

# Ordering in high- $T_c$ superconducting systems: Effective pair interactions in Y-Ba-Cu-O

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Effective pair interactions are examined in the nonstoichiometric as well as the Zn-doped Y-Ba-Cu-O systems in terms of the real-space-scattering-cluster coherent-potential approximation. Large negative pair energies are found for the first and second in-chain neighbors if vacancies occupy the O(1) sublattice, while concomitantly rather small positive pair energies characterize the interchain neighbors. Negative pair energies are also found for a disordered O(2) sublattice if a copper atom bridges the two sites. This result is in good agreement with experiment and with other calculations. For the Zn doped copper sublattices no such clear-cut behavior is observed with regard to the possible ordering of sites occupied by Cu or Zn atoms.

## INTRODUCTION

A large number of experimental studies address the question of ordering of the oxygen-vacancy subsystem in the nonstoichiometric ceramic superconductors, particularly in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (see, e.g., Refs. 1-5). Electron diffraction as well as x-ray-diffraction studies confirm the existence of the ortho-II structure, i.e., a double-period  $\langle \frac{1}{2}, 0, 0 \rangle$  orthorhombic structure, around  $\delta=0.5$ , with alternating chains occupied by either oxygen atoms or vacancies. For lower vacancy content several types of oxygen-vacancy ordering are observed.<sup>3-5</sup> Some of these are consistent with the absence of oxygen atoms along the chain, which then leaves the intermediate monovalent copper atoms with a twofold coordination along the  $c$  direction.

It was shown<sup>6,7</sup> by using a simple Ising model with nearest- and next-nearest-neighbor interactions that the experimental phase diagram could be fairly well reproduced through the choice of appropriate interaction parameters. These parameters were computed from first-principles total energy calculations using the linear muffin-tin orbitals (LMTO) method for the  $\text{O}_6$ ,  $\text{O}_{6.5}$ , and  $\text{O}_7$  structures.<sup>8</sup> These calculations show considerable repulsive O(1)-O(1) interactions along the chain while the interactions belonging to pairs with no bridging copper atoms have attractive character. Configurational entropy calculations by means of the cluster-variation method in the square-lattice approximation assuming repulsive nearest-neighbor interactions can also qualitatively describe the order-disorder phase transition.<sup>9</sup> In Ref. 10 the ordering of the oxygen-vacancy subsystem is explained in terms of long-range Coulomb interactions between the oxygen ions, the ionization potential of copper, and the electron affinity of oxygen.

## THEORY

As was shown by Gonis *et al.*,<sup>11</sup> the configurational free energy of a binary alloy at zero temperature can be evaluated in terms of effective cluster interactions. For a particular pair of sites  $i$  and  $j$ , occupied by atoms of species

$\alpha, \beta = A$  or  $B$ , these interactions are defined by

$$V_{ij}^{\alpha\beta} = \frac{1}{\pi} \text{Im} \int_{-\infty}^{\mu} \text{Tr} \ln Q_{ij}^{\alpha\beta}(E) dE, \quad (1)$$

where  $\mu$  is the chemical potential. Within the coherent-potential approximation (CPA)  $Q_{ij}^{\alpha\beta}(E)$  is given<sup>12</sup> as

$$Q_{ij}^{\alpha\beta}(E) = 1 - \underline{X}_{ij}^{\alpha\beta}(E) \underline{\hat{c}}^c(E). \quad (2)$$

In (2),  $\underline{X}_{ij}^{\alpha\beta}(E)$  is the site-diagonal excess-scattering matrix

$$\underline{X}_{ij}^{\alpha\beta}(E) = \begin{pmatrix} \underline{X}_i^{\alpha}(E) & \underline{0} \\ \underline{0} & \underline{X}_j^{\beta}(E) \end{pmatrix}, \quad (3)$$

$$\underline{X}_i^{\alpha}(E) = \{ [\underline{t}_i^{\alpha}(E)]^{-1} - [\underline{t}_i^{\alpha}(E)]^{-1} - \underline{t}_{ii}^{\alpha}(E) \}^{-1}, \quad (4)$$

and  $\underline{\hat{c}}^c(E)$  is the nondiagonal part of the scattering-path operator of the CPA medium

