group methods.[15,18,19)] Almost all important properties of the phase diagram are well-known, but some aspects of the low-temperature thermodynamics are still not elucidated to a satisfying degree. Although these low temperature equilibrium structures are not attainable in experiments (either because of sluggish oxygen diffusion or because further neighbor interactions may become significant at low temperatures) the problem of the low-temperature statistics of the model is far from being of purely academic importance. It has been proposed recently that some low-temperature characteristics are retained up to those higher temperatures that are experimentally attainable.[20)] It is therefore important to explain the nature of the ASYNNNI model in the region of low temperatures. Moreover, the results are interesting in their own right as they shed light on the properties of two-dimensional Ising models, a subject of fundamental interest in statistical physics.

2. Basic Thermodynamic Functions of the ASYNNNI Model at Low Temperature

The basal plane of $YBa_2Cu_3O_{6+2c}$ is represented in Fig. 1 together with the pair interactions considered in the ASYNNNI model. As is known,[1,2)] at $T = 0$ and for $0 < c < 1/2$, the basal plane lattice contains infinite Cu–O chains located on columns of α sites (Fig. 1). In contrast, β sites are completely unocupied due to the NN repulsion $V_1 > 0$. The α columns can be either completely occupied or completely empty depending on the value of oxygen concentration c. The OII phase, in which every second α column is occupied (α_1) and the remaining columns (α_2) are empty, is

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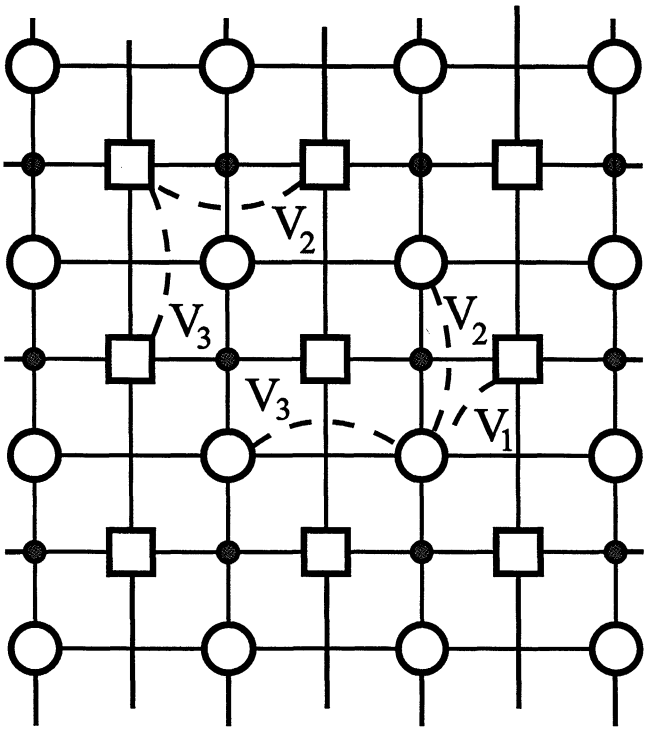

Fig. 1 The basal plane lattice of $YBa_2Cu_3O_{6+2c}$. Open circles and squares denote oxygen sites on α and β sublattices, while small black circles represent Cu(1) ions. V_1 (NN), V_2 (NNN) and V_3 (NNN) are the pair interaction constants of the model.

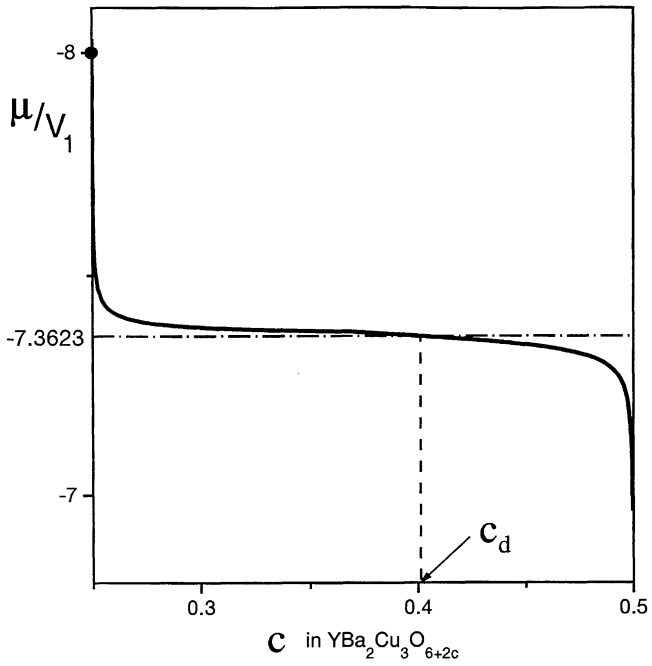

Fig. 2 Chemical potential μ (in units of V_1) as a function of oxygen concentration c at constant temperature $\tau \equiv k_B T/V_1 = 0.23 = const.$ Calculations were made in the 5+4 point approximation of the CVM and for the LMTO values[30] of interaction constants $V_2 = -0.37V_1$, $V_3 = 0.17V_1$.

stable for $c = 1/4$ owing to the repulsive V_3 interaction.[1,2] For $c = 1/2$ all α sites are occupied corresponding to the OI structural phase. It should be noted that in equilibrium at $T = 0$ no chain ends can be present in the system, *i.e.* all the chains are intact (infinite). The ground state energy as a function of oxygen concentration c is given by:

$$\frac{1}{N}E_0(c) = -2V_1(4c-1) + V_2 \mp V_3(4c-1), \qquad (2)$$

where the upper sign corresponds to $0 < c < 1/4$ and the lower to $1/4 < c < 1/2$.

