One Dimensional Oxygen Ordering in YBa$_2$Cu$_3$O$_{7-\delta}$

A.A. Aligia

Comisión Nacional de Energía Atómica

Centro Atómico Bariloche e Instituto Balseiro

8400 S.C. de Bariloche, Río Negro, Argentina

A model consisting of oxygen-occupied and -vacant chains is considered, with repulsive first and second nearest-neighbor interactions $V_1$ and $V_2$, respectively. The statistical mechanics and the diffraction spectrum of the model is solved exactly and analytically with the only assumption $V_1 >> V_2$. At temperatures $T \sim V_1$ only a broad maximum at $(1/2,0,0)$ is present, while for $|\delta - 1/2| > 1/14$ at low enough $T$, the peak splits into two. The simple expression for the diffraction intensity obtained for $T << V_1$ represents in a more compact form previous results of Khachatryan and Morris, extends them to all $\delta$ and $T/V_2$ and leads to a good agreement with experiment.

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It is now clear that the superconducting transition temperature of YBa$_2$Cu$_3$O$_{7-\delta}$ depends not only on $\delta$ but also on the oxygen ordering [1]. Therefore, detailed knowledge of this ordering in the whole oxygen concentration range is important for an understanding of the electronic properties of the system and the superconducting mechanism.

At low enough temperatures, at least for $1/4 < \delta \leq 1/2$, the oxygen atoms in the basal planes are ordered in infinite CuO chains [2,3]. Experimental [3-6] and theoretical [7-10] evidence favoring alternative types of oxygen ordering is restricted to $\delta > 0.6$ and $\delta \leq 0.25$.

Concerning the ordering among different CuO chains at $T = 0$, the experimental situation [2,3] favors structures that are given by the ground state of a one-dimensional (1D) Ising model in which the interactions $V_n$ between chains at a distance $na$, where $a$ is the lattice parameter, satisfy the inequality $V_{n+1} + V_{n-1} > 2V_n$ [10-13]. The low temperature thermodynamics of the two-dimensional asymmetric next-nearest-neighbor Ising model (ASYNNNI) [14] is also governed by the simplest one-dimensional Ising model ($V_1 > 0$ and $V_n = 0$ for $n > 1$) [13].

Due to the sluggish oxygen kinetics at low temperatures, the system often does not reach a completely ordered state at $T=0$, as is required by the third principle of thermodynamics. In this case, in the range $1/4 \leq \delta \leq 1/2$, diffuse diffraction peaks are observed [2,16]. For the largest values of $\delta$, and diffraction vectors $\mathbf{q} = (2\pi/a)(h,0,0)$, only one peak in the interval $0 < h < 1$, centered at $h = 1/2$, is present. For the smallest values of $\delta$ in the above mentioned range, two maxima centered at $h = 1/2 \pm \epsilon$ are observed. Khachaturyan and Morris (KM) [17] explained qualitatively these observations in the range $1/3 \leq \delta \leq 1/2$, assuming a random faulting of the double period ordered structure with $\delta = 1/2$ (alternating Cu-O and Cu-vacancy chains [3]). This work has been criticized in a Comment [18] because of the restricted composition range of the theory and the assumptions on the interactions that would be implicit in the model. In their Reply [19] KM state that Ref. [17] does not assume a particular type of interaction and that, while it would be nice to have a tractable analysis for all $\delta$, it was not necessary to establish that random faulting can produce split peaks. In another Comment to [17], it was shown that the short-range order implicitly
assumed by KM, minimizes the free energy of the 1D Ising model with repulsive $V_1$, $V_2$ and $V_n=0$ for $n > 2$ at $T \to 0$ [20]. $V_1 > 2V_2$ should hold to stabilize the double period structure at $\delta = 1/2$. While interactions at larger distances are important in determining the ground state of the system [10–13], it will be shown in this letter that this model is the simplest one which leads to a reasonable agreement with the experimentally observed diffraction peaks. However, for $T \to 0$ the free energy should be minimized by long-range ordered structures and this model becomes unrealistic. In addition, the results of KM predict too narrow and intense split peaks near $\delta = 1/3$ when compared with experiment [2,16]. Since one expects that these peaks should broaden and lose intensity when the temperature is increased, it is of interest not only to extend the theory of KM to all compositions, but also to study the model at finite temperatures. This task is carried out in the present letter.