$$\underline{\hat{c}}^c(E) = \begin{pmatrix} \underline{0} & \underline{t}_{ij}^c(E) \\ \underline{t}_{ji}^c(E) & \underline{0} \end{pmatrix}, \quad (5)$$

where  $\underline{t}$  denotes single-site  $t$  matrices and the superscript  $c$  labels quantities referring to the coherent potential. Now the well-known effective pair interaction,

$$V_{ij}^{(2)} = V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB}, \quad (6)$$

can be written in the form,

$$V_{ij}^{(2)} = \frac{1}{\pi} \text{Im} \int_{-\infty}^{\mu} \text{Tr} \ln [Q_{ij}^{AA}(E) Q_{ij}^{BB}(E)] \times [Q_{ij}^{AB}(E) Q_{ij}^{BA}(E)]^{-1} dE. \quad (7)$$

The present calculations were performed by using our previous results in terms of the real-space-scattering-cluster coherent-potential approximation<sup>13,14</sup> for two types of disorder, the nonstoichiometric  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and the  $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$  systems. For example, for the nonstoichiometric case we obtain

$$V_{ij}^{(2)} = V_{ij}^{\text{O}(n)-\text{O}(n)} + V_{ij}^{\text{O}(n)-\text{vac}} - 2V_{ij}^{\text{vac}-\text{vac}}, \quad (8)$$

where  $\text{O}(n)$  ( $n=1, \dots, 4$ ) denotes one type of oxygen atom with different crystallographic positions.

It should be noted that by characterizing a thermo-

dynamical system in terms of pair interactions the sign of  $V_{ij}^{(2)}$  determines the tendency of the rearrangement of  $A$  and  $B$  species on a given sublattice with respect to the fully random distribution: positive or negative signs suggest ordering or phase separation, respectively.

### RESULTS

The effective pair interactions for both the nonstoichiometric and the Zn-doped systems are listed in Table I, with the corresponding pairs denoted in each case by 1–5. With reference to Fig. 1, we label as pair No. 1 those which correspond to first neighbors between O(1)- or Cu(1)-type sites along a chain, as well as those corresponding to first neighbors in the planes between O(2)- or Cu(2)-type sites, and along the  $x$  direction. Furthermore, for each geometric arrangement, chains and planes, there are two types of pairs, corresponding to the disordered systems considered. For the case of the nonstoichiometric alloy, we calculate nearest-neighbor interactions between sites of O(1) type and between O(2)-type sites. Similarly, for the Cu(1) and Cu(2) sites in the case of the Zn-doped system. This clearly gives four different nearest-neighbor interactions with label No. 1, the values of which are listed in Table I. Analogous considerations apply to pairs labeled 2, 3, and 4. Interaction No. 5 represents the two interactions that correspond to nearest-neighbors between planes formed by O(2) sites in the case of the nonstoichiometric alloy, and by Cu(2) sites in the Zn-doped system.

Care has to be taken when discussing our results in terms of the last paragraph in the first section and the commonly used terminology for oxygen-vacancy ordering in the Y-Ba-Cu-O system. This is because the lattice in question is complex and gives rise to interactions that are

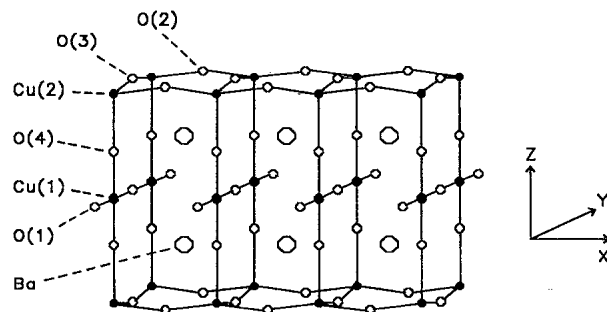


FIG. 1. The orthorhombic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  with the notation of inequivalent sites used in the paper.

anisotropic, whereas the ordering tendencies mentioned above are usually referred to a simple lattice.

