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Structure and superconductivity in Co doped $YBa_2Cu_3O_{6+x}$

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Abstract

The effect of Co doping on the oxygen disordering and superconducting transition temperature in $YBa_2Cu_{3-y}Co_yO_{6+x}$ has been studied experimentally and by Monte Carlo simulations. Samples with Co doping levels, $0 \leq y \leq 0.5$, have been prepared and their superconducting transition temperatures have been determined by DC resistivity and ac susceptibility measurements. Structural ordering phenomena have been studied by neutron powder diffraction and EXAFS measurements. Model calculations based on a modified version of the so-called ASYNNNI model, which takes into account the increased probability of excess oxygen around the Co sites, have been carried out and compared with the experimental results of oxygen coordination number around the Co atoms and the oxygen stoichiometry in the basal $Cu_{1-y}Co_yO_x$ plane of the structure. Using a previously established minimal model relating the superconducting transition temperature, $T_c(x)$, in the undoped material to the presence of specific ordered oxygen domains we show that the detrimental effect on $T_c(y)$ by Co doping is a result of oxygen disordering.

1. Introduction

Oxygen depletion [1,2] and chemical substitutions[3] in the basal CuO_x-plane of the high-temperature superconductor $YBa_2Cu_3O_{6+x}$ ($0 < x < 1$), YBCO, have a significant influence on the superconducting properties. In all cases the superconducting transition temperature, T_c, is observed to decrease. For oxygen deficient YBCO dynamic[4] and static[5] variations of T_c have been correlated with similar variations in the coherence of the oxygen ordering.[1,2] Metal atom substitutions into the basal CuO_x plane, with M = Co, Fe, or Al, have a similar effect, but the role of the M dopants in suppression of T_c is not yet well understood. Since Co, Fe, and Al have preference for higher oxidation levels than Cu,[3] they tend to increase their oxygen coordination number, and consequently they cause oxygen disordering.

In this paper we report results of a combined experimental and computer simulation study of the oxygen disordering phenomena and their effect on the superconducting transition temperature in Co doped YBCO, $YBa_2Cu_{3-y}Co_yO_{6+x}$.

2. Experimental

Powder samples of oxidized $YBa_2Cu_{3-y}Co_yO_{6+x}$ with y = 0.0, 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, 0.50, were prepared from stoichiometric amounts of the metal nitrates by use of the citrate/ethyleneglycol based polymerized complex technique.[6] X-ray powder diffraction showed no impurity phases within the detection limit, which for CuO, $BaCuO_2$ and Y_2BaCuO_5 is 0.5 weight %. The oxygen content was determined by iodometric titration assuming that cobalt is present as Co^{3+}.

The superconducting properties of the samples have been studied by standard four probe DC resistivity and ac susceptibility (132 Hz, 10–100 mOe) measurements.

The neutron powder diffraction studies were carried out by use of the multi detector neutron powder diffractometer at the DR3 reactor, Risø National Laboratory. A neutron wavelength of 1.058 Å with Ge(711) as a monochromator was used for the experiments in order to access a large range of Q transfer ($Q_{max} = 10$ Å^{-1}) with optimal resolution.

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EXAFS studies were carried out at the SRS, Daresbury Laboratory on beamline 8.1. Measurements were made at the Co K edge with fluorescence detection for all samples, and additional measurements were made in transmission for the higher Co concentrations. Data were analyzed using the EXCURV90 package.

3. Models

The model studies of the oxygen ordering properties in the basal $Cu_{1-y}Co_yO_x$ plane of the crystal structure are based on a modified version[7] of the two-dimensional ASYNNNI model for undoped YBCO. The three interaction parameters in the model are shown in fig. 1. They include a strong repulsive nearest-neighbor, ($V_1 < 0$), and anisotropic attractive, ($V_2 > 0$), and repulsive, ($V_3 < 0$), next-nearest-neighbor oxygen interactions depending on whether or not the oxygen atoms are bridged by a Cu atom. We have modified the ASYNNNI model in a simple way by making the nearest-neighbor interaction parameter, V_1^{Co}, around randomly distributed Co atoms less repulsive.

