Low-temperature thermodynamics of the asymmetric next-nearest-neighbor Ising model

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Low-temperature thermodynamics of the asymmetric next-nearest-neighbor Ising (ASYNNNI) model is analyzed. It is demonstrated that this model at low temperatures is equivalent to one-dimensional (1D) NN Ising model in zero external field with the NN interaction being a copper mediated NNN interaction of the ASYNNNI model, $V_2<0$. It is also shown that the spin correlation function $\xi_{V_2}(r)=\langle\sigma_i\sigma_{i+r}\rangle-\langle\sigma_i\rangle^2$ along Cu-O(1) chains decays exponentially with interspin distance r at $T\approx 0$.

Our results imply that at nonstoichiometric values of oxygen atoms concentration the magnitude of the NNN interaction constant $V_3>0$ has no effect on low-temperature thermodynamics and only repulsive nature of this constant determines the degeneracy of exited states of the ASYNNNI model.

The two-dimensional asymmetric next-nearest-neighbor Ising (ASYNNNI) model is one of the most interesting ''classical'' statistical models introduced[1–10] in 1980's. The model was extensively studied during last decade, mostly because it was proposed to analyze oxygen ordering in the basal, CuO_{2c}, planes of very popular high-temperature superconductor $YBa_2Cu_3O_{6+2c}$. The ASYNNNI model was used to describe not only structural, but also superconducting properties of $YBa_2Cu_3O_{6+2c}$, since superconducting transition temperature of this compound depends as on oxygen content c as well as on oxygen ordering to different phases in the basal planes. The Hamiltonian of the ASYNNNI model has the following form:

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

where $\sigma_i=+1$ (-1) means that the site i of the basal plane lattice is occupied (unoccupied) by an oxygen atom, summation runs over the nearest-neighbor (NN) and next-nearest-neighbor (NNN) oxygen sites, Σ' denotes that summation is taken over all NNN oxygen sites with Cu ion in between, and μ stands for oxygen chemical potential. The NN interaction constant V_1 and NNN interaction constant V_3 are repulsive (positive), while the NNN copper-mediated O(1)-O(1) interaction constant V_2 is assumed to be atractive (negative). Such choice of signs of interaction constants ensures the only three oxygen phases which were unmistakably observed in experiments so far, i.e., tetragonal (tetra), orthorombic I (OI), and orthorombic II (OII), to be correctly included in the ASYNNNI model as ground state phases.[11–13] Thermodynamics of the ASYNNNI model has been studied by use of various numerical techniques, such as cluster variation method (CVM),[3–5,9,10] transfer matrix-renormalization group method,[8,13,14] and Monte Carlo (MC) simulations.[6–8,15–17] General topology of the phase diagram is well-known, but quite little has been done so far to determine low-temperature thermodynamics of the ASYNNNI model.

Some efforts to calculate low-temperature statistics of the model have been made by use of the CVM approach,[4,10] low-temperature series expansion,[9] and MC calculations.[6,7,15] It was suggested in Refs. 6,7 that the ASYNNNI model at low T is equivalent to the one-dimensional (1D) Ising model, with the NN interaction of the 1D Ising model J being equivalent to interchain interaction constant $V_3>0$. Here we demonstrate that the ASYNNNI model at low temperatures is thermodynamically equivalent to the 1D Ising ferromagnet in zero external field with $J\equiv V_2$, where $V_2<0$ is intrachain interaction constant. Such a behavior of the ASYNNNI model thermodynamics at low T is closely related to exponential decay of pair correlation function $\xi_{V_2}(r)$ when the distance r between spins is taken in the direction of the V_2

bonds. A certain relation might be seen between the low-temperature thermodynamics of the ASYNNNI model and broad maximum of isothermal susceptibility $\chi=\partial c/\partial\mu$ which has been experimentally observed at high temperature (923 K) by McKinnon *et al.*[18] This maximum is located within the tetragonal phase and, therefore, it is not related to the susceptibility peak of the tetra-OI phase transition.

