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Joint x-ray and neutron refinement of the structure of superconducting $YBa_2Cu_3O_{7-x}$: Precision structure, anisotropic thermal parameters, strain, and cation disorder

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X-ray and neutron powder diffraction data for superconducting orthorhombic $YBa_2Cu_3O_{7-x}$ have been used in a joint refinement to give a room-temperature structure which includes a very precise set of atom positions and thermal-motion parameters. Broadening of the diffraction peaks indicates that these materials are highly strained, and contrary to a number of suggestions in the literature, no evidence is found for any cation disorder.

Recent neutron powder[1-5] and x-ray single-crystal[6-9] diffraction studies of the $YBa_2Cu_3O_{7-x}$ high-T_c superconductors have provided partial information on their structure and the roles that oxygen vacancies and the orthorhombic-to-tetragonal phase transition play in their superconducting properties. In this paper, we report a simultaneous Rietveld refinement using both neutron and x-ray powder diffraction data which yields a more precise structure, complete anisotropic thermal parameters, and the extent of cation disordering. In addition, we obtained a measure of the strain in this specimen.

The sample was made using standard oxide synthesis techniques. Quantities of Y_2O_5, $BaCO_3$, and CuO, stoichiometric in the metal ions, were mixed and ground, and heated twice at 950 °C in air, with a regrinding between firings. The reground mixture was then pelletized and, after heating once more at 950 °C, was annealed in oxygen at 800 °C for 8 h and allowed to cool slowly in the furnace. The onset of diamagnetism occurred at 91 ± 1 K and a low-density compact of the material excluded ~95% of the field at 7 K, when measured at 100 G, not including a demagnetization factor. The ratio of expelled to excluded flux was 0.4. Thermogravimetric analysis gave an approximate stoichiometry of $YBa_2Cu_3O_{6.9}$.

Neutron powder diffraction data were taken on the High Intensity Powder Diffractometer (HIPD) at the Los Alamos Neutron Scattering Center (LANSCE). A portion of the neutron powder diffraction data is displayed in Fig. 1(a). These data were collected in four detector banks ($\pm 150°$ and $\pm 90°$) for approximately 5 h at a proton current of 30 μA. The x-ray data partially shown in Fig. 1(b) were taken on the same sample two days later using a Siemens D500 diffractometer with Cu $K\alpha$ radiation and a graphite diffracted-beam monochromator in two scans ($2° \leq 2\theta \leq 90°$ and $80° \leq 2\theta \leq 150°$) with 0.02° steps counting for 13 sec per step. Both experiments were carried out at 297 K. For both the x-ray and neutron diffraction data, the limiting resolution was determined by strain broadening in the sample, as was also evident in previously reported neutron powder diffraction studies.[1-5] The difference in the relative scattering factors for the neutron and x-ray experiments as well as the strong preferred orientation in the x-ray sample is clearly seen in Fig. 1. Full advantage was taken of the complementarity of this information by refining the four neutron and two x-ray data sets (~24 000 data points) simultaneously using the generalized crystal-structure analysis system (GSAS) Rietveld refinement program.[10] In this analysis the neutron powder peak profiles were modeled with the standard double exponential Gaussian convolution function[10-12] and the x-ray profiles by a Simpson's rule integration of a pseudo-Voigt function to include low-angle peak asymmetry.[10,13,14] The considerable preferred orientation observed in the x-ray data was accom-