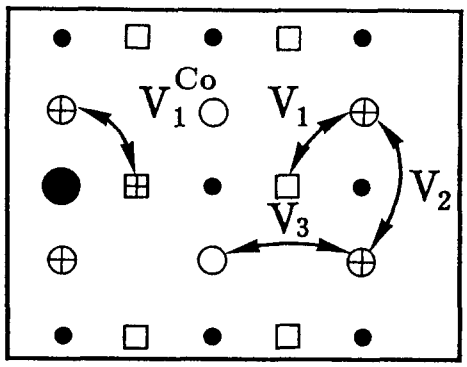

Figure 1. The oxygen interactions in the modified ASYNNNI model for Co doped YBCO. V_1 and V_1^{Co} are the nearest-neighbor oxygen interactions around Cu and Co, respectively, and V_2 and V_3 are the next-nearest-neighbor oxygen interactions depending on whether or not the oxygens are bridged by a Cu/Co atom. • are Cu atoms, and ● a Co atom. ⊕ are occupied oxygen O1 sites in both Ortho-I and Ortho-II, o (O1) sites are only occupied in Ortho-I. □ oxygen (O5) sites are not occupied in the ground state, but Co doping increases the occupation on the ⊞ oxygen sites.

The T_c(y) variation of Co doped YBCO has been calculated by use of the minimal model, originally developed to account for the characteristic two-plateau variation of T_c(x) as function of oxygen stoichiometry.[5] The basic assumption in the minimal model is that only two-dimensional orthorhombic ordered domains exceeding a certain minimal size, Minimal Size Clusters (MSCs), modulate the electronic configurations in a way that favours superconductivity. The MSCs adopted to account for undoped YBCO are 4×4 and 8×8 clusters of the Ortho-I and Ortho-II type ordered structures, respectively. The statistics of the structural ordering is derived from computer simulations based on the ASYNNNI model. The minimal model prediction of T_c is a simple weight of the relative total areas covered by MSCs of the Ortho-I and Ortho-II types multiplied by the T_c values for the corresponding ideal stoichiometric compositions, i.e. 93 K for $x = 1.0$ and 58 K for $x = 0.5$.

4. Results

4.1. Experimental

The superconducting transition temperatures determined from the onset of the diamagnetic response in the ac susceptibility and the midpoint in the resistivity curves are given in fig. 2. Error bars on the data are derived from the full widths of the imaginary part of the susceptibility, and the temperature region of the 10% - 90% variation of the resistive transition.

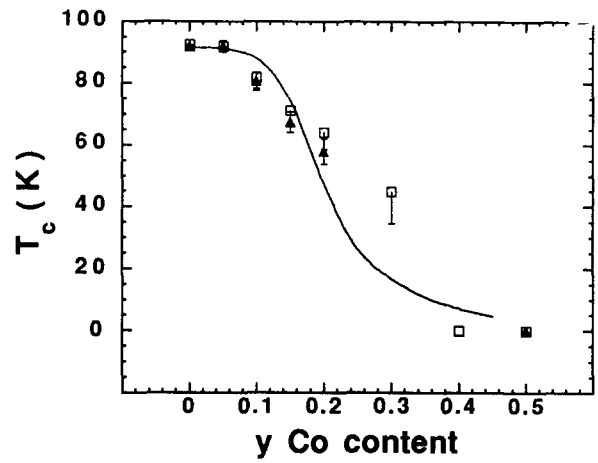

Figure 2. The superconducting transition temperature T_c(y) of $YBa_2Cu_{3-y}Co_yO_{6+x}$. □ are ac susceptibility data and ▲ are resistivity data. The error bars are defined in the text. The full line is the prediction of the minimal model calculation described in the text.

The neutron powder diffraction data were analyzed by use of the EDINP full powder profile refinement program within the orthorhombic Pmmm space group for $y\lesssim0.1$ and the tetragonal space group P4mm for $y\gtrsim0.1$. The oxygen and copper/cobalt sites are indexed as follows: O1 (b-axis) and O5 (a-axis), and Cu1 are oxygen and copper/cobalt sites in the basal plane, O4 is the apical oxygen, and Cu2 and O2 (b-axis) and O3 (a-axis) are sites in the CuO_2 planes.