First we briefly describe the structure of ground and exited states for $0.25<c<0.50$, though all conclusions might be straightforwardly extended for $0<c<0.25$. At $c=0.25$ and $T=0$, all α_1 sites are occupied with oxygen atoms while sites α_2 and β are empty (OII phase) producing perfect, infinite Cu(1)-O(1) chains on α_1 columns (for denotations see, e.g., Ref. 10). At off-stoichiometry $c\in(0.25,0.50)$, aside from completely occupied α_1 columns, there are as many completely occupied α_2 columns as the value of oxygen concentration allows (β sites will be empty because of strong repulsive NN interaction $V_1>0$). It can be shown that the ground state energy per spin is given by the following expression:

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

where the upper sign corresponds to $c\in(0,0.25)$ and lower to $c\in(0.25,0.50)$. For given $c\in(0.25,0.50)$ exited states have the same number of alike and unlike V_1 and V_3 bonds as corresponding ground state, while only unlike V_2 bonds on α columns characterize low-lying energy levels; no (–, –) V_3-bonds on α sublattice exist neither in the ground state nor in exited states of the system. At low temperature the energy is given by[10]

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

Here $n(c,T)$ is the fraction of threefold coordinated Cu ions located in the middle of unlike V_2 bonds. It should be noted that at non-zero (low) temperature there are no completely occupied or unoccupied α columns in an equilibrium state of the ASYNNNI model. The Cu-O(1) chains and empty segments alternate along each of the α columns instead. The chains are allowed to glide almost freely along the b axis, with no change of the total energy, giving decisive contribution to the entropy S at low T. The only limitation is that two empty segments cannot even partially occur alongside each other [because oxygen sites of α sublattice have no (–, –) V_3-bonds in exited states]. From Eqs. (8) and (11) of Ref. 10 it follows that $S/N\approx(1/T)(|V_2|-ak_BT)n(c,T)$ at $T\approx0$, where $a=-0.5$ in the CVM. The equilibrium occupancy of α columns and average length $l=2c/n$ of Cu-O(1) chains are determined by the free energy minimum condition.

Consider the system of chain segments in, e.g., OI phase, consisting of L_1 columns and L_2 rows. Probability $P(n)$ that our system has n chain ends is proportional to the product of the Boltzmann factor $\exp[-E(n)/k_BT]$, where E is given by Eq. (3), and the number of microscopic states with given n, $w(n)=\exp[S(n)/k_B]$, where $S(n)$ is the entropy of the system. The expectation value for n, $\langle n\rangle=\Sigma_n nP(n)/\Sigma_n P(n)$, in the large system limit is equal to the value at which $P(n)$ has its maximum. The maximum of $P(n)$ occurs, since the Boltzmann factor is a decreasing, while the entropy term is an increasing function of $E-E_0$, and $P(n)$ narrows with system size. Thus we are looking for $dP(n)/dn|_{n=\langle n\rangle}=0$. The average number M of occupied chain segments (OS), which is equal to the average number of empty segments (ES), in a column is $L_1n/2$. Thus, the average length of the OS is $l=L_1c/M=2c/n$ and the average length of the ES is $2(1-c)/n$. It is known[4,10] that in the OI phase for $0.25<c<0.5$ only $(+,+)$ and $(+,-)V_3$ bonds are allowed at low temperature. Thus, the distance, for which the ES is allowed to move along the column without the loss of energy averages to the difference in lengths of OS and ES:$2(2c-1)/n$. The number of the ES in our system is $L_1L_2n/2$. Thus the number of states of our moving ES is $w(n)=[2(2c-1)/n]^{(1/2)L_1L_2n}$ and the entropy per site is $s=S/L_1L_2=(k_Bn/2)\ln[2(2c-1)/n]$. After insertion of $w(n)$ into $dP(n)/dn|_{n=\langle n\rangle}=0$ and calculation of derivative we obtain $\langle n\rangle=[2(2c-1)/e]\exp(-2V_2/k_BT)$ with the factor 2 in the exponent which actually comes from the simple argument that the number of chain ends is twice the number of segments.