The large negative first- and second-neighbor interactions along the chain in the case of the disordered O(1) sublattice as well as those along the  $x$  direction for the disordered O(2) sublattice support a tendency towards phase separation of the oxygen atoms and vacancies along these directions. Even for a small vacancy content creation of energetically preferred two-coordinated Cu(1) or four-coordinated Cu(2) ions is probable as also discussed in Ref. 10. The small positive interchain effective pair interactions could result in an ordering of the oxygen atoms and vacancies between chains. For the case  $\delta=0.5$ , this picture is consistent with the experimentally observed existence of the ortho-II structure.

Figure 2 shows that the effective pair interaction on the disordered O(1) sublattice for the nearest neighbors along the chain varies moderately with respect to the vacancy content  $\delta$ , while pairs of sites occupied by only vacancies, oxygen atoms, or both contribute with varying magnitudes

TABLE I. Effective pair interactions for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ . The column labeled by CPA denotes the different types of disordered cases under construction as explained in the text.

CPA		$V_{ij}^{(2)}$ (mRy/atom)				
		Pairs <sup>a</sup>				
		1	2	3	4	5
Vacancies						
O(1)	$\delta=0.1$	-12.09	-3.59	0.11	0.00	
	0.3	-11.20	-1.86	0.15	-0.01	
	0.5	-10.07	-0.75	0.22	0.00	
O(2)	$\delta=0.1$	-16.02	-0.86	0.41	0.48	8.88
	0.3	-15.64	-0.39	0.33	0.29	9.00
	0.5	-15.35	-0.08	0.24	0.14	9.22
Zn subst.						
Cu(1)	$x=0.05$	-0.34	0.40	0.06	-0.01	
	0.15	-0.42	0.31	0.02	-0.04	
Cu(2)	$x=0.05$	0.23	0.04	0.40	0.21	1.31
	0.15	-0.31	-0.30	-0.17	-0.19	0.70

<sup>a</sup>The labeling of pairs is as follows. For O(1) or Cu(1): pair 1, first neighbor in chain; pair 2, second neighbor in chain; pair 3, first interchain neighbor; pair 4, second interchain neighbor. For O(2) or Cu(2): pair 1, first neighbor in plane in  $x$  direction; pair 2, second neighbor in plane in  $x$  direction; pair 3, first neighbor in plane in  $y$  direction; pair 4, second neighbor in plane in  $y$  direction; pair 5, first interplane neighbor.

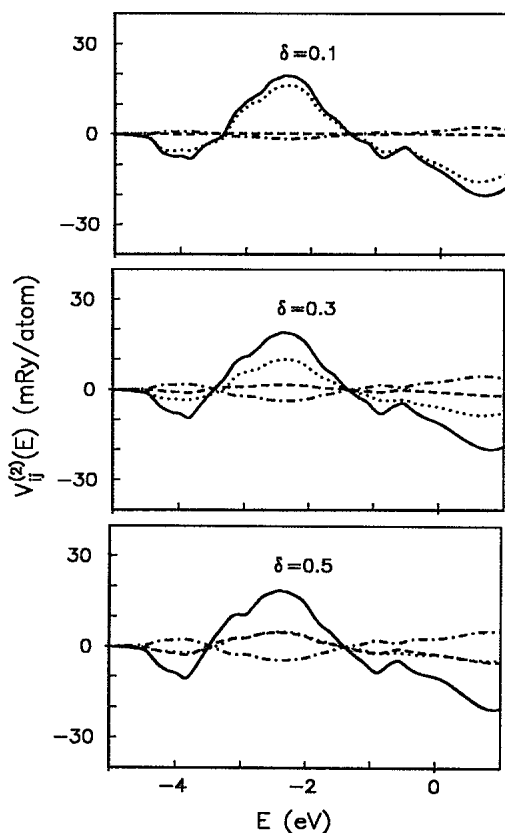


FIG. 2. Effective pair interactions,  $V_{ij}^{(2)}(E)$  (solid line) as a function of energy for the in-chain nearest neighbors of the disordered O(1) sublattice in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The  $V_{ij}^{O(1)-O(1)}$ ,  $V_{ij}^{\text{vac-vac}}$ , and  $V_{ij}^{O(1)-\text{vac}}$  contributions to  $V_{ij}^{(2)}(E)$  are displayed as dashed, dotted, and dash-dotted curves, respectively. The Fermi energy corresponding to the ordered system is indicated by 0.

to the effective interaction, Eq. (8), as the concentration varies. Apparently, a small deviation of the Fermi energy relative to the ordered case (see Refs. 13 and 14) does not result in qualitative changes in  $V_{ij}^{(2)}$ . For small vacancy

concentrations the creation of vacancy-vacancy pairs is preferred throughout: oxygen-oxygen pairs have practically no effect and oxygen-vacancy pairs make merely a small positive energetic contribution with respect to the fully disordered state. In  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  the oxygen-oxygen and vacancy-vacancy pairs have negative contributions of the same order of magnitude, while the effect of the unlike pairs seems to be negligible.