Refinements in the orthorhombic and tetragonal space groups give identical lattice parameters for $y = 0.1$, which most likely is close to the transition between the two structural phases. Systematic refinements have been carried out. The results being reported are obtained from a model without split sites and using isotropic Debye–Waller factors. The occupation factors for the Y, Ba, Cu2, O2 and O3 sites converged to the nominal ones within the uncertainty for all y values. The Cu1 Cu/Co site is slightly deficient for all y, indicating either vacancies or excess Co. Similarly, we find a slight deficiency on the O4 site. These deficiencies may reflect the need for split sites or large anisotropic Debye–Waller factors in the structural models. In the refinements leading to the structural results given in Table 1 we have fixed the occupation numbers to the nominal ones on all sites except O1 and O5. Because only minor unsystematic variations as function of y were found in the isotropic Debye–Waller factors for Y, Ba, Cu1, Cu2, O2, and for O1 and O4 in the tetragonal phase, we use average values for these sites and refine those for O1, O3, O4 and O5 in orthorhombic symmetry (cf. Table 1a). Based on these Debye–Waller factors we obtain the oxygen occupation numbers on the O1 and O5 sites presented in Table 1b. The total oxygen content, x, in the basal plane is shown in fig. 3. Within the model frame considered these x values are rather robust.

Table 1

Structural data from refinements of neutron powder diffraction data of $YBa_2Cu_{3-y}Co_yO_{6+x}$ using isotropic Debye–Waller factors, $B = (8\pi^2/3)\langle u^2\rangle$, as described in the text, and nominal occupation on all sites except on O1 and O5, for which occupation numbers, n, are refined. R_{wexp} and R_w are expected and obtained agreement factors.

a.

Atom	B_{av}	$B_{0.0}$	$B_{0.05}$	$B_{0.1}$
Y	0.42(7)			
Ba	0.56(8)			
Cu1	0.39(9)			
Cu2	0.31(5)			
O2	0.51(9)			
O3		0.55(7)	0.67(8)	0.54(9)
O4	1.47(10)	0.70(10)	0.87(80)	1.00(10)
O5		0.89(8)	0.90(60)	1.20(70)
O1	1.95(20)	0.89(14)	0.90(17)	1.20(17)

b.

y	n(O1)	n(O5)	R_{wexp}	R_w
0.00	0.84(2)	0.11(2)	0.055	0.138
0.05	0.71(3)	0.23(2)	0.056	0.139
0.10_{ort}	0.66(3)	0.27(3)	0.055	0.149
0.10_{tet}	0.987(3)		0.055	0.149
0.15	0.980(3)		0.054	0.135
0.20	0.971(3)		0.054	0.140
0.30	0.978(3)		0.054	0.149
0.40	0.987(3)		0.056	0.151
0.50	1.023(3)		0.057	0.153

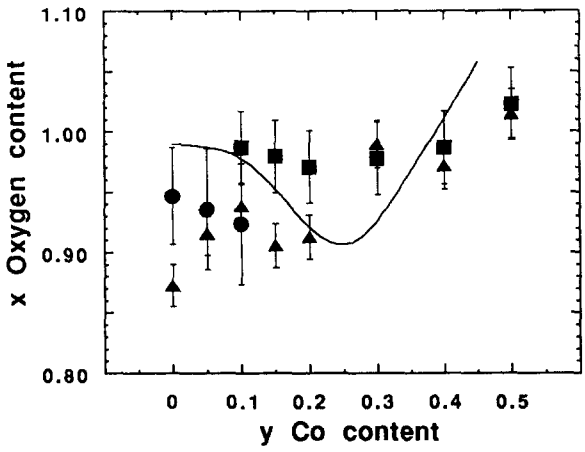

Figure 3. Oxygen content of $YBa_2Cu_{3-y}Co_yO_{6+x}$ determined from neutron powder diffraction data: ■ is from refinements in the tetragonal phase and • is from the orthorhombic phase. The error bars are results from the least squares refinements. ▲ is the oxygen content derived from the iodometric titration analysis. The full line is the result of model calculations by the modified ASYNNNI model as described in the text.

