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1992 J. Phys.: Condens. Matter 4 L585

(http://iopscience.iop.org/0953-8984/4/43/003)

J. Phys.: Condens. Matter 4 (1992) L585–L592. Printed in the UK

LETTER TO THE EDITOR

Long-range interactions, long-range order and a devil's staircase in $YBa_2Cu_3O_z$

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Received 21 August 1992

Abstract. It is shown that the oxygen-ordered superstructures observed experimentally in $YBa_2Cu_3O_z$ can be understood in terms of an Ising Hamiltonian containing screened Coulomb repulsions between any two oxygen sites, augmented with a short-range attractive covalent interaction between oxygen sites adjoined by a copper atom. Spatially modulated commensurate phases separated by smooth soliton-like domain walls are obtained through Monte Carlo simulations. These simulations indicate the existence of a complete devil's staircase of phases. It is predicted that the plateau fine structure of the T_c–z curve and the bond valence sum also exhibit experimentally observable staircase behaviour.

While the high-temperature oxygen-ordering behaviour and the concomitant tetragonal–orthorhombic phase transformation in $YBa_2Cu_3O_z$ are now reasonably well understood [1–2], the nature of the low-temperature ordering remains controversial. Electron microscopy and diffraction [3–9] have provided ample evidence for the presence of small domains containing uniaxially modulated superstructures with reciprocal lattice vectors $\boldsymbol{k} = (\frac{1}{3},0,0)$, $(\frac{1}{4},0,0)$, $(\frac{1}{5},0,0)$, in addition to the generally accepted stable phases, *OrthoI* with $\boldsymbol{k} = (1, 0, 0)$ and *OrthoII* with $\boldsymbol{k} = (\frac{1}{2}, 0, 0)$. However, it is still hotly debated whether these higher-order modulated phases are transient [10, 11], metastable [12, 13] or stable [14–16]. First-principles calculations [17, 18] provided an excellent parameter-free description of the phase diagram [17–20], but did not address the question of the stability of these modulated phases. The residual uncertainties do not definitively exclude the possibility of narrow stability ranges for the modulated phases. It is the purpose of the present contribution to propose a plausible interaction model stabilizing those phases and to analyse some of its statistical properties.

It is now widely accepted that the oxygen ordering in the $YBa_2Cu_3O_z$ basal plane can be accurately described by a two-dimensional Ising model with occupied and

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0953-8984/92/430585+08$04.50

empty oxygen sites as pseudospin variables (σ_i), i.e. with a Hamiltonian of the form:

$$\mathcal{H} = \tfrac{1}{2}\sum_{i\neq j} V_{ij}\sigma_i\sigma_j - \mu\sum_i \sigma_i \tag{1}$$

where V_{ij} denotes the interaction between sites i and j and μ is the chemical potential (related to oxygen partial pressure: $\mu = \mu_0 + \ln p_{O_2}$). The simplest such model [2, 10, 11, 21] that includes *OrthoI* and *OrthoII* as stable phases necessitates the presence of a repulsive first-neighbour interaction, an attractive second-neighbour interaction for oxygen sites with an intervening Cu atom, and a repulsive second-neighbour interaction for oxygen sites without intervening Cu atom. Such behaviour is in agreement with simple chemical bonding argument [2] and is also consistent with first-principles electronic structure calculations. However, the model does not stabilize modulated superstructures beyond *OrthoII* [21], although it does support the occurrence of such phases as transients in small domains [10, 11]. In order to stabilize structures characterized by a rational wave vector $\boldsymbol{k} = (p/q, 0, 0)$ where $q \geqslant 3$, further-neighbour interactions need to be present [22]. A possible choice is to augment the interaction set to include long-range repulsions along the modulation direction, thus explicitly stabilizing the whole range of uniaxially modulated superstructures [14]. While such a choice does indeed lead to the required phases being ground states, Monte Carlo simulations [23] of this model show that the kinetic evolution towards those phases is exceedingly slow and that deviations from stoichiometry are dynamically incorporated by the introduction of 45° twin boundaries, between *OrthoI* or *OrthoII* domains, rather than by formation of the other superstructures. In addition, the presence of one-dimensionally modulated phases does not necessarily imply the existence of one-dimensional interactions and since the repulsions between oxygen sites are expected to be electrostatic in nature it is more natural to allow for a screened Coulomb repulsion between *any* two oxygen sites in the basal plane, but include an attractive covalent interaction between oxygen sites separated by a Cu atom. Similar models have been proposed previously [15, 16, 22] but their low-temperature and kinetic behaviour in particular with respect to the higher-order modulated phases have not been investigated so far. To address this issue, in the present paper the interaction V_{ij} between sites i and j separated by a distance $|\boldsymbol{r}_i - \boldsymbol{r}_j|$ is taken to be of the form:

$$V_{ij} = V_1 \exp\left[-\lambda|\boldsymbol{r}_i - \boldsymbol{r}_j|\right]/|\boldsymbol{r}_i - \boldsymbol{r}_j| + V_2 f_{ij} \tag{2}$$

where $f_{ij} = 1$ for next-nearest-neighbour sites separated by a Cu atom and $f_{ij} = 0$ otherwise. In order to favour chain formation the net interaction between second-neighbour sites separated by a Cu atom must be attractive. Thus the model contains three parameters: an inverse screening length λ (> 0), a Coulomb prefactor V_1 (> 0) and a covalent interaction V_2 (< 0). Within these bound it can be seen that *all* uniaxially modulated phases must be true ground states of the Hamiltonian. If λ is sufficiently large, interactions beyond second neighbours become negligible and this model essentially reduces to that studied before [2, 10, 11, 17–19], except for the presence of the higher-order modulated phases in very narrow stability domains. In order to be consistent with the first-principles calculations [17,18] it is indeed to be expected that λ must be fairly large. The possibility of a concentration-dependent λ has also been recently suggested [16].

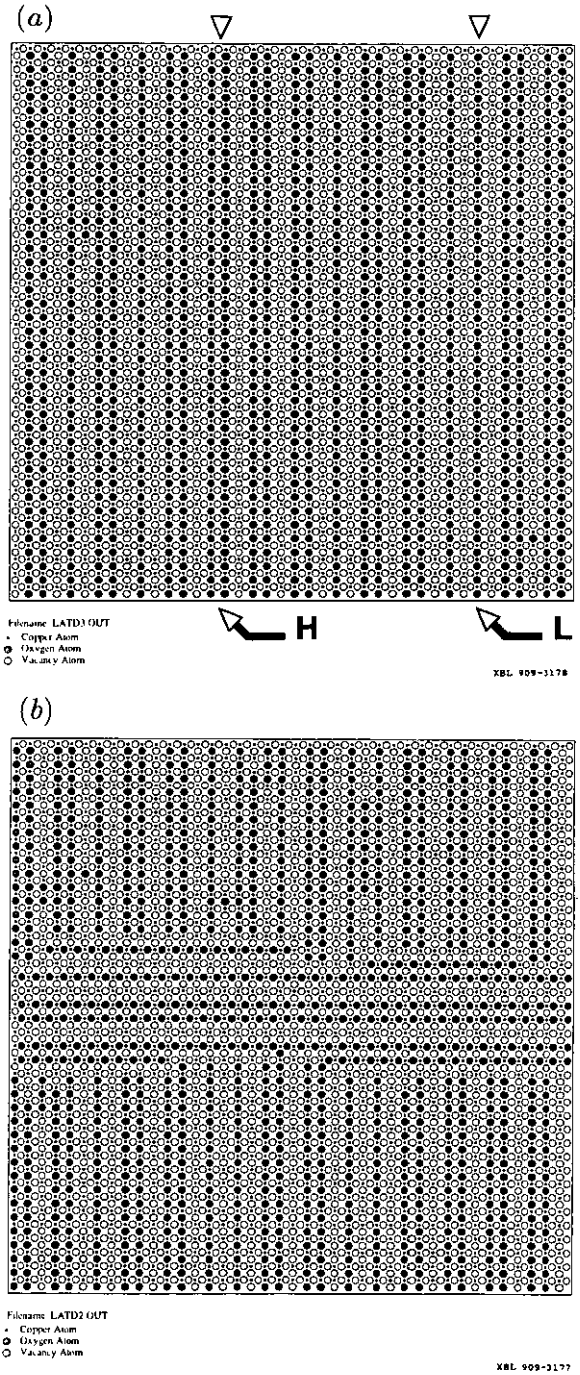

Figure 1. Monte Carlo snapshots of the basal plane in $YBa_2Cu_3O_z$ obtained after 1000 MCS at a reduced temperature $k_BT/V_1 = 0.7$. Black dots denote Cu atoms, shaded circles are oxygen atoms and open circles are vacancies. (a) Fivefold unit cell with $\boldsymbol{k} \approx (\frac{3}{5}, 0, 0)$ obtained at chemical potential $\mu = -3.95$. Typical heavy (H) and light (L) domain walls are indicated. Other line and point defects may be observed. (b) Complex structure with multiple domains corresponding to $\boldsymbol{k} \approx (\frac{4}{7}, 0, 0)$, $(\frac{2}{5}, 0, 0)$ and $(\frac{5}{7}, 0, 0)$, separated by line defects, and a nearly 90° twin boundary was obtained at $\mu = -3.80$. The 90° type of defect was occasionally observed, most often at chemical potential values intermediate between those for structures with low-order modulation periods.

