Neutron Scattering and Stability of Certain Disordered Magneli phases of $YBa_2Cu_3O_{6+x}$

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Abstract

We study two partially ordered phases A and B of the CuO_x planes (those which contain the O vacancies) of $YBa_2Cu_3O_{6+x}$. They consist of a random distribution of two types of parallel strips. In phase A, for $x > 1/2$, one strip is given by a full Cu-O chain and the other is composed of one full and one empty chain. In phase B, for $x > 1/2$ the first strip is replaced by one consisting of three chains, two of them full and the other empty. For $x < 1/2$, full and empty chains are interchanged. While diffraction patterns of phase B are known to consist of two peaks for $x > 0.556$, we obtain that in phase A only one broad peak at $\vec{k} = (\pi/a, 0, 0)$ exists. Comparing the stability of finite domains of both phases, we show that O-O repulsive interactions at distances of at least $2a$ are necessary to explain the diffraction experiments.

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The atomic structure of the CuO_x planes of $YBa_2Cu_3O_{6+x}$ and its relation with electronic and superconducting properties is one of the most interesting and studied problems in the field of high T_c superconductivity. There are at least three different stable phases for the arrangement of O atoms: tetragonal[1], 1×1 orthorhombic[1] and 2×1 orthorhombic[2,3]. For $x \sim 1/8$ and $x \sim 7/8$, $2\sqrt{2} \times 2\sqrt{2}$ structures have been reported[4]. These can be explained if O repulsions are still important at distances ~ 11Å. In other diffraction experiments, diffuse peaks at positions $\vec{q} = (2\pi/a)(1/2\pm\varepsilon, o, o)$ have been observed[5,6,7]. These experiments can be interpreted in terms of (n×1) structures with n = 3,4,5 and 8. There is evidence that these structures, which give rise to split diffraction peaks, are metastable[7]. In spite of this, it is interesting to note that <u>all</u> observed diffraction patterns can be explained as arising from structures that result from the competition of long-range Coulomb repulsion and a tendency of O ions to order in chains[8]. This tendency can be explained from electronic calculations based on the extended Hubbard model[8]. If it is sufficiently large and the temperature sufficiently low, the system consists of full and empty Cu-O chains. Following Ref. 9 we shall denote them by the symbols o and □ respectively. Khachaturyan and Morris[9] explained the split diffuse diffraction peaks in terms of a phase, which can be interpreted as a random assemblage of strips (oo□) with probability α' and (o□) with probability $\beta' = 1-\alpha'$. This phase, which we call B, is thought as metastable. However, if this phase exists at all, it should have lower energy as the phase which we call A, consisting of a random assemblage of strips (o) and (o□). Otherwise, there is no reason why three consecutive full CuO chains should be avoided and phase

A is favoured. This is the case for the model of Ref. 10 where only interactions up to second nearest neighbours are included. These interactions are enough to stabilize the 2×1 structure and the phase A with respect to the completely random phase, since phase A is the most disordered one among those which minimize the repulsion between nearest-neighbour Cu-O chains. Therefore, it should be favoured at T→0.

Are the interactions up to second-nearest-neighbour O atoms[10] enough to explain the split peaks? Since the stable completely ordered phases of the model of Ref. 10 do not give split peaks, it remains to study phase A. The scattering intensity for wave vector $\vec{k} = (2\pi/a)(q,0,0)$ and $0<q<1$ is proportional to[9,11]:

$$I(q) = x \sum_{n=-\infty}^{\infty} e^{i2\pi qm} P(m) \qquad (1)$$

where P(m) is the conditional probability of finding the m^{th} Cu-O chain full if the 0^{th} is also full. P(m) can be related to P(m-1). If P(m-1)=0, then the chain m-1 is empty (it is the second of a strip (o□)) and the chain m is full (it belongs to a strip (o) or is the first chain of a strip (o□)). If instead P(m-1) = 1, then P(m) = 1 if and only if the chain m-1 belongs to a (o) strip (i.e. with probability α). Therefore:

$$P(m) = 1-P(m-1) + P(m-1)\alpha = 1-\beta P(m-1) \qquad (2)$$

Eq. (2) can also be obtained noting that the probability of finding the m^{th} chain empty, (1-P(m)), equals that of finding the chain m-1 full and belonging to a (o□) strip. The solution of Eq. (2) with the boundary condition P(0) = 1, extended also to