We also performed the CVM and MC calculations to show that $n(c,T)$ at very low temperatures has the following form:

$$n(c,T)=\Theta(c)\exp\left(\frac{|V_2|}{ak_BT}\right), \qquad (4)$$

where $a=-1/2$. However, the exact form of $\Theta(c)$ would clearly include $\Theta(c)=0$ for $c=0$ (tetra), $c=0.25$ (OII), and $c=0.5$ (OI). The MC simulations were based on a grand canonical scheme (Glauber dynamics) for systems of size varied from $8\times(60\times60)$ to $8\times(150\times150)$ (our system was divided in eight sublattices). At first we simulated the isothermal processes at constant low values of temperature for several sets of interaction constants V_1, V_2, and V_3 to check the validity of the relation for the entropy.[10] The change of entropy was determined from the changes of energy and free energy. The change of free energy was determined by $\int_a^b\mu(c,T)dc$. To determine this integral numerically for isothermal process we calculated, for example, 11 nearly equidistant points between $c_a=0.279$ and $c_b=0.293$. All calculations (for different low values of temperature, intervals of oxygen concentrations and sets of interaction constants) demonstrated that the value of a lies between -0.49 and -0.50. Then, to verify the validity of expression (4), we calculated the fraction n at different low values of temperature for fixed values of oxygen concentration c. A typical result, shown in Fig. 1, demonstrates that the exponential dependence (4) is correct. From the slope of this straight-line plot we determine the constant a (see inset to Fig. 1). For all other calculations of ln n vs inverse temperature, i.e., for different fixed concentrations of oxygen atoms and different sets of interaction constants V_1, V_2, and V_3, we obtained the same value of $a=-0.5$. Thus, it follows from our MC simulations as well as from calculations by the $5+4$-point CVM[10] that at low temperature the fraction of threefold coordinated Cu ions, the energy and the entropy of the ASYNNNI model are proportional to $\exp(-2|V_2|/k_BT)$. For comparison, the energy and the entropy of an open NN Ising chain of N spins in zero magnetic field with NN interaction

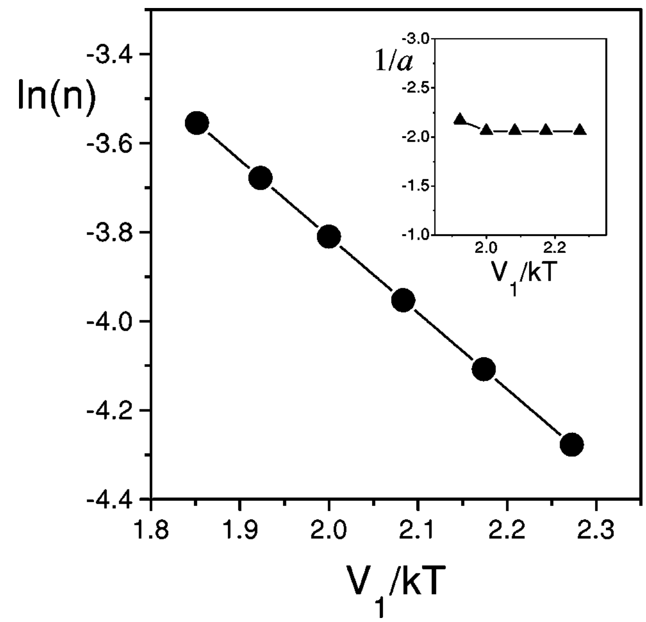

FIG. 1. The result of MC simulation confirming the correctness of formula (4): ln(n) vs inverse temperature $1/\tau = V_1/k_BT$ dependence at $c=0.4$ obtained using ''new'' set of the LMTO interaction constants (Ref. 13). Inset: a dependence on $1/\tau$ calculated from Fig. 1 using Eq. (3).

