Title
VACANCY ORDERING IN THE BASAL PLANE OF YBa2 Cu3Oz

Author
Wille, L.T.

Publication Date
1987-10-01

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Presented at the Materials Research Society
Meeting, Cincinnati, OH, October 10–14, 1987,
and to be published in the Proceedings

Vacancy Ordering in the Basal Plane of $YBa_2Cu_3O_z$

L.T. Wille, A. Berera, D. de Fontaine,
and S.C. Moss

October 1987

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

LBL-24263

VACANCY ORDERING IN THE BASAL PLANE OF $YBa_2Cu_3O_z$

by

L. T. Wille, A. Berera*, D. de Fontaine**
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
and
**Department of Materials Science and
Mineral Engineering
University of California
Berkeley, CA 94720

*Department of Physics
University of California
Berkeley, CA 94720

and

S. C. Moss
Department of Physics
University of Houston
Houston, TX 77004

November 1987

This work was supported by a grant from the Director, Office of Energy Research, Materials Sciences Division, U. S. Department of Energy, under contract DE-AC03-76SF00098.

VACANCY ORDERING IN THE BASAL PLANE OF $YBa_2Cu_3O_z$.

L.T. WILLE *, A. BERERA *,**, D. DE FONTAINE *,† AND S.C. MOSS ‡.
* Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720
** Department of Physics, University of California, Berkeley, CA 94720
† Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720
‡ Department of Physics, University of Houston, TX 77004

ABSTRACT

The ordering in the Cu-O basal plane of the high T_c superconductor $YBa_2Cu_3O_z$ is investigated. Asymmetric pairwise interactions between nearest and next nearest neighbors are assumed. Ordering instabilities in two-dimensional **k**-space are mapped out as a function of the interactions and the ordered ground state superstructures consisting of occupied and empty oxygen sites are determined. A temperature-composition phase diagram is calculated by means of the Cluster Variation Method. The thermodynamic behavior of the superconducting compound is discussed in the light of these results.

INTRODUCTION

The high T_c superconductor $YBa_2Cu_3O_z$ ($z = 7 - \delta$) transforms upon heating from an orthorhombic to a tetragonal structure [1]. This transition is caused by a disordering of the oxygen ions (concentration $c_o = \frac{1}{2}(z-6)$) on the available lattice sites in the Cu-O basal plane. The superconducting critical temperature T_c shows two plateaus as a function of c_o and falls abruptly to zero at the orthorhombic to tetragonal phase transition [2]. Clearly the state of order in this quasi-two-dimensional system has a dramatic effect on superconductivity and it is important to construct theoretical models that are rich enough to analyze this behavior.

In previous work [3,4] the ordering process has been interpreted on the basis of a two-dimensional Ising model as depicted in Fig. 1. Nearest neighbor oxygen sites are coupled by an effective pair interaction (EPI) V_1, while the next nearest neighbor interaction takes the value V_2 or V_3, depending on whether the sites are linked through a Cu ion or not. These EPI's will depend on the full three-dimensional structure of the compound and are in general also concentration dependent. They are conventionally defined in terms of embedded pair energies and are short ranged. The basal plane occupancy in the perfect orthorhombic phase is as shown in Fig. 1 : one sublattice (β) is completely filled by oxygen ions (O), in the other one (α) all sites are vacant ($\square$). Thus, parallel O-Cu-O chains are produced, which are believed to be essential for superconductivity in $YBa_2Cu_3O_z$ and related ceramics.

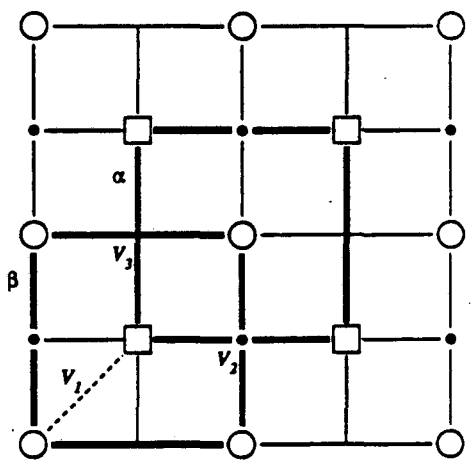

Fig. 1 Model for the $YBa_2Cu_3O_z$ basal plane.