In order to obtain simple analytical results, two cases are considered: a) $T >> V_2$, $V_1/T$ arbitrary [21], b) $V_1 >> T$ and any $V_2/T$ with $V_2 < V_1/2$. The resulting short-range correlations are used as input parameters for the calculation of the diffraction intensity. If the system is metastable, these parameters can be thought of as probabilities that are given by the preparation method, independent of the free energy of the system, or as equilibrium parameters at higher $T$. While KM obtained two different expressions for the diffraction intensity, one for $1/3 \leq \delta \leq 4/9$ and another one for $4/9 \leq \delta \leq 1/2$ [17], in case (b) the elegant method based on generating functions [22] leads to a single expression which simplifies those of KM, extends them to all oxygen compositions, and allows for more than two consecutive oxygen occupied chains (requiring $T \neq 0$ in the 1D Ising model).

Following KM we shall denote by $\bigcirc$ the Cu-O chains and by $\square$ the Cu-vacancy chains. It is convenient to write the model in the form:

$$H = V_1 \sum_i n_in_{i+1} + V_2 \sum_i n_in_{i+2},$$

(1)

where $n_i = 1$ (0) if the ith chain is $\square$($\bigcirc$). The diffraction intensity is given by [17]:

$$I(h) = N |f_{ox}|^2 \delta \sum_{m=-\infty}^{\infty} P(m) \exp(i2\pi hm),$$

(2)
where $N$ is the total number of unit cells, $f_{ox}$ is the oxygen scattering factor and $P(m)$ is the conditional probability that if $n_0 = 1$, also $n_m = 1$. Interchanging $\bigcirc$ and $\square$ it is easily seen that, excluding integer $h$, $I(h)$ is the same for $\delta$ and $1 - \delta$.

In the following $\delta \leq 1/2$ is assumed.

a) $V_2 \ll T$

In this case $V_2$ can be neglected (as will become clearer in case (b)) and the model reduces to the simplest 1D Ising model. This model describes the low-temperature oxygen ordering of the 2D ASYNNNI model [13,15] and is exactly solvable [13]. The quantity that determines the free energy and $I(h)$ for each value of $\delta$, is the probability $y_1$ of finding a pair $\square\square$ of two consecutive $\square$ chains:

$$y_1 = \delta - \gamma_1/2 + \left[ (\delta - \gamma_1/2)^2 + \delta^2 (\gamma_1 - 1) \right]^{1/2},$$  \hfill (3)

where $\gamma_1 = [1 - \exp(-V_1/T)]^{-1}$. $P(m)$ satisfies the following non-homogeneous difference equation:

$$P(m) = \eta - \beta P(m - 1),$$  \hfill (4)

where $\eta = (\delta - y_1)/(1 - \delta)$ is the conditional probability that if $n_{m-1} = 0$, then $n_m = 1$. Similarly $\eta - \beta = y_1/\delta = P(1)$ is the probability that if $n_{m-1} = 1$ then $n_m = 1$. The solution of Eq. (4) with the boundary condition $P(0) = 1$ is:

$$P(m) = \delta + (1 - \delta)(-\beta)^{|m|},$$  \hfill (5)

and replacing this in Eq. (2)

$$I(h) = N \cdot f_{ox} \cdot | f_{ox} |^2 \delta \frac{(1 - \beta)(1 + \beta - \eta)}{1 + \beta^2 + 2\beta \cos(2\pi h)}.$$  \hfill (6)

For any $\delta$ and $T$ this expression gives only one peak centered at $h = 1/2$. If enough statistics and Monte Carlo steps are allowed, Monte Carlo results using the ASYNNNI [13] at low enough temperatures should converge to this simple expression. Thus, the ASYNNNI should be extended to include longer range repulsions in order to explain split diffraction peaks [10,13], as shown before [20].
In the limit $T >> V_1$ \cite{21}, then $\gamma_1 = T/V_1$, $y_1 = \delta^2 [1 - (1 - \delta)^2 V_1 / T]$, $\eta = \delta + \delta^2 (1 - \delta) V_1 / T$, $\beta = \delta (1 - \delta) V_1 / T$ and:

$$I(h) \simeq N |f_{ox}|^2 \delta (1 - \delta) [1 - 2\delta (1 - \delta) (V_1 / T) \cos (2\pi h)]. \quad (7)$$

Thus, at high enough $T$, $I(h)$ is a constant plus a small harmonic term with maximum at $h = 1/2$ and minimum at $h \to 0$ and $h \to 1$.