negative m, is:

$$P(m) = \frac{1-(-\beta)^{|m|+1}}{1+\beta} \qquad (3)$$

α or β can be related to x in the following way: the average O content per strip is:

$$x_s = \alpha L + \beta L = L \qquad (4)$$

where L is the length of the strips in units of the lattice parameter *b*. The average number of unit cells per strip is:

$$n_s = \alpha L + 2\beta L = (1+\beta)L \qquad (5)$$

and dividing

$$x = \frac{x_s}{n_s} = \frac{1}{1+\beta} \qquad (6)$$

which coincides with $P(\infty)$ as it should be. Replacing (3) and (6) in (1) one obtains:

$$I(q) = \frac{x\beta\,(1-\beta)}{1+\beta^2+2\beta\,\cos(2\pi q)} \qquad (7)$$

The above derivation assumed $x \geq 1/2$. For $x \leq 1/2$, full and empty chains are interchanged, and Eq. (7) is still valid if x is replaced by 1-x in Eqs. (6) and (7).

I(q) is represented in Fig. 1. It always has the form of a peak centered at $q = 1/2$. For $x \to 1/2$ the peak becomes extremely narrow, since the 2×1 stoichiometric phase is reached in this limit. Instead, for $x \to 0$ or $x \to 1$ the peak broadens and disappears.

In the thermodynamic limit $L\to\infty$, the entropy of phase A vanishes due to the fact that the order along the chains is perfect. However, experimentally in the Monte Carlo calculations[10] L~50, which leads to a finite entropy. The entropy per strip is the ideal one (in units of the Boltzmann constant):

$$S_s = -(\alpha \ln\alpha + \beta \ln\beta), \qquad (8)$$

Dividing by n_s given by Eq. (5) and using (6), we obtain the entropy per unit cell:

$$S = \frac{1}{L} \left| x \ln x - (1-x)\ln(1-x) - (2x-1) \ln|2x-1| \right| \qquad (9)$$

Eq. (9) has been written in a way such that it is valid for all compositions $0\le x\le 1$. Thus, phase A can be defined as that of largest entropy among those which minimize the interactions up to the 4th nearest-neighbour O atoms (assuming $a=b$), because as it will become clear later, these do not have nearest-neighbour empty (full) chains for $x\ge 1/2 (x\le 1/2)$. Therefore if interactions of longer range are not included, phase A dominates the scenario for $T\to 0$ and no split peaks can be observed. At finite T, phase A is not that of minimum thermodynamic potential, because it is convenient for the system to lose some energy in order to increase the entropy, particularly for $x\to 1/2$. However, this disordering can only broaden and not split the peak at $q = 1/2$. In any case, the agreement between these simple results and those obtained using Monte Carlo[10] at low temperature is noticeable.

Thus, the experimental results indicate that repulsive interactions at distances of at least $2a$ (5th nearest neighbours)

should be included. This brings support to the model of Ref. 8. These interactions are enough to stabilize 3×1 structures at $x = 1/3$ and $x = 2/3$, whose diffraction patterns present peaks at $q = 1/3$ and $q = 2/3$. However, for intermediate compositions, $1/3<x<1/2$ or $1/2 < x < 2/3$, the B phase proposed in Ref. 9, is favoured by the entropy if the size of the domains is finite, as we shall show, or by the slow kinetics of the decomposition reaction.

In order to compare the free energy of the A and B phases, we assume that the energy can be described in terms of the following model[8,11]:

$$H = \varepsilon_o \sum_i n_i + \frac{1}{2} \sum_{i,j} V_{ij}\, n_i n_j \qquad (10)$$

where n_i is the atomic occupation number at position i, ε_o the binding energy of a single oxygen atom and V_{ij} the interaction energy between two O ions at positions i and j. We assume that the attraction between second-neighbour O atoms with a Cu in between is sufficiently strong and the temperature sufficiently low, so that the O ions are arranged in chains parallel to $\vec{b}$. Thus, the model written in terms of the occupation numbers $m_i = 1,0$ of the chains becomes one-dimensional:

$$H = \frac{L}{2} \sum_{i1} W_1 m_i m_{i+1} = \frac{L}{2} \left[\sum_i W_o m_i + \sum_{i,1\neq o} W_1 m_i m_{i+1} \right] \qquad (11)$$

where

$$W_1 = 2\varepsilon_o \delta_{o1} + \sum_j V_{ij}\, \delta\left[\left(\vec{R}_j - \vec{R}_i \right) . \vec{a} - 1 \right] \qquad (12)$$