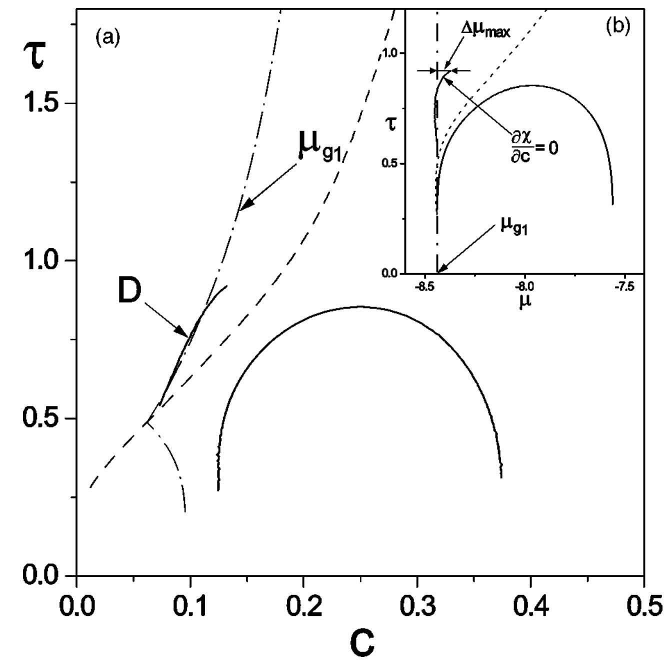

FIG. 2. The curve of disorder points $D(\partial c/\partial\mu = 0)$ as compared to μ_{g1}=const curve in (c,τ) (a) and $(\mu,\ \tau)$ (b) coordinates. Calculations were performed by the $(4+5)$-point CVM using the ''new'' set of LMTO interaction constants (Ref. 13).

$J<0$ at $T\approx 0$ are proportional to $\exp(-2|J|/k_BT)$.[19] It can be easily checked that, at $T\approx 0$ all basic thermodynamic functions of the ASYNNNI model are identical to those of the 1D Ising model with one-to-one correspondence between the interaction constants V_2 and J. This means that the ASYNNNI model and the V_2-coupled Ising chain are thermodynamically equivalent at low temperatures.

An important property of the 1D Ising model in zero external field is that pair correlation functions at any temperature decay exponentially with the distance r between spins, i.e., $\xi(r) = \langle\sigma_i\sigma_{i+r}\rangle = (\xi_{NN})^r$, where $\xi_{NN}\equiv\xi(1) = \tanh(J/k_BT)$ denotes the NN pair correlation function. For the ASYNNNI model at $T\approx 0$, the average magnetization $\langle\sigma_i\rangle$ on either of the α_1 or α_2 column is not equal to zero. On the other hand, assuming one-dimensionality of this model at low temperatures, one obtains the following expression:

$$\xi_{V_2}(r)\equiv\langle\sigma_i\sigma_{i+r}\rangle-\langle\sigma_i\rangle^2=(1-\langle\sigma_i\rangle^2)\left[\frac{\xi_{V_2}(1)}{1-\langle\sigma i\rangle^2}\right]^r, \quad (5)$$

where $\langle\sigma_i\rangle = 4c-1$ and $\xi_{V_2}(1) = 1-2n(c,T)-(4c-1)^2$, which is exact for $1d$-dimensional Ising model with fixed $\langle\sigma_i\rangle$. To confirm this result, we studied the behavior of the first 20 correlation functions $\xi_{V_2}(r)$ by use of the MC simulations. For the OI phase ($c>0.375$) and temperature range $0.20<\tau<0.30$, we obtained absolute agreement, and the similar behavior of the correlation functions can be found for the OII phase. It is clear then that one-dimensional fluctuations along the V_2 bonds contribute mainly to the singularity of the susceptibility χ, since from $\partial\mu(c,T)/\partial c = -\frac{1}{2}k_BT\partial^2 n(c,T)/\partial c^2$, it follows $\chi = (2/\Theta''(c)k_BT)\times\exp(2|V_2|/k_BT)$[10]. Such a behavior is expected for the system which at $T\approx 0$ is mapped onto a 1D Ising model with $J\equiv V_2$. Therefore the pair correlation functions along the direction of V_2 bonds, when normalized to their maximal value $1-\langle\sigma_i\rangle^2$ (for fixed magnetization $\langle\sigma_i\rangle$), decay exponentially with the interspin distance for all off-stoichiometric values of oxygen concentration.