XBL 8711-4810

ORDERED STRUCTURES

In order to investigate which ordered superstructures are to be expected one can perform a stability analysis [3]. In this approach the disordered state is perturbed by imposing a concentration wave and it is determined for which wave vector the free energy first becomes unstable. This instability occurs for concentration wave vectors located at the absolute minimum of the Fourier transform of the EPI's [5]. Moreover, for short ranged interactions, the search for minima can be limited to the so-called special points in the Brillouin zone. At these points, where symmetry elements intersect, any **k**-space function necessarily attains an

extremum (Lifshitz criterion). For the present case it has been shown [3] that the special points are <0 0>, <½ 0> and <½ ½>. In the following, V_1 will be taken to be positive, since a negative value would correspond to a phase separating system and then the structure shown in Fig. 1 would not be a ground state (unless V_2 or V_3 have unphysically large values). Obviously the magnitude of V_1 is merely a scale factor and hence one can define normalized interaction parameters $x = V_2/V_1$ and $y = V_3/V_1$. One can then mark out the region in the xy-plane where a given special point wave is most unstable. Such a stability map is shown in Fig. 2a.

The stability analysis does not yield actual ground states and needs to be complemented by a ground state study. To this end all possible configurations on a 2x4 lattice have been enumerated and the lowest energy structure was mapped out in the xy-plane [4]. Only three values of the concentration give rise to periodic structures : c_o = .25, .50 and .75. The latter corresponds to an interchange of oxygens and vacancies and will not be considered henceforth. The ground state maps are depicted in Fig. 2. The results from an exhaustive search over a multiple unit cell have to be interpreted with some caution as can be seen from Fig. 2b. The structure in the third quadrant corresponds to a phase separating system which can not be inferred from a calculation on a small system. Likewise, the structure in the first quadrant is infinitely degenerate since the O-□ diagonals can slide parallel to each other without any cost in energy. A small third neighbor interaction would be necessary to lift the degeneracy and stabilize one of two possible ground states.

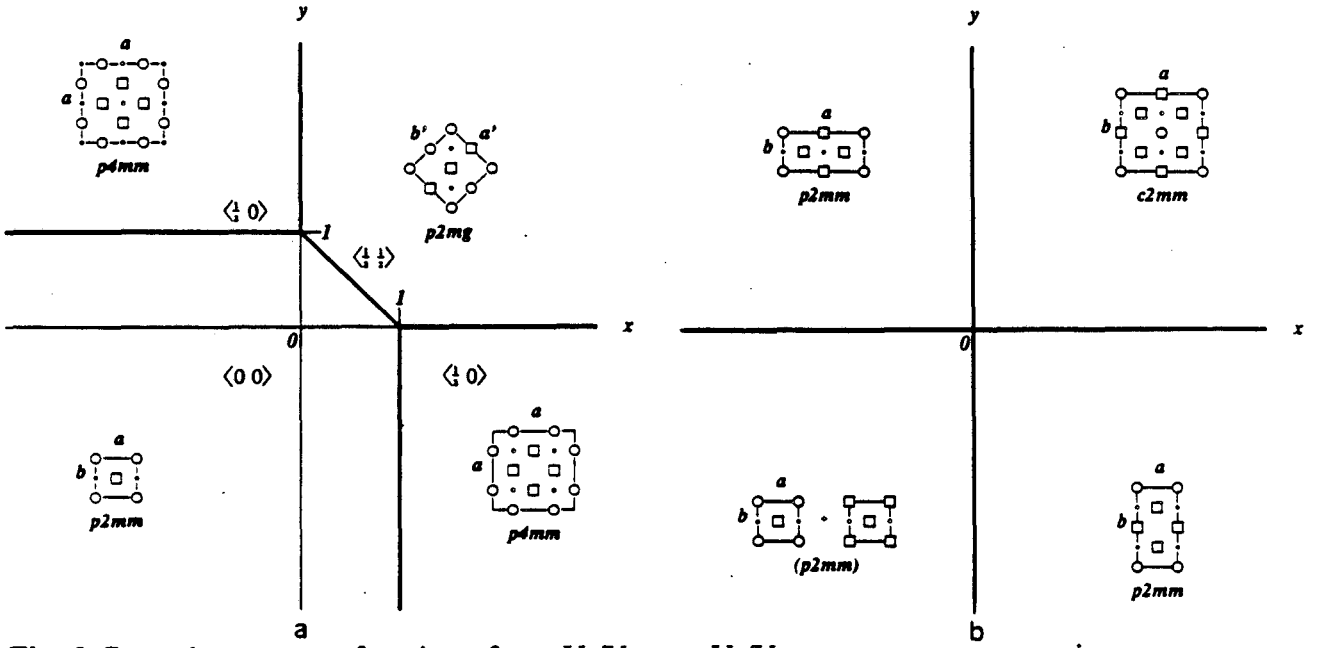

Fig. 2 Ground states as a function of $x = V_2/V_1$, $y = V_3/V_1$, at oxygen concentration : (a) 0.50 (b) 0.25.