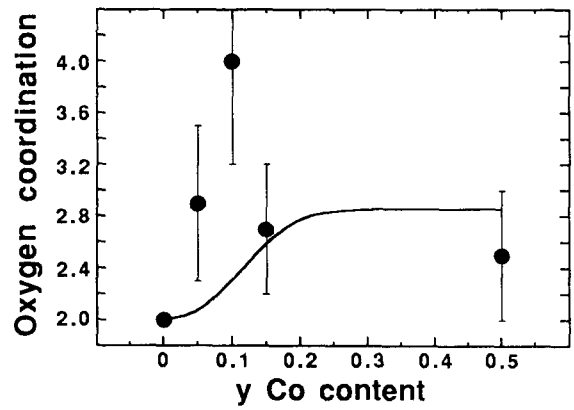

Figure 4. Oxygen coordination numbers around Co in the basal $Cu_{1-y}Co_yO_x$ plane of $YBa_2Cu_{3-y}Co_yO_{6+x}$ determined from EXAFS data assuming that two apical oxygen atoms are present. The full line is the results obtained by model calculations using the modified ASYNNNI model as described in the text.

Analysis of the EXAFS spectra have been carried out on the samples with y = 0.05, 0.1, 0.15 and 0.5 using models including one Ba and Cu shell, and one or two O shells. Because no improvements in the fits were obtained by including two oxygen shells we shall report only on the results from the one shell model. The oxygen coordination numbers in the basal plane, obtained by assuming that two apical O4 oxygen are present are shown in fig. 4. The error bars shown are the widths corresponding to a 5% significance level assuming a fixed Debye–Waller factors of $B = 0.8\AA^2$ for the Co–O distance. Due to correlation effects the uncertainty will double if the Debye–Waller factor is also allowed to vary.

4.2. Model calculations

The statistics of the oxygen ordering properties of $YBa_2Cu_{3-y}Co_yO_{6+x}$ have been derived from the modified ASYNNNI model using Monte Carlo simulation technique. The interaction parameters for undoped YBCO have been determined from comparison with the structural phase diagram[8], which gives $V_2/V_1 = -0.36$, $V_3/V_1 = 0.12$, $k_BT_{room} = -0.07V_1$, where $T_{room} = 300K$, and a chemical potential, $\mu = -0.05V_1$, for one atmosphere of oxygen. Analysis of existing structural data for Co doped YBCO suggested that $V_1^{Co}/V_1 = 0.0$ is a likely interaction parameter around Co atoms.[7] The oxygen equilibrium stoichimetry, x, determined from the model simulations at room temperature, T_{room}, and one atmosphere of oxygen (chemical potential μ), is compared with the experimental results in fig. 3. In fig. 4 we compare the oxygen coordination numbers derived from the model calculations with the similar data deduced from the EXAFS studies.

Allowing that the modified ASYNNNI model gives an appropriate description of the oxygen ordering properties in $YBa_2Cu_{3-y}Co_yO_{6+x}$ we may calculate T_c(y) without further adjustable parameters by use of the minimal model with the same MSCs as for undoped YBCO. For Co doped only Ortho-I domains and disordered phase are found from the analysis. Within the minimal model picture the decrease in T_c(y), shown in fig. 2, is a result of disordered structures being formed in the basal plane by Co doping.

5. Discussion

In the present paper we have presented initial results of an extensive study on Co doped YBCO of the structural disordering phenomena and how they influence the superconducting properties. More elaborate models and refinement techniques are definitely needed to establish more accurate models for the disorder phenomena. The use of several techniques is imperative for establishing a detailed defect structure model, as has been shown recently by Renevier et al.[9] In order to progress we intend to use the Reverse Monte Carlo technique for simultanous analysis of our neutron powder diffraction and EXAFS data,[10] and use the results for comparison with model calculations by computer simulations. Studies of the lattice dynamics by Raman scattering technique are also included.[11]

Finite conclusions about the validity of the modified ASYNNNI model for description of the oxygen ordering properties in Co doped YBCO cannot be drawn on the basis of the present accuracy of the experimental data, but the agreement is sufficiently good for adopting it as an appropriate starting model. The minimal model description of the T_c(y) variation supplies an additional indication that structural ordering at least on a local scale is needed for superconductivity in YBCO. In this respect it is interesting to note that the linear charge transfer model relating the average Cu valence in the superconducting CuO_2 planes and T_c has been established for both oxygen deficient[2] and Co doped YBCO[12], and that the relation between T_c and the axial stretching vibration of the apical oxygen is valid for both Co doped and oxygen deficient YBCO,[11] indicating that a unified description of the mechanisms underlying superconductivity in these systems is applicable.

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