The thermodynamics of the ASYNNNI model at low temperatures is determined by the energy and degeneracy of the excited states. It is known[9–11] that the excited states of the ASYNNNI model are characterized by an alternation of Cu–O chains of finite length and empty segments along the α columns. For a given oxygen concentration c and temperature T ($T \approx 0$), the equilibrium occupancies c_1 and c_2 of the sublattices α_1 and α_2, and the lengths of the Cu–O chains are determined by the minimum condition on the free energy. The chains and empty segments can glide almost freely along the α columns without any change in total energy, the only limitation being that no two empty segments (on two adjacent α columns) can even partially be positioned against one another, because $(-, -)$ V_3 bonds between α sites are not allowed in the excited states.[9–11] Denoting by N_s the number of oxygen sites on one α column, at finite temperatures the square of the average magnetization $M_\alpha = (1/N_s)\sum_{i=1}^{N_s}\sigma_i$ equals to $(2c_1-1)^2$ on an α_1 column, and $(2c_2-1)^2$ on an α_2 column, while $M_\alpha^2 = +1$ at absolute zero temperature. Such a 'sudden' jump of the sublattice magnetization indicates that the model undergoes a second order phase transition at absolute zero. For a given concentration c, the excited states differ from the ground state only in that some of the like V_2 bonds are transformed into unlike V_2 bonds. Thus, at $T \approx 0$, the energy has the form:[9–11]

$$\frac{1}{N}E(c, T) = \frac{1}{N}E_0(c) + |V_2|n(c, T). \qquad (3)$$

Here $n(c, T)$ denotes the fraction of 3-fold coordinated Cu(1) ions (located in the middle of unlike V_2 bonds).

From eq. (2) we see that at $T = 0$ the chemical potential $\mu = (1/N)\partial E_0(c)/\partial c$ equals $\mu_1 = -8V_1 - 4V_3$ for $0 < c < 1/4$, and $\mu_2 = -8V_1 + 4V_3$ for $1/4 < c < 1/2$. At low temperatures the chemical potential attains values that are very close to μ_1, or to μ_2, away from the stoichiometric values $c = 1/4$ and $c = 1/2$. The transition between these two μ values takes place in a narrow interval arround the OII stoichiometry $c = 1/4$. At exactly this concentration the chemical potential equals $-8V_1 = (\mu_1 + \mu_2)/2$. Likewise at the OI stoichiometry $c = 1/2\mu = 0$. The results of CVM calculations are shown in Fig. 2. We see that the chemical potential indeed varies from $-8V_1$ to 0, when the concentration c increases from 1/4 to 1/2, whereas it is approximately equal to its ground state value μ_2 in a wide range of oxygen off-stoichiometry. Moreover, the chemical potential μ differs from μ_2 only within very narrow intervals around $c = 1/4$ and $c = 1/2$, while it attains exactly the value μ_2 for some value of concentration marked with c_d in Fig. 2. A similar behavior of the $\mu(c)$ dependence has also been obtained for $0 < c < 1/4$ and for other sets of interaction parameters V_1, V_2, and V_3. For the sake of simplicity we shall confine our further analysis to the case $1/4 < c < 1/2$.

From the basic thermodynamic relation $\mu = \partial f/\partial c$ (where f denotes the free energy per site) and taking into account

eq. (3) it follows that, at $T \approx 0$ and for $c = c_d$, one has:

$$\mu_2 \equiv \frac{\partial f}{\partial c} = \frac{1}{N}\frac{\partial E_0(c)}{\partial c} + |V_2|\frac{\partial n}{\partial c}\bigg|_{c=c_d} - T\frac{\partial s}{\partial c}\bigg|_{c=c_d}, \quad (4)$$

where s denotes the entropy per lattice site. Since the first term in the right-hand side of the above equation is equal to μ_2, we obtain:

$$\frac{\partial s}{\partial c}\bigg|_{c=c_d} \approx \frac{|V_2|}{T}\frac{\partial n}{\partial c}\bigg|_{c=c_d}, \quad (5)$$

where δc and δn denote small increments in concentration and in the number of 3-fold coordinated Cu(1) ions, around the value c_d. In the excited states of the system, for $1/4 < c < 1/2$, two types of unoccupied oxygen sites on the α sublattice can be distinguished with respect to the change of energy obtained when the sites are filled with an oxygen atom. The first type (denoted by A) corresponds to vacant oxygen sites located in the ends of empty segments; placing an oxygen atom on such a site produces a change in energy $\Delta E_A = -8V_1 + 4V_3 \equiv \mu_2$. The second type (denoted by B) corresponds to vacant oxygen sites located within empty segments on α columns; filling such a site with an oxygen atom produces an energy change $\Delta E_D = -8V_1 - 4V_2 + 4V_3$. If w_A and w_B denote the probabilities that oxygen atoms are added on sites A and B, then we can write for the increment of the concentration: $\delta c = \delta c_A + \delta c_B = w_A\delta c + w_B\delta c$ (where $w_A + w_B = 1$). Since only oxygen atoms added on sites B lead to the creation of new chain ends it follows that $\delta n = w_B\delta c$ and thus eq. (5) transforms into:

$$\frac{\partial s}{\partial c}\bigg|_{c=c_d} = |V_2|\frac{w_B}{T}. \quad (6)$$

In this equation the probability w_B generally depends on temperature. Moreover since the right-hand side of eq. (6) must remain finite as T approaches zero (third law of thermodynamics[21]), it follows that $w_B \to 0$ as $T \to 0$, *i.e.* for $c = c_d$ all oxygen atoms are added on chain ends ($\delta c = \delta c_A$ because $w_B \approx 0$ and $w_A \approx 1$ at $c = c_d$). This implics that at $T \approx 0$ both the entropy per site and the fraction of 3-fold coordinated Cu(1) ions attain their maximal values at the concentration $c = c_d$ (when they are considered as functions of oxygen concentration c at fixed $T = \approx 0$).