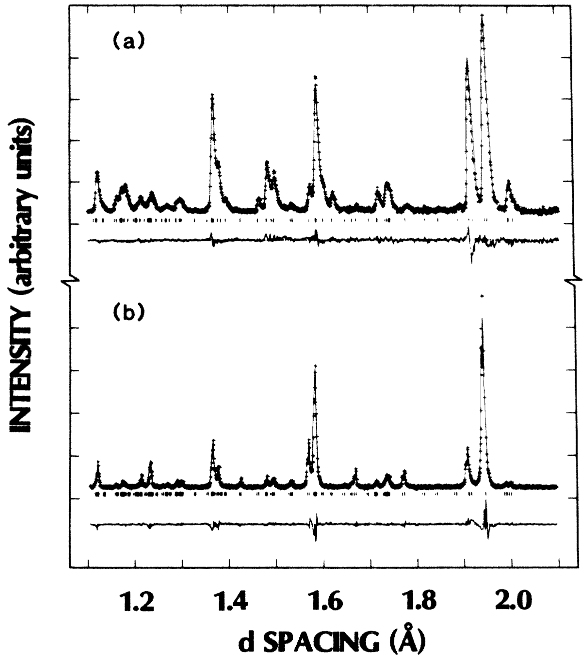

FIG. 1. Part of the x-ray and neutron diffraction data for orthorhombic $YBa_2Cu_3O_{7-x}$. Data shown by plus (+) marks in (a) represent only data collected on the +153-degree detector band of the HIPD while the data shown in (b) were taken on a Siemens D500 x-ray diffractometer. The continuous line through both sets of data points is the calculated profile from the Rietveld refinement. Tick marks below the data indicate the positions for the allowed reflections. Both Cu $K\alpha_1$ and Cu $K\alpha_2$ positions are marked in the x-ray pattern; the d spacings are computed from $K\alpha_1$. The lower curve in each panel represents the difference between the observed and calculated profiles.

modated extremely well using the March model;[10,15,16] the neutron data showed no preferred orientation. The final overall weighted residual on all data was 5.24% (R_w = 7.33% and 4.30% for x-ray and neutron data, respectively).

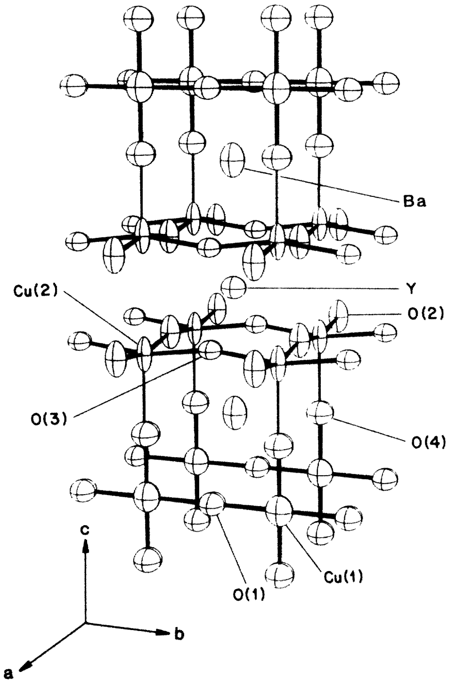

FIG. 2. Structure of orthorhombic $YBa_2Cu_3O_{7-x}$. Nearest-neighbor oxygen atoms from adjacent units cells are included to show full Cu-O coordination. The thermal ellipsoids are drawn as 99% probability surfaces.

The resulting lattice parameters and atomic coordinates given in Table I are in close agreement with the previous structure determinations using neutron powder diffraction[1-5] and the most recent single-crystal x-ray diffraction study.[9] In all cases, our estimated standard deviations for these parameters are considerably better, in some cases by an order of magnitude, than the earlier studies. The combined data and the excellent quality of the simultaneous refinement also allowed a precise determination of the anisotropic thermal parameters for all the atoms in the structure. We are aware of only one previous determination of all anisotropic thermal factors,[9] but the values obtained do not appear physically reasonable and have estimated standard deviations which are too large for the results to be useful. The other reported refinements of anisotropic thermal parameters included only those for a few of the O atom sites, while constraining the remaining thermal parameters to be isotropic.[1,2,5] Unfortunately, this practice reduces the reliability of the few anisotropic values obtained, especially when the other atom thermal motions are quite anisotropic. In fact, when subject to the same constraint on the thermal parameters, we obtain a set of values similar to those obtained by others. Our fully anisotropic model thus gives a different description of the motion of O(1); we find that the ellipsoid is cigar shaped with the major axis along a perpendicular to the Cu–O–Cu bond. The other studies show a more pancakelike thermal ellipsoid perpendicular to this bond. Examination of the other anisotropic thermal parameters in Table I and Fig. 2 suggests that there may be a high degree of concerted motion involving the Ba, Cu(2), and O(2) atoms. All three atoms have essentially identical U_{33} values, which are larger than their respective U_{11} or U_{22} values and represent rms displacements of 0.14 Å along c. The Y and O(3) atoms do not participate in this motion. It is interesting to note that the isotope shift in T_c for ^{18}O doped samples[17] (-0.4 K) is the same as that naively computed from Bardeen-Cooper-Schrieffer (BCS) theory for a mass change of 2 in the total mass (217) of these three atoms.

No particle size broadening of the Bragg peaks was observable in either the neutron or x-ray diffraction data, from which a lower limit of about 1 μm can be placed on the grain size in the sample. Furthermore, no extinction was observed from which an upper limit of about 3 μm can be estimated. This is in contrast with high-resolution electron microscopy (HREM) experiments,[18,19] which show the sample particles to be divided into long lamellar domains about 500 Å wide with boundaries oriented along the diagonal in the (110) plane. Twinning occurs at the boundaries of adjacent domains where the stacking se-

TABLE I. Structure parameters for $YBa_2Cu_3O_{7-x}$ determined by joint refinement of x-ray and neutron powder diffraction data taken at 297 K. The numbers in parentheses are the estimated standard deviations in the last significant digit(s).