XBL 878-3718

The resulting ground states can now be interpreted by means of the concentration wave idea. For example, the <0 0> instability will place infinite wavelength modulations on the α and β sublattice in full agreement with the ground state structure. For other special points and off-stoichiometry it may be necessary to consider superpositions of ordering waves to obtain the correct ground states. As noted before, the effect of the observed <0 0> wave will be to enrich one sublattice (say β) and deplete the other one accordingly. However, in another region of the sample the reverse process may have been initiated. This mechanism will create a twin boundary between two ordered domains as shown in Fig. 3. These domains are at an angle θ = (b - a)/a, where a and b are the basal axes in the orthorhombic unit cell. Since adjacent atoms have the wrong occupancy across the boundary this process is energetically unfavorable. In fact the energy per unit cell can be evaluated as $E_b/4V_1 = [1 - (x+y)]$, which is positive quantity throughout the <0 0> stability domain in Fig. 2a. If an additional elastic interaction is included the twin boundaries will form a regularly spaced array to minimize the total boundary energy [3,6].

Finally we note that the double cell phase at c_o = .25 shown in the second quadrant in Fig.

2b has been observed independently by Van Tendeloo et al [7] by means of electron microscopy and diffraction. This means that in the neighborhood of $c_o = .25$ the EPI's are likely to have values corresponding to the overlap of the appropriate regions in Fig. 2a and 2b, i.e. $V_1 > 0$, $V_2 < 0$, $0 < V_3 < V_1$. It is also tempting to speculate that the two plateaus in T_c vs. c_o found by Cava et al [2] correspond to coexistence regions around the ordered structures at $c_o = .25$ and $c_o = .50$. To prove this point more convincingly it is necessary to calculate a phase diagram for this model, a problem that will be addressed in the next section.

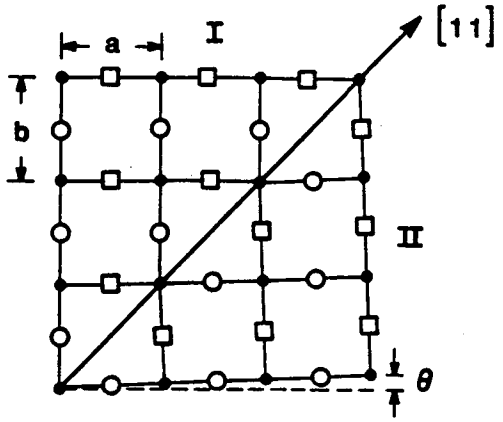

Fig. 3 Twin boundary along the [11] direction.

XBL 8711-4808

PHASE DIAGRAM

It has just been argued that it is essential to calculate phase diagrams for various x,y values and attempt to relate the amount of short range order to the experimental results of Cava et al [2]. As a first step in this direction the case $V_2 = V_3 = -½V_1$ has been examined [8] by means of the Cluster Variation Method (CVM) [9] in the four and five point approximation. The CVM, although a mean field theory, gives fairly accurate results, in particular the correct order for the phase transitions, and, being formulated in terms of correlation functions, contains a wealth of information about ordering parameters, not easily accessible to other methods. As a test of the accuracy, the zero field critical temperature (for $V_2 = V_3 = 0$) is only 4 % higher than the exact Onsager solution.

The CVM phase diagram, symmetric about $c_o = .50$ for concentration independent EPI's, is shown in Fig. 4. In the upper part of the diagram a two-dimensional disordered phase, corresponding to the tetragonal structure, is obtained. It is separated from the ordered phase (orthorhombic structure) by a line of second order transitions (heavy dashed line). The second order transition line ends in a tricritical point (t) where it joins smoothly onto a disordered phase boundary line and discontinuously to an ordered phase boundary line. Below these first order transition lines the system exhibits phase separation as predicted by the ground state analysis (Fig. 2b). The fine dashed line is an ordering spinodal [10] below which the disordered phase becomes unstable to small ordering fluctuations (as shown by the vanishing of the Hessian). The fine dot-dash curve is the locus of instability for phase separation on the partially filled β sublattice. In terms of the stability analysis, the fine dashed curve is the stability limit for two <0 0> ordering waves out of phase on the α and β sublattice, whereas the dot-dash curve is the stability limit for a single <0 0> wave on the β sublattice.