Taking into account that at $T \approx 0$ both quantities $\Delta\mu \equiv \mu(c, T) - \mu_2$ and $n_c' \equiv \delta n(c, T)/\partial c$ equal zero for $c = c_d$, we expand $\Delta\mu$ in a Taylor scries with respect to n_c' around the value c_d. Thus, we can write $\Delta\mu = a(T)n_c' + b(T)(n_c')^2 + \cdots$ where the expansion coefficients depend only on temperature. Since $\Delta\mu$ is small for a wide range of oxygen off-stoichiometries (see Fig. 2) we retain only the first term of the series. Since the coefficient $a(T)$ depends only on temperature, we also expand it in a Taylor series arround absolute zero, i.e. $a(T) = a_0 + a_1k_BT + \cdots$ (where k_B denotes the Boltzmann constant). Hence, for the chemical potential $\mu(c, T)$ at low temperatures we finaly obtain:

$$\mu(c, T) \approx \mu_2 + (a_0 + a_1k_BT)n_c'. \quad (7)$$

From eqs. (3) and (7) the expression for the entropy per site can be obtained as follows. Consider an isothermal reversible process at a (constant) low temperature between two states with concentrations c_a and c_b (for the sake of simplicity, we assume $1/4 < c_a < c_b < 1/2$). The change of the free energy per site equals $\Delta f = \int_a^b \mu(c, T)\,dc$, but it also obeys: $\Delta f = (1/N(E_b - E_a) - T(s_b - s_a)$. Inserting eqs. (3) and (7) into the expression for Δf, we obtain:

$$s(c, T) = \frac{1}{T}[|V_2| - a_0 - a_1k_BT]n(c, T). \quad (8)$$

From eqs. (3) and (8) we see that, at low temperatures, the two basic thermodynamic functions of the ASYNNNI model, the energy and the entropy, are proportional to the fraction of 3-fold coordinated Cu(1) ions. Moreover, from eqs. (7) and (8) it follows that the low-temperature thermodynamics also depends on two constants a_0 and a_1. However, the temperature dependence of the fraction $n(c, T)$ is also determined through these two constants which can be shown using the basic thermodynamic relations $C_c = T\partial S/\partial T$ and $C_c = \partial E/\partial T$ (C_c stands for the heat capacity at fixed oxygen concentration). Combining these two relations we arrive at the following differential equation for the fraction $n(c, T)$:

$$\frac{dn(c, T)}{n(c, T)} = \frac{(a_0 - |V_2|)\,dT}{T(a_0 + a_1k_BT)}. \quad (9)$$

From the above equation it becomes evident that the fraction $n(c, T)$ can be expressed as a product $n(c, T) = \Theta(c)\Phi(T)$. The solution of the differential eq. (9) has the form:

$$n(c, T) = \Theta(c)\left(\frac{a_1k_BT}{a_0 + a_1k_BT}\right)^{1-\frac{|V_2|}{a_0}}. \quad (10)$$

We now analyze the relative fluctuations of the energy in the neighborhood of absolute zero temperature in order to show that the constant a_0 must be equal to zero. If the energy of the system under study is measured from its ground state value, *i.e.* $E' = E - E_0$, then we have for the relative fluctuations of the energy (see, for example, Ref. 22)):

$$\frac{k_BT^2C_c}{E'^2} = \frac{\langle E'^2\rangle - \langle E'\rangle^2}{E'^2}. \quad (11)$$

Generally, the relative energy fluctuations diverge as $T \to 0$ due to the third law of thermodynamics. To show this, let us observe that (as has been noted, for example, by Landau and Lifshitz[21]) in the majority of model systems the entropy at low temperature depends on temperature according to a power law $S \propto T^m$, which implies $C_c \propto T^m$ and $E' \propto T^{m+1}$ (m denotes a positive quantity). For such systems $TC_c \approx \text{const} \times E'$ at $T \approx 0$ and, consequently, the behavior of the left-hand side of eq. (11) is determined by the behavior of the ratio k_BT/E' for which we find (applying L'Hôpital's rule) $k_BT/E' \propto 1/C_c \to \infty$, as $T \to 0$. The last relation follows from the Nernst principle[21] ($C_c \to 0$, as $T \to 0$).

However, since the ASYNNNI model exibits a phase transition at $T = 0$ the left-hand side of eq. (11) must be characterized by a stronger divergence than that which follows solely from the third law of thermodynamics. The only physically acceptable way to obtain such divergence is to assume:

$$\lim_{T\to 0}\frac{T^2C_c}{E'} = \text{const} \neq 0. \quad (12)$$

For all other possible relations between the quantities T, E', and C_c it can be shown[23] that they are, either unphysical

or included in the case $S \propto T^m$. That the above condition ensures a stronger divergence of the relative energy fluctuations can be directly seen by comparing the ratios $k_B T/E'$ and const$/E'$ (in the limit $T \to 0$). Using eqs. (3) and (10) we obtain that the ratio in the left-hand side of eq. (12) attains the form (note that from eq. (3) one has: $E'/N = |V_2| n(c, T)$):

$$\frac{T^2 n'_T(c, T)}{n(c, T)} = \frac{a_0 - |V_2|}{a_1 k_B + \dfrac{a_0}{T}}. \tag{13}$$

From the above equation we see that, if $a_0 \neq 0$, the expression in the right-hand side becomes arbitrarily small if the temperature is low enough. Thus, we conclude that the condition (12) will be fullfilled if and only if $a_0 = 0$. In order to obtain the correct expression for the fraction $n(c, T)$ for the case $a_0 = 0$ we rewrite eq. (10) as:

$$\begin{aligned} n(c, T) &= \Theta(c) \left(\frac{a_1 k_B T}{a_0 + a_1 k_B T} \right)^{1 - \frac{|V_2|}{a_0}} \\ &= \Theta(c) \left(1 - \frac{a_0}{a_0 + a_1 k_B T} \right)^{-\frac{a_0 + a_1 k_B T}{a_0} - \frac{|V_2|}{a_0 + a_1 + k_B T}} \\ &\quad \times \left(1 - \frac{a_0}{a_0 + a_1 k_B T} \right). \end{aligned} \tag{14}$$

Since the second factor in the above expression tends to unity as $a_0 \to 0$, we finally obtain:

$$\lim_{a_0 \to 0} n(c, T) = \Theta(c) e^{\frac{|V_2|}{a_1 k_B T}}. \tag{15}$$

It can easily be shown that this expression is the solution of eq. (9) for $a_0 = 0$.

The results presented in this section can be summarized as follows: a) all basic thermodynamic functions of the ASYNNNI model at low temperatures are proportional to the fraction $n(c, T)$ of 3-fold coordinated Cu(1) ions, b) the concentration dependence of the basic thermodynamic functions occurs only through the fraction $n(c, T)$ (determined by the function $\Theta(c)$) while the fraction n depends exponentially on inverse temperature $1/k_B T$, and c) the dimensionless constant a_1 determines quantitatively the low-temperature thermodynamics of the ASYNNNI model. Moreover, the function $\Theta(c)$ must be equal to zero for $c = 0$, 1/4, 1/2, while, on grounds of symmetry, in the interval $0 < c < 1/2 \Theta(c)$ must be symmetric arround the value 1/4, *i.e.* $\Theta(1/4 + \delta) = (\Theta(1/4 - \delta)$. Also, $\Theta(c)$ attains its maximum for $c = c_d$ and $c = 1/2 - c_d$.