For $V_1 >> T >> V_2$, neglecting exponentially small terms, $\gamma_1 = 1$, $y_1 = 0$, $\eta = \beta = \delta / (1 - \delta)$ and:

$$I(h) = \frac{N |f_{ox}|^2 \delta (1 - \delta) (1 - 2\delta)}{1 + 2\delta (1 - \delta) \cos (2\pi h)}, \quad (8)$$

in agreement with Ref. \cite{20}. For $\delta \to 0$, $I(h)$ is small and flat, while for $\delta \to 1/2$, the second member of Eq. (9) gives the extremely narrow peak at $h = 1/2$ corresponding to the double periodic long-range ordered structure.

b) $V_1 >> T$

As shown above, for $\delta \leq 1/2$ the probability $y_1$ of finding a strip $\square \square$ is of order $\delta^2 (1 - 2\delta)^{-1} \exp (-V_1 / T)$ and can be neglected if $\delta \neq 1/2$. This allows to represent any possible structure in terms of a sequence of two strips: $\bigcirc$ and $\square \bigcirc$. The energy per strip is given by $V_2 y$ where $y$ is the probability of finding two nearest-neighbors $\square \bigcirc$ strips. Calling $x$ the probability of finding one $\square \bigcirc$ strip, it is easy to see that the problem can be mapped into the 1D Ising model with only $V_1 \neq 0$, already considered in case (a). The mapping is given by the correspondence $\square \bigcirc \to \square, x \to \delta$, $y \to y_1$, $V_2 \to V_1$. The free energy per chain $F$ is given by:

$$(1 + x) F = V_2 y - T [x \ln x + (1 - x) \ln (1 - x) - y \ln y - 2(x - y) \ln (x - y) - (1 - 2x + y) \ln (1 - 2x + y)], \quad (9)$$

where $1 + x$ is the average number of chains per strip. The average number of $\square$ chains per strip is $x / (1 + x) = \delta$. Thus:

$$x = \delta / (1 - \delta), \quad (10)$$
and minimizing $F$ one obtains:

$$y = x - \gamma/2 + [(x - \gamma/2)^2 + x^2(\gamma - 1)]^{1/2},$$  \hspace{1cm} (11)$$

where

$$\gamma = [1 - \exp(-V_2/T)]^{-1}. \hspace{1cm} (12)$$

The probability of finding three consecutive $\bigcirc$ chains, which is given by $1 + \delta(y/x - 3)$ can be used instead of $T$ as independent variable.

$P(m)$ can be determined from $P(m - 1)$ and $P(m - 2)$ from the following reasoning. Since $P(m) = P(-m), m \geq 0$ will be assumed. The pair of chains $m - 2$ and $m - 1$ can be in one of the three following states: 1) $\bigcirc\bigcirc$, 2) $\square\bigcirc$, 3) $\bigcirc\square$. The probability of state $i$ is denoted $p_i$. Since $\square\square$ is excluded, if the third state is realized ($p_3=1$) then $P(m)=0$. In state 1, the chain $m - 1$ should belong to a $\bigcirc$ strip and if $p_1=1, P(m)$ is given by the conditional probability $(x - y)/(1 - x)$ that after a strip $\bigcirc$, a strip $\square\bigcirc$ follows. Similarly, if $p_2 = 1, P(m)$ is the conditional probability $y/x$ that after a strip $\square\bigcirc$, another of the same kind follows. Thus:

$$P(m) = p_1(x - y)/(1 - x) + p_2y/x,$$  \hspace{1cm} (13)$$

and using $P(m - 2) = p_2$, $P(m - 1) = p_3$, $p_1 + p_2 + p_3 = 1$, Eq. (13) takes the form:

$$P(m) = \beta [1 - P(m - 1)] - \alpha P(m - 2),$$  \hspace{1cm} (14)$$

where

$$\beta = (x - y)/(1 - x) ; \hspace{0.2cm} \alpha = \beta - y/x. \hspace{1cm} (15)$$