In some Ising-type model systems the exponential decay of pair correlation functions along certain crystalographic axes is essentially connected with the concept of so-called disorder point,[20] defined as $\partial c/\partial\mu = 0$. These points exist well above critical temperature of the phase transition, inside the disordered (tetra) phase. On the other hand, it was shown by Rikvold *et al.*[14] that broad maximum of isothermal susceptibility (BMS), $\chi = \partial c/\partial\mu$, experimentally observed by McKinnon *et al.*[18] at $T=923$ K, is accompanied by nearly exponential decay of $\xi_{V_2}(r)$ [i.e., the same as in Eq. (5)]. Therefore we think that the existence of BMS at high T is a manifestation of a retained low temperature V_2-coupled Ising chain nature of the ASYNNNI model. In addition, analyzing the $\mu(c,T)$=const curves in the $(c,\ T)$ phase diagram we found that maximal fluctuations of oxygen atoms in the tetra phase should occur at all temperatures in the proximity of the ground state curve $\mu_{g1} = -8V_1-4V_3$. As is shown in Fig. 2 the line of disorder points calculated by the $(4+5)$-point approximation of the CVM is close to the curve μ_{g1} for all temperatures including those lying well above the top of the OII phase. We also performed the same calculations for the 13-point CVM and used various sets of interaction constants, but this result did not change. It should be also noted that small values of oxygen concentration, at which the BMS was observed,[18] are quite advantageous for manifestation of the chainlike nature of the ASYNNNI model, since at low c Cu-O(1) chains are quite isolated and there are no forbidden V_3 bonds.

Since the value of oxygen chemical potential in the gas phase, which corresponds to the top of the BMS, is nearly equal to μ_{g1}, we can evaluate the on-site energy ϵ of a basal plane oxygen atoms. The evaluation of this parameter might be important for the studies of oxygen diffusion or desorption. It follows from the experiment[18] that the chemical potential of oxygen atoms in $YBa_2Cu_3O_{6+2c}$ at $T=923$ K is equal to $\mu/k_BT=-11.7$, i.e., $\mu=\epsilon+\mu_{g1}=-0.93$ eV at the peak of the BMS. To express μ_{g1}, instead of Eq. (1), we use the lattice-gas formalism, since it directly gives us the real chemical potential. Then $\mu_{g1}=V_2^{lg}=4V_2$. Consequently, $\epsilon=-0.93-4V_2$ in eV. That gives $\epsilon=-0.8$ eV for an ''old'' set of LMTO interaction constants[12] and $\epsilon=-0.6$ eV for a new, ''realistic,'' set.[13]

Thermodynamics of the ASYNNNI model at low temperature was also numerically studied by de Fontaine, Ceder *et al.*[6,7] Analyzing the behavior of the NN pair correlation function along Cu-O(1) chain, it was obtained that $\xi_{V_2}(1)\to+1$ at $T\to0$ independently of oxygen concentration c. Thus, α columns at $T\approx0$ were considered as either completely occupied or completely empty, and the ASYNNNI model was claimed to be thermodynamically equivalent to the V_3-coupled Ising chain.[7] We argue here that, although such one-to-one mapping might be established at absolute zero temperature, it cannot be extended to $T\neq0$. Our results show (see also Ref. 4) that the low-energy excitations do display themselves via breaking the chains into shorter segments, but not via creation or destruction of full and empty chains. As a consequence, the ASYNNNI model at $T\approx0$ is thermodynamically equivalent to the V_2-coupled Ising chain. The magnitude of the interaction constant V_3 makes no influence on low temperature thermodynamics of the model. Only the repulsive nature of $V_3(>0)$ determines the degeneracy of the exited states leading to a distribution when two empty segments on adjacent α columns cannot be alongside each other, because for $0.25<c<0.5$ no (–, –) V_3 bonds on α sublattice are allowed for exited states. The magnitude of V_3 affects only the temperature range at which the ASYNNNI model turns to $1dV_2$-coupled Ising model.

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