Space group *Pmmm*, a = 3.82030(8) Å, b = 3.88548(10) Å, c = 11.68349(23) Å							
Atom	x	y	z	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	Occupancy
Y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0085(8)	0.0106(8)	0.0085(6)	1
Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.18393(6)	0.0078(6)	0.0096(7)	0.0198(5)	1
Cu(1)	0	0	0	0.0080(9)	0.0115(9)	0.0150(7)	1
Cu(2)	0	0	0.35501(8)	0.0033(5)	0.0036(5)	0.0207(5)	1
O(1)	0	$\frac{1}{2}$	0	0.0161(16)	0.0104(11)	0.0080(14)	0.910(8)
O(2)	$\frac{1}{2}$	0	0.37819(15)	0.0039(6)	0.0068(7)	0.0203(11)	1
O(3)	0	$\frac{1}{2}$	0.37693(16)	0.0109(8)	0.0084(7)	0.0056(11)	1
O(4)	0	0	0.15840(13)	0.0162(11)	0.0123(9)	0.0097(7)	1

quence can be seen to change from *ab* to *ba*. These domains then form a coherent intergrowth giving powder grains that appear to be much larger than the domain size. Although the density of twinning faults observed may be artificially high in the HREM studies due to the sample preparation requirements, it is possible that the naturally high twin density in this material is responsible for the highly strain-broadened powder diffraction line shapes observed. Using the simplifying assumption of a homogeneous, isotropic strain distribution, both the x-ray and neutron diffraction data yield a strain of about 0.23%. As a result, it is quite likely that, locally at least, substantial stresses exist in the 1:2:3 superconductors. Given the positive pressure dependence found for the T_c,[20] it is conceivable that the recent reports of changes in the superconducting properties of the 1:2:3 superconductors which have been attributed to structural transformations[21] and nitrogen absorption[22] may in fact be the result of changes in the microstructural strain distribution induced by thermal cycling of the system.[23]

A recent interpretation by Lytle, Greegor, and Panson[24] of the Cu *K* x-ray near-edge absorption and extended x-ray-absorption fine structure (EXAFS) spectra of this compound suggests that substantial Cu-Y substitution is present and that this may be related to the superconducting properties. The neutron scattering lengths for Cu and Y are very nearly identical and neutron scattering data are, therefore, insensitive to any Cu-Y disordering. However, the x-ray scattering factors for the various cations differ substantially, and the joint refinement is very sensitive to such disorder. Despite deliberate introduction of up to 50% Y-Ba, Ba-Cu, or Y-Cu substitution in the model, the structure in all cases immediately refined to give the completely ordered compound within the limits of precision of 1–2 at.% and residuals that are about half those for the disordered model. From a comparison of the bond distances determined from the crystal structure with those computed from standard ionic radii,[25] it is also quite clear that Y-Cu substitution is unlikely strictly from size considerations. Moreover, a fifth oxygen atom O(4) occupies the apical position of a square pyramid 2.298 Å from Cu(2) thus giving a 5-coordination geometry very commonly found for Cu^{2+} and not for Y^{3+}. Thus, the suggestion by Lytle *et al.* of up to 30% Y occupation in Cu sites is clearly contradicted by both the powder diffraction data and the crystal chemistry of these materials. Although Van Tendeloo *et al.*[26] have reported evidence of Y-Ba disorder on the basis of electron diffraction and microscopy experiments, their samples were very rapidly quenched from the preparation temperatures and were not superconducting. Other electron microscopy studies of more slowly cooled samples showed occasional structural defects but no Y-Ba disorder.[18,27] A physically reasonable valence distribution for the two copper sites, for which charge is balanced and reasonable Cu-O bond lengths exist, is trivalent Cu(1) and divalent Cu(2), in agreement with David *et al.*[2]

We have shown that the technique of joint neutron and x-ray powder diffraction Rietveld refinement is a very powerful one and allows a much more complete structural determination than either a neutron or x-ray experiment by itself and virtually eliminates problems encountered with false minima. In the case of the 1:2:3 superconductors, we have used this technique to obtain the most precise structure determination to date, which gives all of the anisotropic thermal parameters, a measure of the strain, and conclusively demonstrates the absence of any significant cation disorder.

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