Eq. (14) can be solved using the generating function [22]:

$$G(z) = \sum_{m=0}^{\infty} P(m)z^m. \hspace{1cm} (16)$$

Using Eq. (14) and the boundary conditions $P(0) = 1, P(1) = 0$, an equation for $G(z)$ is obtained, the solution of which reads:
\[ G(z) = \frac{1 + (\beta - 1)z}{(1 - z)(1 + \beta z + \alpha z^2)}. \]  

(17)

By integration in the complex plane it can be shown that

\[ P(m) = \delta - R_{m+1}(z_1) - R_{m+1}(z_2), \]  

(18)

where \( R_n(z_i) \) is the residue of \( G(z)/z^n \) at the pole \( z_i \), and \( z_1 \) and \( z_2 \) are the two roots of the polynomial \( \alpha z^2 + \beta z + 1 \). However, the diffraction intensity can be obtained directly from the generating function. Using Eqs. (2) and (16) one has:

\[ I(h) = N | f_{ox} |^2 \delta \left[ G(\exp(i2\pi h)) + G(\exp(-i2\pi h)) - 1 \right], \]  

(19)

and after some algebra, this expression is simplified to:

\[ I(h) = \frac{N | f_{ox} |^2 \delta(1 - \alpha)(1 + \alpha - \beta)}{4\alpha \cos^2(2\pi h) + 2\beta(1 + \alpha) \cos(2\pi h) + (1 - \alpha)^2 + \beta^2} \]  

(20)

Eq. (20), together with Eqs. (10) to (12) and (15) describes the scattering intensity for all \( \delta \leq 1/2 \) and \( T << V_1 \). For \( \delta > 1/2 \), \( I(h) \) is given by the same equation with \( \delta \) replaced by \( 1 - \delta \). The condition for the existence of two split maxima is obtained requiring that the denominator of Eq. (20) as a function of \( \cos(2\pi h) \) has a minimum in the interval \((-1,1)\). One obtains \( 4\alpha > \beta(1 + \alpha) \), or equivalently \( \gamma < \gamma_c \), where

\[ \gamma_c = \frac{4(1 - 2\delta)}{(1 - \delta)} \]  

(21)

Since \( \gamma \geq 1 \), split peaks are possible only for \( \delta < 3/7 = 0.429 \). For these values of \( \delta \), the simple Eqs. (12) and (21) give the critical temperature above which only one peak exists. In the region of compositions and temperatures for which two intensity maxima exist \( (\delta < 3/7 \) and \( \gamma < \gamma_c \)), their positions are given by a very simple expression:

\[ h_{\text{max}} = \frac{1}{2\pi} \arccos \left[ -\frac{\gamma(1 - \delta)}{4(1 - 2\delta)} \right]. \]  

(22)

In the limit \( V_1 >> T >> V_2 \), neglecting terms of order \( \exp(-V_1/T) \) and of order \( V_2/T \), which do not bring any qualitative change in \( I(h) \), one has \( \gamma = T/V_2, y = x^2, \beta = x, \alpha = 0 \)
and \(I(h)\) takes the form of Eq. (8). For \(T << V_2\), neglecting exponentially small terms one has \(\gamma = 1\) and i) for \(\delta \leq 1/3\), \(y = 0\), \(\alpha = \beta = \delta/(1 - 2\delta)\); ii) for \(\delta \geq 1/3\), \(y = (3\delta - 1)/(1 - \delta)\), \(\beta = 1\), \(\alpha = (1 - 2\delta)/\delta\). Case (ii) coincides with the one previously solved by KM \[17\], since Eq. (14) takes the form of the nonhomogeneous difference equation of KM. In both cases, \(I(h)\) takes the form (for \(T << V_2\) and any \(\delta\)):

\[
I(h) = \frac{N \mid f_{ox} \mid^2 \delta(1 - 2\delta) \mid 1 - 3\delta \mid}{4\delta(1 - 2\delta) \cos^2(2\pi h) + 2\delta(1 - \delta) \cos(2\pi h) + 10\delta^2 + 1 - 6\delta} \tag{23}
\]