3. Results of Numerical Calculations

We used the cluster variation method (CVM) to determine the constant a_1 numerically. The CVM was originally proposed by Kikuchi[24–26] for the treatment of orderdisorder processes. The CVM formalism is based on the expression for the entropy per lattice site:

$$s = -k_B \sum_l \gamma_l \sum_{i=1}^{b(l)} \alpha_{l,i} x_{l,i} \ln x_{l,i}, \tag{16}$$

where the index l enumerates elements of the Kikuchi cluster family, the Kikuchi coefficients γ_j take account of possible cluster overlap, the index i enumerates all nonequivalent microstates of the cluster l, $x_{l,i}$ is the probability of occurrence of the microstate i of the cluster l, and $\alpha_{l,i}$ is the degeneracy factor of the microstate i of the cluster l. One or several clusters are taken as basic clusters (whose size defines the level of the CVM approximation), while the remaining clusters l are included in (16) in order to correctly take into consideration extensive thermodynamic quantities. Cluster probabilities $x_{l,i}$ are connected with the multisite correlation functions ξ_j (j denoting subclusters) as follows:

$$x_{l,i} = \frac{1}{2^{p(l)}} \left[1 + \sum_j \nu_{l,i,j} \xi_j \right], \tag{17}$$

where $p(l)$ denotes the number of lattice sites included in the cluster l and the index j runs over the set of all nonequivalent clusters of the cluster family. The coefficients $\nu_{l,i,j}$ are determined according to the following condition: for a given subcluster j of the cluster l (the cluster l being in its microstate i), the product of its spins is calculated and the corresponding products of all such subclusters of the type j are summed. Combining eq. (16) with the expression for the energy of the system $E = N \sum_j n_j V_j \xi_j$, where n_j denotes the number of clusters of the type j per lattice site and V_j is the interaction energy associated with the cluster j, we obtain the expression for the free energy (or for the thermodynamic potential). The equilibrium state of the system under study corresponds to the minimum of the free energy in the space of the multisite correlation functions ξ_j:

$$\begin{aligned} \frac{\partial f}{\partial \xi_j} &= 0 \Rightarrow n_j V_j \\ &= -k_B T \sum_j \frac{\gamma_j}{2^{p(l)}} \sum i = 1^{b(l)} \alpha_{l,i} \nu_{l,i,j} \ln x_{l,i}. \end{aligned} \tag{18}$$

If, instead of the concentration c and the temperature T, we search for the equilibrium state for a given value of the chemical potential μ and the temperature T, then the thermodynamical potential Ω should be used in eq. (18).

However, for some model systems it is more convenient to use the so-called cluster fields as variational variables instead of the multisite correlation functions. This approach to the CVM is free of logarithmic terms in (18) which usually cause convergence problems at low temperatures because some of the cluster probabilities $x_{l,i}$ become vanishingly small. The cluster fields are introduced in the CVM *via* the relation:

$$x_{l,i} = \frac{1}{Z_l} \exp \left(-\frac{1}{k_B T} \sum_j \nu_{l,i,j} (V_j + \psi_{l,j}) \right), \tag{19}$$

where Z_l denotes the statistical sum of the cluster l and $\psi_{l,j}$ is the cluster field attached to cluster j when it is considered as a subcluster of cluster l. Not all of the cluster fields $\psi_{l,j}$ are linearly independent since they must satisfy certain relations,[24,25] connected with the consistency relations among the cluster probabilities $x_{l,i}$. In order to obtain these relations, we insert the expressions (19) into (18) and, after a few trans-

formations, obtain:

$$\sum_l \gamma_l \nu_{l,1,j} \psi_{l,j} = 0, \tag{20}$$

where $\nu_{l,1,j}$ equals the number of subclusters j contained in the cluster l (here, we adopted a convention acording to which the first microstate $i = 1$ of any cluster l is that in which all its spins are oriented upwards). The implementation of the cluster fields approach to the CVM ends with a search for the minimum of the free energy (or, of the thermodynamic potential Ω) in the space of linearly independent fields $\psi_{l,j}$ *i.e.*

$$\frac{\partial f}{\partial \psi_{l,j}} = 0. \tag{21}$$

We used the CVM in the cluster fields approach to analyze the thermodynamics of the ASYNNNI model at low temperatures and especially to determine the value of the parameter a_1. The set of six basic clusters, consisting of three 5-point and three 4-point clusters, is that used previously[3,4] and has proven itself capable of embracing all the relevant physics of the ASYNNNI model. Recently higher-order CVM approximations including clusters as large as the 9-point basic clusters[27] and the 13-point basic clusters[28] were used, but the resulting phase diagrams were practically identical to those obtained with the 5 + 4-point approximation. The Kikuchi cluster family for the 5 + 4-point approximation contains 15 clusters (*i.e.* $l = 1, 2, \cdots, 15$) which define $N_m = 41$ multisite correlation functions $\xi_j[3,4]$ (*i.e.* $j = 1, 2, \cdots, 41$) and $N_p = \sum_{i=1}^{15} b(l) = 130$ cluster probabilities $x_{l,i}$. Since the probabilities were subjected to normalization conditions[29] (for each cluster l of the cluster family) there were a total of $N_c = N_p - N_m - 15 = 74$ consistency relations imposed on the cluster probabilities $x_{l,i}$ and as many linearly independent cluster effective field $\psi_{l,j}$. Thus, the problem was reduced to a system of 74 nonlinear eqs. (21) which were solved numerically using a Newton-Raphson iteration scheme. Our numerical algorithms were able to work properly at very low temperatures (as low as $\tau = k_B T / V_1 \approx 0.26(7)$), but, since we were interested in obtaining results at even lower temperatures, we applied a simplified version of the CVM. This reduced version of the CVM algorithm, which included a smaller number of 60 cluster fields, was able to work successfully at $\tau \approx 0.18$ in a wide range of oxygen off-stoichiometry. Although such a reduction of the numerical algorithms was made at the expense of the consistency of the CVM, in the sense that some of 3-site correlation functions became dependent on the cluster l from which they were expressed, the equilibrium values of the cluster probabilities $x_{l,i}$ (19) thus obtained nevertheless satisfied the system (18).