Monte Carlo simulations were performed in the grand canonical ensemble on lattices varying in size from 32×32 to 64×64 (with two oxygen sites per unit cell) and up to 10^5 Monte Carlo steps per spin (MCS). A variety of interaction parameters were studied and it was found that for all values within the stability domain delineated above, modulated phases were consistently formed. In order to accelerate the kinetics of domain formation a fairly small value of $\lambda = 1.0$ (in units of the inverse lattice constant) was adopted in the simulations reported here. While this choice modifies the time scale and the extent of the phase fields, it was found not to affect the qualitative discussion of the kinetic behaviour. For this value of λ, formation of modulated domains was generally very rapid and was usually achieved within the first 10^3 Monte Carlo steps. The Ising interaction parameters V_1 and V_2 were taken to be 1.0 and -0.5, with V_1 used as a temperature scaling factor.

Depending on chemical potential, phases were observed with modulation period $q = 3$, 4, 5, and 7, although it was difficult to distinguish the $q = 7$ structures from faulted lower-order phases. Triple-unit-cell phases could usually be grown into almost perfect single domains over a relatively wide range of chemical potential values. Snapshots exhibiting some of these phases and their typical defects are shown in figure 1. These were obtained by following the evolution of an initially empty lattice at a fixed temperature of $k_B T/V_1 = 0.7$, where k_B is Boltzmann's constant. Depending on chemical potential and commensurability with the lattice size the final configuration contained single or mixed phase modulated structures, occasionally separated by nearly 90° and, less frequently, nearly 45° domain boundaries. Figure 1(a) shows a phase of predominantly $\boldsymbol{k} = (\frac{3}{5}, 0, 0)$ character with a number of point and line defects (heavy and light domain walls, as indicated), obtained at a chemical potential $\mu = -3.95$. The corresponding Fourier transform intensity shown in figure 2(a) shows a striking similarity to experimental diffraction patterns interpreted as originating in a fivefold unit cell [4, 5, 8]. Figure 1(a) shows a preponderance of heavy domain walls, indicating a slight 'overpressure' in chemical potential. As the chemical potential was decreased (at finite temperature), a nearly perfect $\frac{3}{5}$ phase ($z = 6.6$) was obtained, followed by a structure containing more light than heavy domain walls ($6.57 < z < 6.6$) and finally a transition to a predominantly $\frac{4}{7}$ ($z = 6.57$) phase. Another occasional observation in the simulations was the occurrence of (approximately) 90° twin boundaries, of which a typical example is shown in figure 1(b) obtained under the same preparation conditions as figure 1(a) but at a chemical potential $\mu = -3.80$. Such structural defects have been observed experimentally [24], although they have not received the same degree of attention as the strain-related 45° twin boundaries. This domain boundary is accompanied by a substantial number of line defects, leading to considerable streaking in the Fourier transform intensity shown in figure 2(b). It is thus not possible to assign a unique wavevector to the structure in figure 1(b). As can be seen it contains mixed domains corresponding mainly to $\boldsymbol{k} = (\frac{4}{7}, 0, 0)$, $(\frac{2}{3}, 0, 0)$ and $(\frac{5}{7}, 0, 0)$. For chemical potential μ near -3.60 at the same temperature, nearly perfect $\boldsymbol{k} = (\frac{2}{3}, 0, 0)$ structures were obtained in the simulations, while for μ near -3.95 a predominantly fivefold unit cell was found with $\boldsymbol{k} \approx (\frac{3}{5}, 0, 0)$ (see figure 1(a)). This type of complex domain formation was frequently observed at chemical potential values intermediate between low-order single phases. In general, the higher the order (q) of the phases the more difficult they are to grow in the simulation, with the highest-order phases observed in reasonably large domains corresponding to $q = 7$. This can be understood in terms of the general topology of the phase diagram [23]