Eq. (11) has the same form if full and empty chains are interchanged. Calling $\tilde{m}_1 = 1-m_1$, one has:

$$H = \frac{L}{2}\left[\sum_{i1} W_1 - \sum_i \left(W_o + 2\sum_{1\neq o} W_1\right)\tilde{m}_1 + \sum_{1,1\neq o} W_1 \tilde{m}_1 \tilde{m}_{1+1}\right] \qquad (13)$$

Therefore, for a given composition, the minimum energy is obtained minimizing the last term of Eq. (11) or equivalently the last term of Eq. (13). In particular if $W_1 = 0$ for $1 \geq 2$ and $W_1>0$, the minimum energy for $x>1/2$ ($x<1/2$) is obtained if nearest neighbour empty (full) chains are avoided, which is a property of phase A. In terms of the conditional probabilities P(i), the energy per unit cell of Hamiltonian (11) is:

$$E = \frac{x}{2}\left[W_o + \sum_{1\neq o} W_1 P(1)\right] \qquad (14)$$

We consider here only interactions V_{ij} for which $|\vec{R}_i-\vec{R}_j|<3a$. Thus $W_1 = 0$ if $i>2$. We assume $W_1>W_2>0$. Using Eqs. (3) and (14) we find for phase A:

$$x \geq 1/2,\ E_A = \frac{W_o}{2} x + W_1(2x-1) + W_2\left[\frac{1}{x} - 3(1-x)\right] \qquad (15)$$

and using the full-empty chain transformation given by Eq. (13):

$$x \leq 1/2,\ E_A = \frac{W_o}{2} x + W_2\left[\frac{1}{1-x} - x - 1\right] \qquad (16)$$

For $x > 1/2$, phase B is composed of strips (oo□) with probability α' and (o□) with probability $\beta' = 1-\alpha'$. It is the most disordered among those which minimize the terms in W_1 and W_2

for given $x > 1/2$. The energy per strip is given by:

$$n'_s E_B = \alpha'(W_o + W_1 + W_2) + \beta'(W_o/2 + W_2) \qquad (17)$$

Following the same reasoning that led to Eqs. (4), (5), (6) and (9), we obtain for phase B if $x > 1/2$:

$$x'_s = 2\alpha' L + \beta' L = (1+\alpha')L \qquad (18)$$

$$n'_s = 3\alpha' L + 2\beta' L = (2+\alpha')L \qquad (19)$$

$$x = 1 - \frac{1}{2+\alpha'} \qquad (20)$$

$$S_B = (1-x)\ln(1-x) - (2x-1)\ln(2x-1) - (2-3x)\ln(2-3x) \qquad (21)$$

Eq. (20) was already obtained in Ref. 9. From Eqs. (17), (19) and (20) one obtains:

$$x \geq 1/2, \quad E_B = \left[\frac{W_o}{2} + 2W_1\right]x - W_1 + (1-x)W_2 \qquad (22)$$

And using again the full-empty chain transformation:

$$x \leq 1/2, \quad E_B = \frac{W_o}{2}x + (3x-1)W_2 \qquad (23)$$

$$S_B = x\ln x - (1-2x)\ln(1-2x) - (3x-1)\ln(3x-1) \qquad (24)$$

In Fig. 2 we show for different values of W_2/W_1, the result of comparing the four different expressions (phase A or B, $x \geq 1/2$ or $x \leq 1/2$) of the thermodynamic potential $\Omega = E - TS - \mu x$ in

the μ, T plane. The relevant equations are (9), (15), (16), and (21) to (24). The composition x that corresponds to a given chemical potential μ for each phase is determined by the equation:

$$\mu = \frac{\partial(E-TS)}{\partial x} \tag{25}$$

All transitions are first order. Due to the fact that both phases are perfectly ordered at all temperatures for x=1/2 (as a consequence of the assumption that the structures always have minimum energy), both phases near x=1/2 are unstable against decomposition in two phases of the same type (A or B) but with compositions more different from 1/2. This is clearly seen in Fig. 3(a). The chemical potential at which this first order transition occurs is determined by the symmetry transformation that interchanges full and empty chains and is given by:

$$\mu_o = W_o/2 + W_1 + W_2 \tag{26}$$

In Fig. 3(a) the phase diagram is shown in the x-T plane. Split diffraction peaks can only occur for $0.556 < x < 2/3$ (or 1-x in the same interval)[9] and in the B phase. According to Fig. 3(a), split peaks can only be seen if roughly $W_2 > T/L$. For these parameters and similar compositions, we obtain a first order transition between phases A and B. This might be related to the observations of Tetenbaum et al.[12], which suggest the existence of a region of constant μ for $x \sim 0.6$, qualitatively similar to that shown in Fig. 3(b). Concerning this figure, we should note that the first order transition near 1/2 is artificial, for reasons explained before, while the results for $x < 1/3$ might be

unrealistic, since the screening length is expected to be much larger and then it is more difficult to stabilize the Cu-O chains against other structures[8,11] that minimize the Coulomb repulsion. Phase B is in fact stable for T = 0 and $1/3 \leq x \leq 2/3$ if $W_2 > 0$ and $W_i = 0$ for $i>2$. If interactions of longer range are included in the model, then other stoichiometric phases with x = 4/7, 3/5, 5/8, 5/7 and the symmetric compositions with respect to 1/2 ($x \rightarrow 1-x$), have lower energy for the corresponding values of x (Ref. 8).

If $W_2 = 0$, there is no reason for the system to prefer phase B with respect to phase A, even if one or both of them are metastable. However, if $W_2 > 0$, then phases with x = 1/3 and x = 2/3, which correspond to limiting cases of phase B, are stable and have diffraction peaks at q = 1/3 and q = 2/3. If the W_i with $i>2$ are important, other phases with split diffraction peaks become stable. In this reasoning, we are assuming that full and empty chains are always stable. In this case, it is clear that one can consider the split peaks to be originated by stable phases (or slightly metastable with excitation energies W_i with $i>2$ and composition very near to the one corresponding to a stable phase). The other possibility is that the chains themselves are metastable against formation of regularly spaced vacancies. In this case, the structures $2\sqrt{2} \times 2\sqrt{2}$ seen by Alario-Franco et al.[4] would be stable and the chain structures could be stable or metastable depending on the composition (more stable for $x \rightarrow 1/2$), the relative strength of the Coulomb repulsion and the tendency to order in chains, as was shown in Ref. 8.

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Figure Captions

Figure 1: Diffraction intensity as a function of wave vector $(2\pi/a)$ $(q,0,0)$, $0<q<1$, for phase A and different compositions x denoted inside the figure. The intensities corresponding to compositions x and 1-x are the same.

Figure 2: Temperature-chemical potential phase diagram showing the regions of stability of phases A and B. Full line $W_2/W_1 = 0.2$, dashed line $W_2/W_1 = 0.1$, dotted line $W_2/W_1 = 0.05$.

Figure 3: (a) Temperature-composition phase diagram showing the regions of stability and coexistence of the different phases. Parameters are the same as in Fig. 2.

(b) Chemical potential as function of composition for $W_2/W_1 = 0.2$ and $T = 0.08W_1$.