Figure 2 shows the chemical potential μ as a function of oxygen concentration c at constant reduced temperature $\tau = 0.24$, in the interval $1/4 < c < 1/2$. Our numerical calculations were based on the grand canonical scheme, *i.e.* for a given value of the chemical potential μ and temperature T we calculated the equilibrium values of the oxygen concentration c, the fraction $n(c, T)$ of 3-fold coordinated Cu(1) ions, and other relevant statistical quantities. It should be noted here that the difference δc between the concentrations of two adjacent calculated points on the isotherm was maintained to be very small, *i.e.* $0.002 < c < 0.003$. We achieved this goal by suitably modifying the increment of the chemical potential $\delta\mu$ every time before calculating a new point (using the previously solved point in the starting iteration, in the space of the $\psi_{l,j}$ variables, for implementation of the Newton-Raphson procedure). Working this way we were

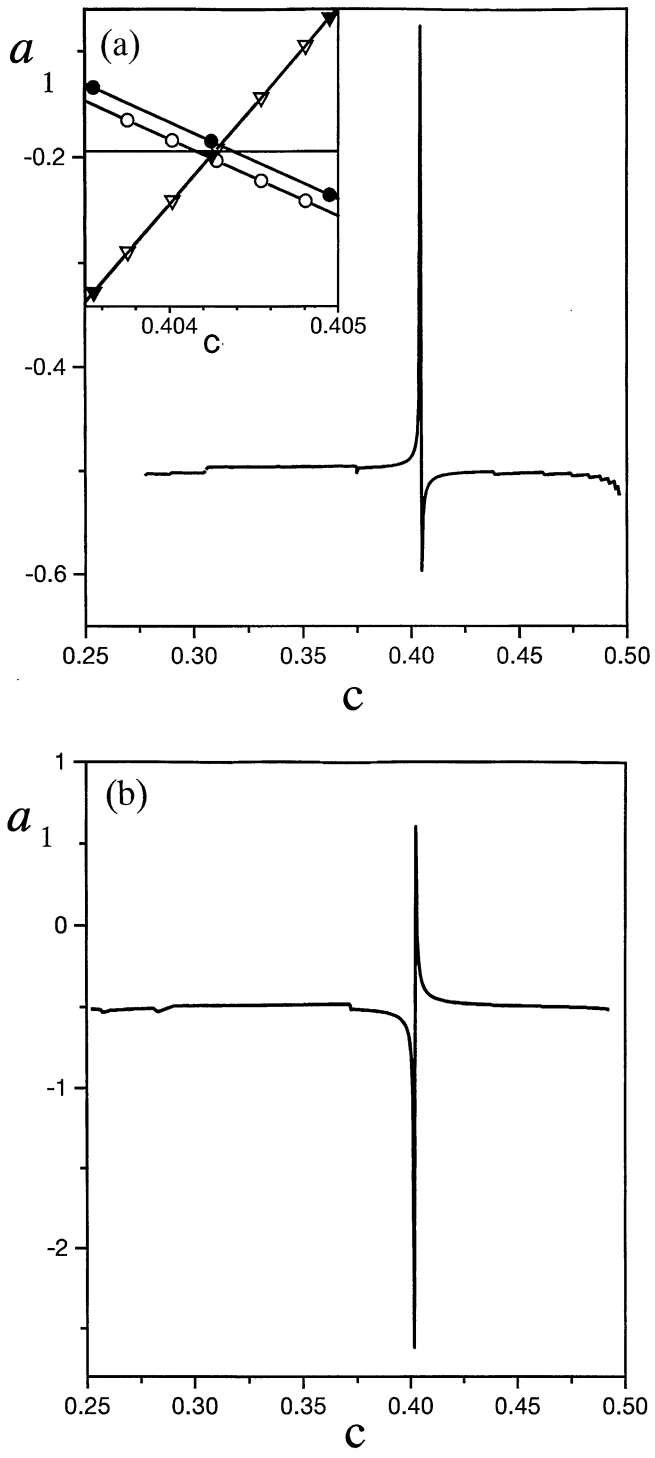

Fig. 3 Expansion coefficient a_1, as a function of concentration c at constant temperature, calculated from eq. (7). Calculations were made for (a) the canonical values of interaction constants[1,2] ($V_2 = -0.5V_1$, $V_3 = 0.5V_1$) at $\tau = 0.190 = const$ for $0.0005 < \delta c < 0.001$, and (b) the LMTO values[30] at $\tau = 0.195 = const$. Inset: open (black) circles denote calculated values of $k_B T \delta n(c, T)$ while open (black) inverted triangles denote the values of $\Delta\mu$ for $0.0005 < \delta c < 0.001$ ($0.0002 < \delta c < 0.0004$).

able to determine very accurately the partial derivative $\partial n/\partial c$ as the ratio $\delta n/\delta c$. Figure 3(a) shows the calculated values of the parameter a_1, as a function of oxygen concentration c, obtained from the ratio between $\delta n/\delta c$ and $\Delta\mu$ (where $\Delta\mu$, as before, stands for $\mu(c, T) - \mu_2$) according to eq. (7). The results shown in Fig. 3(a) were obtained for the interaction constants $V_2 = -0.37V_1$, $V_3 = 0.17V_1$, determined from first principles linearized muffin-tin orbital (LMTO) calculations.[30] From these results we see that a_1 is equal to $-1/2$ at practically all values of the concentration except in the near proximity of the concentration c_d, where a_1 diverges. We have also observed that the way a_1 tends to infinity, as c approaches c_d, is highly influenced by the magnitude of δc. The results shown in Fig. 3(a) were obtained for $0.0005 < \delta c < 0.001$, but when δc was kept between 0.0002 and 0.0004 the singular behavior around c_d became similar to that shown in Fig. 3(b) (see the inset of Fig. 3(a)). Such singular behavior around $c = c_d$ is therefore an artifact of the way we determined the derivative n'_c in the sense that, although δc in our calculations was a very small quantity, it still was finite causing $\Delta\mu$ and δn not to change their signs at exactly the same value of the concentration (*i.e.* at $c = c_d$) as they should in an exact calculation. Figure 3(b) shows results for the $a_1(c)$ dependence obtained for the canonical interaction constant[1,2] $V_2 = -0.5V_1$, $V_3 = 0.5V_1$. We see that again $a_1 = -1/2$ for all oxygen concentrations (except in the vicinity of $c = 1/4$ and $c = 1/2$), as in Fig. 3(a). Since the same result were also obtained for other sets of interaction parameters and at all low temperatures it follows that $a_1 = -1/2$ is indeed a general property of the ASYNNNI model at $T \approx 0$ independent of the particular values of interactions.