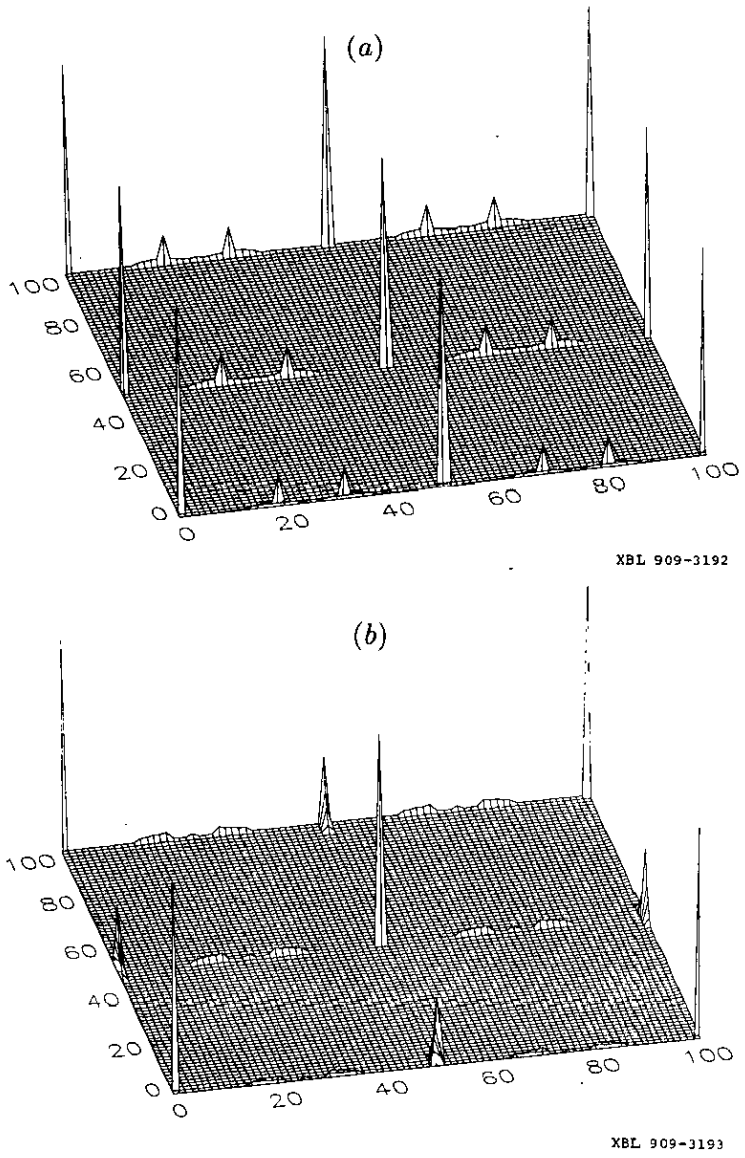

Figure 2. Fourier transform intensities corresponding to the snapshots shown in figure 1.

for the type of interactions studied here, which is very similar to that proposed for graphite intercalation compounds [25]. Below the order–disorder line, such phase diagrams exhibit wide stability regions corresponding to the low-order phases, in this instance to *OrthoI* and *OrthoII*, and in addition narrow stability domains for the higher-order modulated phases, with the width generally decreasing as the order of modulation increases, and, in particular, near absence of even-order phases beyond $q = 2$. This is consistent with the present simulations which show that it is very difficult to grow phases with quadruple unit cells in large domains, and it also explains why fivefold unit cells are more frequently observed experimentally than fourfold unit cells.

In general, the narrowness of the stability domain of the higher-order modulated phases compared to those of *OrthoI* and *OrthoII* explains why careful preparation conditions, such as Zr gettering [4,5] or constant stoichiometric cooling [6–8], are needed to grow modulated domains with $q \gtrsim 3$.

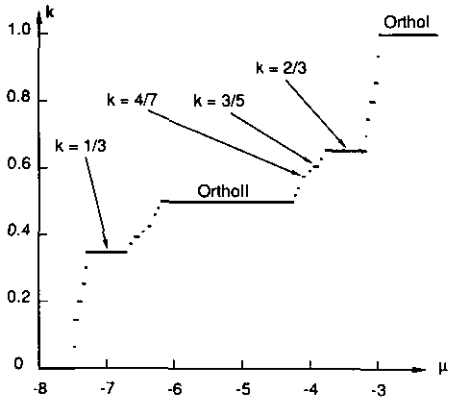

Figure 3. Principal modulation vector k ($\approx z - 6$), estimated from Monte Carlo simulations, plotted against chemical potential μ strongly suggests the presence of a complete devil's staircase.