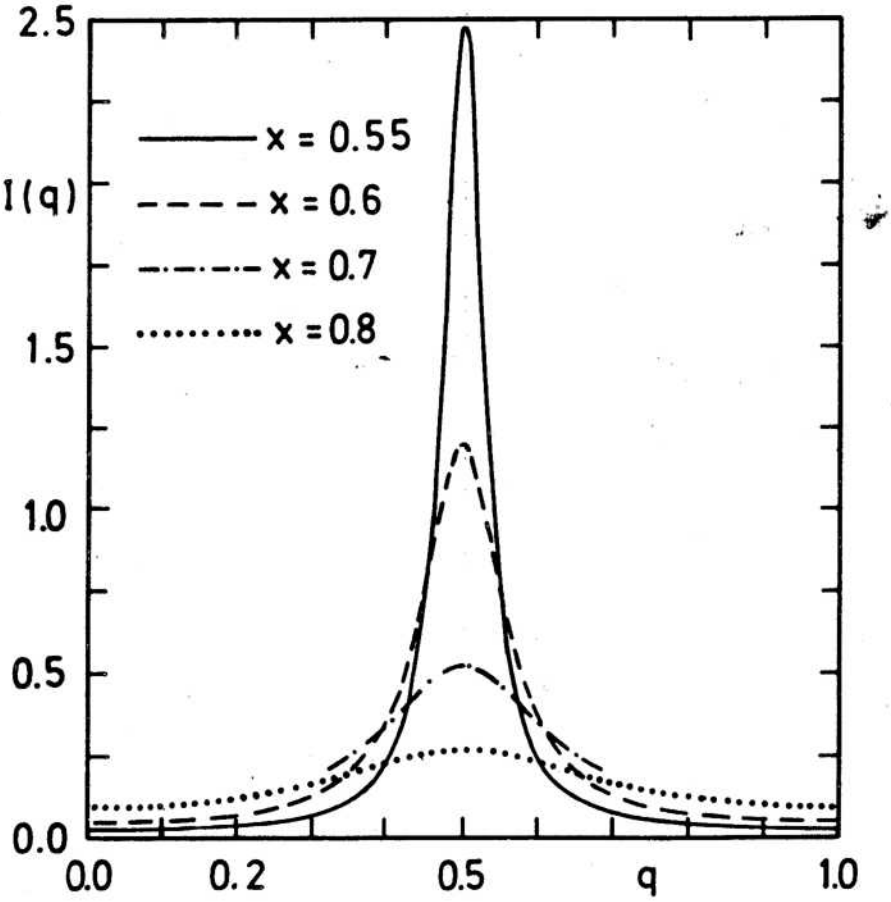

Fig. 1

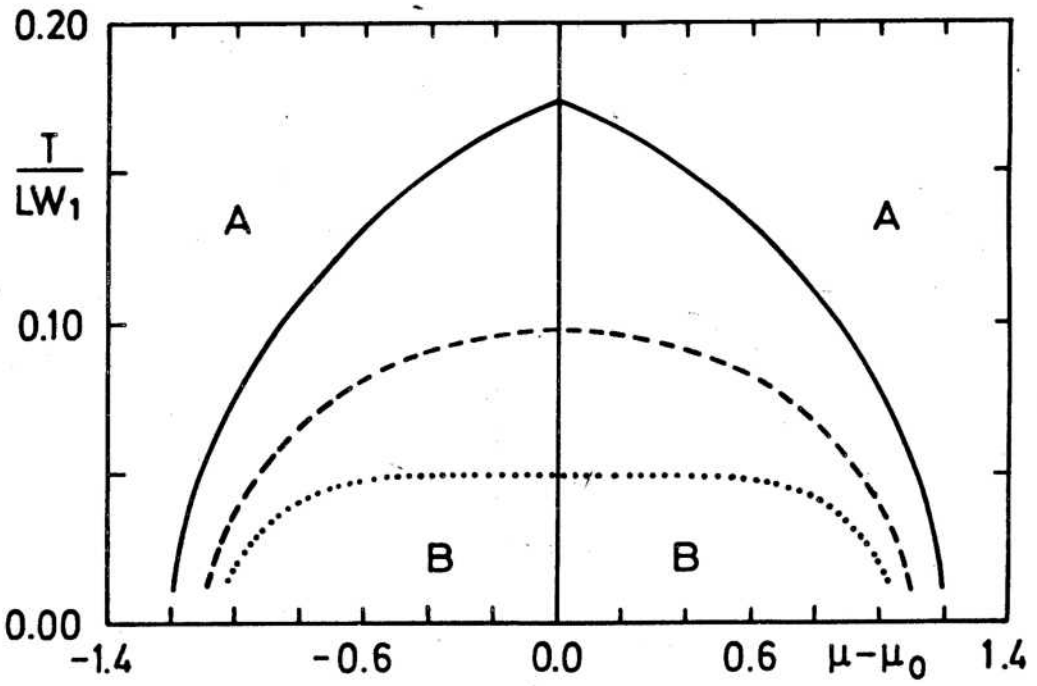