To confirm this result we have calculated a_1 as a function

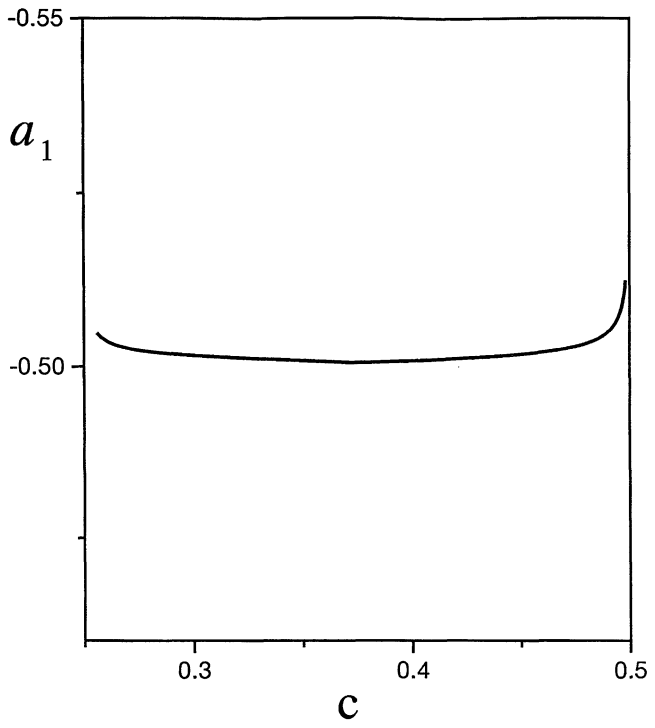

Fig. 4 Expansion coefficient a_1 as a function of concentration c, calculated from eq. (8). The CVM calculations were performed for the canonical set of interaction constants at $\tau = 0.190 = const.$

of c at constant (low) temperature using eq. (8). From eq. (8) it follows that $a_1 = (|V_2|/k_BT) - (s/k_Bn(c, T))$, where the fraction $n(c, T)$ and the entropy s were determined from the CVM calculations. These results, shown in Fig. 4, are in excellent agreement with the results of Fig. 3, indicating once again that $a_1 = -1/2$. The fact that $a_1(c)$ attains the same value at different concentrations c confirms the validity of eq. (8). This is a truly remarkable result in view of the CVM expression for the entropy (16). In order to explain this in some more detail, let us observe that at $T \approx 0$ the collection of all cluster microstates can be divided in two classes: the first class contains the cluster microstates present in the structure of the ground state, while the second class contains the cluster microstates characteristics only for excited states. The equilibrium values of the cluster probabilities of the first class are of the order of unity, while the probabilities of the second class are vanishing quantities as $T \approx 0$ (the cluster microstates of the latter class obviously contain unlike V_2 bonds and are proportional to the fraction $n(c, T)$). Taking into account that the CVM entropy (16) represents a sum of terms proportional to $x_{l,i} \ln x_{l,i}$ we have $s = s_{grs} + s_{exs}$, where s_{grs} includes the terms with probabilities from the first class while s_{exs} includes the terms with probabilities from the second class. Thus, one would expect $s_{grs} \gg s_{exs}$ and consequently $s \approx s_{grs}$ at $T \approx 0$. However, such a conclusion is incorrect since our numerical simulations clearly show that $s_{exs} \gg s_{grs}$ at $T \approx 0$, which is in accordance with eq. (8). We explain such behavior by the fact that some of the Kikuchi coefficients γ_l enter in eq. (16) with a negative sign and, thus, positive and negative terms cancel causing s_{grs} to be negligible in comparison with s_{exs}. Such behavior was also observed for all other sets of interaction constants V_1, V_2, and V_3.

Having obtained numerically that $a_1 = -1/2$, either by use of eq. (7) or through eq. (8), we can now state that the basic thermodynamic functions of the ASYNNNI model at $T \approx 0$ are determined by the following expressions.

The deviation of the energy per site from the energy of the ground state per site is given by:

$$\frac{E - E_0}{N} = \Theta(c)|V_2| \exp\left(-\frac{2|V_2|}{k_BT}\right). \tag{22}$$

From eq. (8) we find that the entropy per site is given by:

$$s = \frac{\Theta(c)}{T}\left[|V_2| + \frac{k_BT}{2}\right] \exp\left(-\frac{2|V_2|}{k_BT}\right). \tag{23}$$

Finally, the chemical potential μ, as a function of the concentration c and the temperature T, is determined by:

$$\mu(c, T) = -8V_1 \mp 4V_3 - \frac{k_BT}{2}\Theta'(c) \exp\left(-\frac{2|V_2|}{k_BT}\right). \tag{24}$$

All other important thermodynamic functions can be directly obtained from (22–24).

4. Discussion and Conclusions

The low-temperature thermodynamics of the ASYNNNI model has also been studied in Refs. 31)–33) in which the authors concluded that the ASYNNNI model is equivalent to a one-dimensional (1-D) Ising model with characteristic param-

eter V_3. Such a conclusion was based on the fact that at $T = 0$ all α columns are either completely occupied with oxygen atoms or completely empty. It appears, then, that a completely occupied α column can be replaced by a single Ising spin oriented upwards, while any completely unoccupied α column corresponds to an Ising spin oriented downwards. Taking into account that the repulsive V_3 bonds act between adjacent α columns it therefore seems as if the whole basal plane lattice is visually mapped onto a sequence of Ising spins coupled by V_3 bonds (the sequence of spins being aligned along the direction perpendicular to the α columns). Assuming further that at finite (low) temperatures the α columns are practically intact (as at $T = 0$) the authors of Refs. 31)–33) thus concluded that at low temperatures the ASYNNNI model is thermodynamically equivalent to a 1-D Ising model with NN interaction $J \equiv V_3$.