Hamiltonians similar to the one studied here, exhibiting uniaxial, commensurately modulated phases, and in particular, their domain walls and the associated phase transitions, have been extensively studied [26,27]. It was shown that the topology of the phase diagram and the domain wall behaviour depend only on the general features of the interactions. In particular, it is very likely, although not rigorously proven, that for convex interactions a complete devil's staircase [22,28] is obtained at low temperatures, and this is entirely consistent with the previous discussion of the Monte Carlo snapshots. To illustrate this possibility further, figure 3 shows the dominant wave vector as a function of chemical potential derived from a large number of Monte Carlo simulations (at $k_B T/V_1 = 0.7$). Some of the major low-order phases have been indicated; it is to be particularly noted that the complex structure in figure 1(b) obtained at $\mu = -3.80$ corresponds to a higher-order modulation period. While care must be taken in extracting this from the simulations and no corrections have been made for finite-size and kinetic effects, the resemblance to a true devil's staircase is striking indeed. Since T_c has been shown to correlate with the degree of order via the hole doping [29,30], this strongly suggests that the plateau structure in the curve of T_c versus oxygen content [8,29,30] is in reality also a devil's staircase smeared out by experimental resolution. This provides a compelling explanation for many observations that the 60 K plateau is not completely flat and is also consistent with the observation [8] that this plateau extends beyond the *OrthoII* stability domain, indicating that T_c for the nearby modulated phases may be distinct from 60 K but is probably very close to it. A thorough analysis of the experimental T_c–z relation may be able to find additional steps, most likely to be detected near $z = 6.67$ ($k = \frac{2}{3}$). For the same reasons the bond valence sum [30,31] is expected to exhibit a devil's staircase. This is not incompatible with the results of de Leeuw *et al* [31], but the scatter in their data is too large to allow one to draw any definitive conclusions. As devil's staircase phases are known to be very

sensitive to metastability problems, the present results also explain the conflicting reports on possible phase separation between *OrthoI* and *OrthoII* that have appeared [32]. The inclusion of elastic distortions in the Hamiltonian would exacerbate the metastable behaviour. Finally, in agreement with the general analysis of [26] and [27], at elevated temperatures the domain walls observed in figure 1 were found to lead to interfacial wetting between modulated phases, most likely accompanied by a domain wall roughening transition [23].

Recently, there have been a series of experimental studies reporting x-ray, electron, and neutron diffraction evidence [33–36] for an additional type of ordering attributed to superstructures with either $2\sqrt{2}a_0 \times 2\sqrt{2}a_0$ or $2\sqrt{2}a_0 \times \sqrt{2}a_0$ unit cells. In the present study, only uniaxially modulated chain-ordered oxygen superstructures are observed to form. This finding is consistent with the interpretation that the $\sqrt{2}$ superstructures most likely arise via the action of a Jahn–Teller deformation [33] or by Cu and Ba loss [35,36] rather than through long-range static Coulomb interactions between oxygens in the basal plane of $YBa_2Cu_3O_z$.

In summary, it has been argued that isotropic screened Coulomb interactions with a second-neighbour Cu mediated attractive interaction are able to explain the observed oxygen-ordered superstructures in $YBa_2Cu_3O_z$. The resulting phase diagram and the associated devil's staircase have been discussed and typical defect structures obtained in Monte Carlo simulations have been found to be in excellent agreement with experiment. It is suggested that experimental T_c–z curves or bond valence sums be carefully investigated for the presence of steps. If observed, these would lend considerable support to the present model. It is worth pointing out that the proposed long-range interaction model for the modulated phases in $YBa_2Cu_3O_z$ is of considerable interest in its own right and has been shown to exhibit rich critical behaviour.

DA and LTW were supported by the US Defense Advanced Research Projects Agency (DARPA) under grant No MDA 972-88-J-1006. CPB and RG were supported by a Texas Center for Superconductivity, University of Houston, subcontract under DARPA Grant No MDA 972-88-J-1002, using facilities at Lawrence Berkeley Laboratory (funded by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the US Department of Energy under Contract No DE-AC03-76SF00098. The work of PAS was performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under Contract No W-7405-ENG-48. The authors are indebted to Drs Aligia, Mouritsen, and Rikvold for making available preprints of their papers.

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