Fig. 2

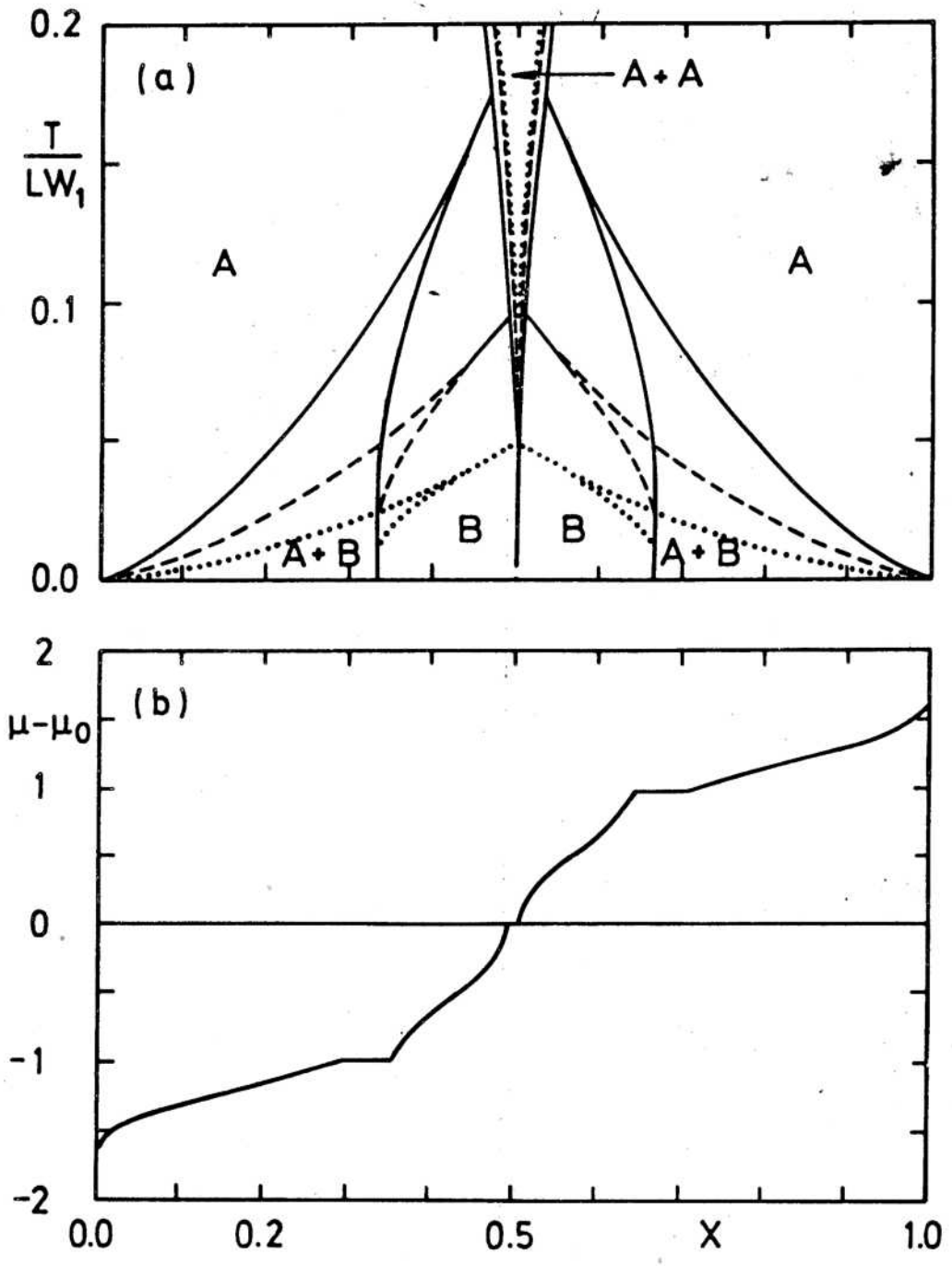

Fig. 3