Eq. (10a) (valid for \(4/9 \leq \delta \leq 1/2\)) and also Eq. (10b) of KM (\(1/3 \leq \delta < 4/9\)) should reduce to the much simpler Eq. (23). Moreover, Eq. (23) extends the results of KM to all values of \(\delta\), and Eq. (22) with \(\gamma = 1\) gives the position of the split maxima. This low temperature limit can be described as an uncorrelated sequence of i) strips \(\bigcirc\) and \(\square\) \(\bigcirc\) \(\bigcirc\) for \(\delta \leq 1/3\) or ii) strips \(\square\) \(\bigcirc\) \(\square\) \(\bigcirc\) \(\bigcirc\) for \(\delta \geq 1/3\). These strips would become correlated if \(V_3\) (and \(V_4\) for \(\delta \geq 1/3\)) were included in the model.

For a comparison with experiment, the low temperature limit Eq. (23) is not good enough and Eqs. (10) to (12), (15) and (20) should be used. In Fig. 1, the evolution of \(I(h)\) with temperature is represented. For \(\delta = 0.364\) and \(T = 0 \ (\gamma = 1)\), \(I(h)\) shows two sharp peaks as already shown in Fig. 1 of KM \[17\]. As expected, the peaks broaden and lose intensity, keeping the same total area, when the temperature is increased. However, as long as two well defined maxima exist, the positions of the peaks do not depend strongly on temperature. For \(\gamma = 1.2\), the result is very similar to one of those obtained by Beyers \textit{et al.} for \(\delta = 0.35\) \[2,16\]. For \(\delta = 0.25\), the experimental peaks are somewhat sharper, suggesting that repulsions at larger distances than two lattice parameters are also present \[10,13\]. Other difficulties in the comparison between theory and experiment are the possibility of phase separation \[2,16\] and that a fraction of oxygen atoms always remains disordered \[24\], particularly for quenched samples. For comparison with the experimental results in quenched samples \[16\] with \(\delta = 0.27\), \(\delta = 0.35\) and \(\delta = 0.43\), \(\delta\) is replaced by \(5\delta/4\) in the theoretical curves, following Ref. \[24\]. The corresponding results for \(\gamma = 1.2\), shown in Fig. 2, are in good agreement with experiment. The intensity for \(\delta = 0.35 \times 5/4\) is somewhat higher than the
experimental one.

The agreement with experiment can be improved by adding more interactions. Also a quantitative agreement with experiment was obtained postulating that $P(2n+1) = 0$ within domains, the size of which is adjusted for each $\delta$ \cite{16}. However, except in unrealistic limits, an analytical treatment of the problem is no longer possible in these cases and a further improvement of the present results can only be done at the cost of a loss in simplicity and physical transparency. Furthermore, in view of the above mentioned experimental uncertainties, the analytical results are already satisfactory.

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When the 1D model is regarded as a limiting case of 2D models of O ordering \cite{14,10}, the temperature should be low enough to ensure a correlation length of several lattice parameters along the CuO chains. A study of the relevant correlation functions suggests that the limiting temperature lies roughly 30\% below the tetragonal-orthorhombic transition temperature for $\delta = 1/2$ \cite{13,10}.

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FIGURES

FIG. 1. Intensity as a function of diffraction vector for several values of $V_2/T$ (see Eq. (12)), $V_1 >> T$ and (a) $\delta = 4/11$, (b) $\delta = 1/4$. In (a), the critical temperature above which only one peak exists is given by $\gamma = \gamma_c = 12/7$ (see Eqs. (12) and (21))

FIG. 2. Intensity as a function of diffraction vector for $\gamma = 1/2$, $V_1 >> T$ and several values of $\delta$. 

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