For the Zn-doped copper sublattices the effective pair interactions are relatively small and—as can be seen from Table I in the case of the disordered Cu(2) sublattice—the sign can change with respect to the concentration. Because of negative first-neighbor and positive second-neighbor interactions along the chain for the doped Cu(1) sublattice the ordering on this sublattice—if any—would imply a much more complicated (ordered) structure than that for the oxygen-vacancy system. Therefore the copper sublattices substituted by Zn seem to remain statistically disordered. Nevertheless the positive values for the interplanar pair interactions for the disordered Cu(2) sublattice suggest a phase separation with respect to the plane “sandwiches.”

In summary it can be said that the effective cluster interactions are consistent with the onset of ortho-II structure in the nonstoichiometric Y-Ba-Cu-O system around a  $\delta=0.5$  vacancy content. Creation of isolated copper atoms is also indicated in the low vacancy concentration limit. For the Zn-doped system, however, a random distribution of Cu and Zn atoms seems to be more probable.

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- <sup>1</sup>E. G. Derouane, Z. Gabelica, J.-L. Brédas, J.-M. André, Ph. Lambin, A. A. Lucas, and J.-P. Vigneron, *Solid State Commun.* **64**, 1061 (1987).
- <sup>2</sup>C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chenavas, P. Strobel, and M. Marezio, *Solid State Commun.* **65**, 283 (1988).
- <sup>3</sup>D. J. Werder, C. H. Chen, R. J. Cava, and B. Batlogg, *Phys. Rev. B* **38**, 5130 (1988).
- <sup>4</sup>R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. P. Parkin, M. L. Ramirez, K. P. Roche, J. E. Vazquez, T. M. Gür, and R. A. Huggins, *Physica C* **162-164**, 548 (1989).
- <sup>5</sup>B. W. Veal, A. P. Paulikas, Hoydoo You, Hao Shi, Y. Fang, and J. W. Downey, *Phys. Rev. B* **42**, 6305 (1990).
- <sup>6</sup>D. de Fontaine, L. T. Wille, and S. C. Moss, *Phys. Rev. B* **36**, 5709 (1987); L. T. Wille and D. de Fontaine, *ibid.* **37**, 2227

- (1988); L. T. Wille, A. Berera, and D. de Fontaine, *Phys. Rev. Lett.* **60**, 1065 (1988).
- <sup>7</sup>J. Stolze, *Phys. Rev. Lett.* **64**, 970 (1990).
- <sup>8</sup>P. A. Sterne and L. T. Wille, *Physica C* **162-164**, 223 (1989).
- <sup>9</sup>J. M. Sanchez, F. Mejía-Lira, and J. L. Morán-López, *Phys. Rev. B* **37**, 3678 (1988).
- <sup>10</sup>J. Kondo, *J. Phys. Soc. Jpn.* **59**, 819 (1990).
- <sup>11</sup>A. Gonis, X.-G. Zhang, A. J. Freeman, P. Turchi, G. M. Stocks, and D. M. Nicholson, *Phys. Rev. B* **36**, 4630 (1987).
- <sup>12</sup>P. E. A. Turchi, G. M. Stocks, W. H. Butler, D. M. Nicholson, and A. Gonis, *Phys. Rev. B* **37**, 5982 (1988).
- <sup>13</sup>L. Szunyogh, G. H. Schadler, P. Weinberger, R. Monnier, and R. Podloucky, *Phys. Rev. B* **41**, 1973 (1990).
- <sup>14</sup>L. Szunyogh, U. König, P. Weinberger, R. Podloucky, and P. Herzig, *Phys. Rev. B* **42**, 432 (1990).