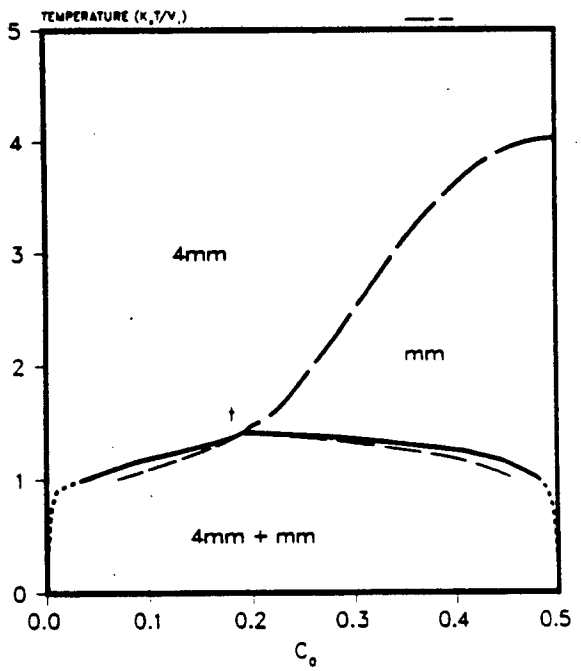

Fig. 4 Phase diagram for $V_2 = V_3 = -½V_1$.

XBL 8711-4809

Some details of this diagram are mean field features and are not properly described by the

CVM. In particular, the coexistence curve in the neighborhood of t should be very flat and the line of second order transitions is much steeper in more elaborate calculations [11,12]. (However, note again that correlation functions can be more readily obtained in the CVM [8].) Jorgensen et al [1] also observed that the orthorhombic to tetragonal phase transitions occurs at an oxygen concentration of c_o = .32 regardless of oxygen partial pressure, which can only happen if the transition line is very steep in the relevant temperature range. This is already partly so in Fig. 4 and even more so in the renormalization group [11] or Monte Carlo [12] calculations. The dependence on oxygen partial pressure was also analyzed by Brynestad et al [13]. These authors observed second order transitions at z = 6.7 (c_o = .35) and T ≅ 635 C and at z = 6.5 (c_o = 0.25) and T ≅ 500 C. It is seen in Fig. 4 that both of these transitions occur at concentrations greater than that of the calculated triple point t (c_o ≅ 0.2) to the "right" of which, indeed, the transition is predicted to be second order, provided that the observed temperatures lie above T_t. For measurements performed under Helium atmosphere, the transition is reported to be an "irreversible" one at T ≅ 425 C. It is here suggested that the latter temperature lies below T_t so that the observed transition is the one predicted by the (first-order) phase separation (full lines in Fig. 4). The transition from the phase separated to the single phase tetragonal state would be completed at very low oxygen content, which is expected for samples held in He atmosphere. Thus there is good qualitative agreement between theory and experiment, although the temperature scales do not match quantitatively. Other choices of interaction parameters should improve the fit.

In conclusion, our results so far have provided excellent qualitative agreement with the experimentally observed thermodynamic properties of the superconducting compound. Work currently in progress focuses on the double cell phase expected near c_o = .25.

ACKNOWLEDGEMENTS

Work performed at U. C. Berkeley was supported by the Director, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098, and that performed at Houston was supported by the National Science Foundation under Grant No. DMR-8603662.

REFERENCES

1. J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D, Grace, I. K. Schuller, C. U. Segre, K. Zhang and M. S. Kleefisch, Phys. Rev. B**36**, 3608 (1987).
2. R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zakuriah and D. Weder, preprint.
3. D. de Fontaine, L. T. Wille and S. C. Moss, Phys. Rev. B, in press.
4. L. T. Wille and D. de Fontaine, preprint.
5. D. de Fontaine, Acta Metall. **23**, 533 (1975).
6. G. R. Barsch, B. Horovitz and J. A. Krumhansl, Phys. Rev. Lett. **59**, 1251 (1987).
7. G. Van Tendeloo, H. W. Zandbergen and S. Amelinckx, Sol. St. Comm., **63**, 603 (1987).
8. A. Berera, L. T. Wille and D. de Fontaine, preprint.
9. R. Kikuchi, Phys. Rev. **81**, 988 (1951).
10. D. de Fontaine, Sol. St. Phys. **34**, 73 (1979).
11. F. Claro and V. Kumar, Surf. Sci. **119**, L371 (1982).
12. K. Binder and D. P. Landau, Phys. Rev. B**21**, 1941 (1980).
13. J. Brynestad, E.D. Specht, C.J. Sparks, A.G. Dhere, O.B. Cavin, D.M. Kroeger, R.K. Williams, H.A. Oye and F.J. Seiler, presented at the TMS Topical Symposium, Cincinnati OH (1987).

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720