However, our results stand in a sharp contradiction to the conclusions reached in Refs. 31)–33). In order to show this, we shall briefly recapitulate the basic thermodynamic functions of the 1-D Ising model at low temperatures. The energy of an open linear Ising chain, consisting of N spins in zero external field, is determined by: $(E - E_0)/N = |J|(1 - \tanh(J/k_BT))$ which at $T \approx 0$ attains the following approximate form

$$\frac{E - E_0}{N} = 2|J| \exp\left(-\frac{2|J|}{k_BT}\right). \tag{25}$$

The entropy of the 1-D Ising model in zero external field is given by[34)]

$$S = k_B\left[N \ln 2 + (N-1)\ln\left(\cos h\frac{|J|}{k_BT}\right) - (N-1)\frac{|J|}{k_BT}\tan h\frac{|J|}{k_BT}\right], \tag{26}$$

which when taken per site, at low temperature, and in the thermodynamic limit ($N \to \infty$) transforms into:

$$s = \frac{2}{T}\left[|J| + \frac{1}{2}k_BT\right]\exp\left(-\frac{2|J|}{k_BT}\right). \tag{27}$$

At low temperature and in zero external field the heat capacity C and the susceptibility χ are approximately equal to

$$C \approx \frac{1}{k_BT^2}\exp\left(-\frac{2|J|}{k_BT}\right), \tag{28a}$$

$$\chi \approx \frac{1}{T}\exp\left(\frac{2|J|}{k_BT}\right), \tag{28b}$$

revealing singular behavior at $T = 0$.

Another fundamental property of the 1-D Ising model is that the pair correlation functions $\xi(r) = \langle\sigma_i\sigma_{i+r}\rangle$ decay exponentially with the distance r between spins, *i.e.* $\langle\sigma_i\sigma_{i+r}\rangle = \langle\sigma_i\sigma_{i+1}\rangle^r$. Since the magnetization per spin $\langle\sigma_i\rangle$ is equal to zero at all temperatures, in zero external field, such exponential decay can be rewritten as:

$$\frac{\langle\sigma_i\sigma_{i+r}\rangle - \langle\sigma_i\rangle^2}{1 - \langle\sigma_i\rangle^2} = \left[\frac{\langle\sigma_i\sigma_{i+1}\rangle - \langle\sigma_i\rangle^2}{1 - \langle\sigma_i\rangle^2}\right]^r, \tag{29}$$

which remains applicable when $\langle\sigma_i\rangle \neq 0$.

Thus, at low temperatures, the basic thermodynamic functions of the 1-D Ising model are determined by eqs. (25), (27), and (28a), (28b), while the pair correlation functions along the Ising chain satisfy the relation (29). We see that the temperature dependences of the energy (25) and the entropy (27) of the 1-D Ising model have the same forms as those of the corresponding quantities of the ASYNNNI model (given by eqs. (22) and (23)). We further realize that the role of the interaction V_2 in formulas (22) and (23) is played by the NN interaction J in eq. (25) and (27) of the 1-D Ising model, while the role of the quantity $\Theta(c)$ (in (22) and (23)) is played by the number 2 in eqs. (25) and (27). Such one-to-one correspondence between the interactions V_2 and J makes it possible to establish a full thermodynamical equivalence between the ASYNNNI model and the 1-D Ising model with $J \equiv V_2$ in the region of low temperatures. That a conclusion of this kind is very well grounded can also be seen from the heat capacity and the susceptibility of the ASYNNNI model which show the same behavior as in eqs. (28a) and (28b), respectively. The heat capacity of the ASYNNNI model is obtained by taking the derivative of eq. (22), while the susceptibility can be obtained as the inverse of the derivative of eq. (24) per concentration c yielding

$$\chi \equiv \frac{\partial c}{\partial \mu} = \frac{2}{\Theta''(c)}\frac{1}{k_BT}\exp\left(-\frac{2|V_2|}{k_BT}\right). \tag{30}$$

It has recently been shown[20)] by Monte Carlo simulations that, at low temperatures, the pair correlation functions of the ASYNNNI model, along the direction of the V_2 bonds $\xi_{V_2(r)} = \langle\sigma_i\sigma_{i+r}\rangle_{V_2} - \langle\sigma_i\rangle_\alpha^2$, behave almost exactly in accordance with eq. (29) up to $r \approx 20$. However, such behavior was not observed for the pair correlation functions along the V_3 and V_1 bond[20,35)] implying that the correlation functions along the V_2 bonds might produce the largest contribution to the susceptibility at low temperatures. That the fluctuations of the oxygen atoms along the V_2 bonds contribute the dominant part in the singular behavior of the susceptibility (30) around $T = 0$ can be most directly seen if we recall the fluctuation-dissipation result:[34)]

$$\chi \equiv \frac{\partial c}{\partial \mu} = \frac{1}{4Nk_BT}\sum_i\sum_j(\langle\sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle). \tag{31}$$

The indices i and j in the above equation run over all sites in the lattice. Assuming that only the fluctuations along the V_2 bonds on α columns are of importance at low T, eq. (31) transforms to:

$$\chi \propto \frac{1}{4Nk_BT}\frac{N}{2}\sum_{r=-\infty}^{+\infty}(\langle\sigma_i\sigma_{i+r}\rangle_{V_2} - \langle\sigma_i\rangle_\alpha^2). \tag{32}$$

Taking into account that for the case of, for example, the OI structural phase $\langle\sigma_i\rangle = 4c - 1$ (consequently, $1 - \langle\sigma_i\rangle_\alpha^2 = 8c(1-2c)$) and $\langle\sigma_i\sigma_{i+1}\rangle - \langle\sigma_i\rangle_\alpha^2 = 8c(1-2c) - 2\Theta(c)\exp(-2|V_2|/k_BT)$, and inserting the expression (29) into (32) we obtain:

$$\chi \propto \frac{[8c(1-2c)]^2}{16\Theta(c)}\frac{1}{k_BT}\exp\left(\frac{2|V_2|}{k_BT}\right). \tag{33}$$

This relation expresses the same type of singular behavior near absolute zero temperature as the CVM expression (30).

Although the CVM generally does not give accurate results near critical points, where the correlation length becomes in-

finite, it seems, according to (30) and (33), that it is nevertheless able to approach the exact solution very closely near critical points in those cases in which the critical singularities are due to the exponential decay of pair correlation functions (29) along a certain direction. We believe that, even in the framework of relatively simple approximations of the CVM, the contribution of such long-distance pair correlation functions appears to be included in the response functions of the system owing to the way the CVM entropy expression is constructed: as a product of combinatorial expressions counting local configurations of small clusters. This is supported by the fact that for the 1-D Ising model using only the NN pairs as the largest basic cluster in the CVM, yields the *exact* solution which is characterized by the exponential decay of the pair correlation functions.[34)]

It is important to emphasize that the exponential decay of the pair correlation functions along the V_2 bonds, being one of the most important characteristics of the ASYNNNI model at low temperatures, is maintained up to fairly high temperatures which are obtainable in experiments (800–900 K, corresponding to $\tau \approx 0.9$). Also, the range of these correlation functions is much greater than that of the pair correlation functions along the V_1 or V_3 bonds. For example, in the tetragonal (disordered) phase at $\tau \approx 50$, the first 6 (7) pair correlation functions along the V_2 bonds are still significant (they also fit excellently into exponential decay, as expressed by eq. (29)), while the correlation functions along the V_3 and V_1 bonds are negligible, except for NNN pairs.[35)] Therefore, the short-range order in the system at high temperatures is, to a high degree, determined by some maintained characteristics of the V_2-coupled Ising chain nature of the ASYNNNI model which prevails at low temperatures.

REFERENCES

1) L. T. Wille and D. de Fontaine: Phys. Rev. B **37** (1988) 2227–2230.
2) D. de Fontaine, L. T. Wille and S. C. Moss: Phys. Rev. B **36** (1987) 5709–5712.
3) L. T. Wille, A. Berera and D. de Fontaine: Phys. Rev. Lett. **60** (1988) 1065–1068.
4) A. Berera, L. T. Wille and D. de Fontaine: Physica A 153–155 (1988) 598–601.
5) V. E. Zubkus, E. E. Tornau, S. Lapinskas and P. J. Kundrotas: Phys. Rev. B **43** (1991) 13112–13117.
6) V. E. Zubkus, S. Lapinskas and E. E. Tornau: Phys. Status Solidi B **156** (1989) 93–104.
7) V. E. Zubkus, S. Lapinskas and E. E. Tornau: Physica C **156** (1989) 501–504.
8) V. E. Zubkus, S. Lapinskas and E. E. Tornau: Physica C **166** (1990) 472–475.
9) V. M. Matic: Physica C **230** (1994) 61–74.
10) V. M. Matic: Physica C **211** (1993) 217–226.
11) V. M. Matic: Physica A **184** (1992) 571–586.
12) W. Selke and G. V. Uimin: Physica C **214** (1993) 37–44.
13) G. Uimin: Phys. Rev. B **50** (1994) 9531–9547.
14) T. Fiig, J. V. Andersen, N. H. Andersen, P. A. Lindgard, O. G. Mouritsen and H. F. Poulsen: Physica C **217** (1993) 34–52.
15) T. Aukrust, M. A. Novotny, P. A. Rikvold and D. P. Landau: Phys. Rev. B **41** (1990) 8772–8791.
16) M. Goldman, C. P. Burmester, L. T. Wille and R. Gronsky: Phys. Rev. B **50** (1994) 1337–1340.
17) J. V. Andersen, H. Bohr and O. G. Mouritsen: Comput. Mater. Sci. **1** (1992) 25.
18) D. J. Liu, T. L. Einstein, P. A. Sterne and L. T. Wille: Phys. Rev. B **52** (1995) 9784–9792.
19) P. A. Rikvold, M. A. Novotny and T. Aukrust: Phys. Rev. B **43** (1991) 202–209.
20) V. M. Matic, N. Dj. Lazarov, E. E. Tornau, S. Lapinskas, M. Milic and V. Spasojevic: Phys. Rev. B **62** (2000) 107–110.
21) L. D. Landau and E. M. Lifshitz: Theoretical Physics V—Statistical Mechanics, Third Edition, NAUKA Publishers, Moscow (in Russian) (1976).
22) J. E. Mayer and M. G. Mayer: Statistical Mechanics, Second Edition, MIR Publishers, Moscow (in Russian) (1976).
23) N. Dj. Lazarov: Magistration Thesis, Belgrade (2000).
24) R. Kikuchi: Phys. Rev. **81** (1951) 988–1003.
25) R. Kikuchi: J. Chem. Phys. **19** (1951) 1230–1241.
26) M. Kurata, R. Kikuchi and T. Watari: J. Chem. Phys. **21** (1953) 434–448.
27) J. L. Moran-Lopez and J. M. Sanchez: Physica C **210** (1993) 401–407.
28) G. Grigelionis, S. Lapinskas, A. Rosengren and E. E. Tornau: Physica C **242** (1995) 183–190.
29) V. M. Matic and S. Milosevic: Physica A **262** (1999) 215–231.
30) P. A. Sterne and L. T. Wille: Physica A **162** 223–224.
31) G. Ceder, M. Asta, W. C. Carter, M. Kraitchman, D. de Fontaine, M. E. Mann and M. Sluiter: Phys. Rev. B **41** (1990) 8698–8701.
32) D. de Fontaine, M. E. Mann and G. Ceder: Phys. Rev. Lett. **63** (1989) 1300–1303.
33) G. Ceder, R. McCormack and D. de Fontaine: Phys. Rev. B **44** (1991) 2377–2380.
34) H. E. Stanley: Introduction to Phase Transitions and Critical Phenomena (Clarendon Press, Oxford, 1971).
35) N. Dj. Lazarov and V. M. Matic: unpublished work.