RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 13 1 MAY 1987

High-resolution synchrotron x-ray study of the structure of $La_{1.8}Ba_{0.2}CuO_{4-y}$

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(Received 20 February 1987)

X-ray diffraction of $La_{1.8}Ba_{0.2}CuO_{4-y}$ reveals two macroscopically segregated tetragonal (K_2NiF_4-type) phases of nearly identical lattice parameter. Many peaks show additional broadening upon cooling. This broadening is consistent with a spontaneous monoclinic distortion, with an onset temperature of ≈ 150 K, and is possibly relevant to the superconducting properties. Small single crystals of ≈ 70 μm diameter within the powder aggregate are also studied and show a similar two-phase constituency and a resolvable peak splitting at low temperature.

We present here the results of a high-resolution synchrotron x-ray diffraction study of a $La_{1.8}Ba_{0.2}CuO_{4-y}$ powder sample belonging to a new class of high-T_c superconductors.[1-5] The structure of the orthorhombic phase of pure La_2CuO_4, which is not superconducting, was studied by Grande, Müller-Buschbaum, and Schweizer;[6] it has axes a_0 and b_0 which are related to the (undistorted) tetragonal axis, a_T, of the K_2NiF_4-type structure by $a_0 \approx b_0 \approx \sqrt{2}a_T$. The series $La_{2-x}A_xCuO_{4-y}$ (A = Ba, Ca, Sr) was examined in detail by Michel and Raveau,[7] who showed that, with increasing x, the Ba- and Sr-substituted structures revert to this tetragonal K_2NiF_4-type structure. Jorgensen *et al.*[8] confirmed[4,7] the tetragonal structure of $La_{1.85}Ba_{0.15}CuO_{4-y}$ compound and determined the c-axis (z) parameters of La(Ba) and O. On cooling to 10 K, they found essentially no change in structure.

The present study used a high-resolution diffractometer[9] at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) on Beam Line X22 with an x-ray wavelength $\lambda = 1.719$ Å. To ensure a random powder pattern the sample was oscillated while doing θ-2θ scans. Our powder was similar to that studied in Ref. 2 and was sealed in a He-filled Be can and mounted on a Displex cryostat.

Both 300- and 10-K diffraction patterns showed a set of *hkl* reflections which could all be indexed to the tetragonal K_2NiF_4-type structure.[4,7,8] But the detailed profiles of the individual peaks revealed distinct shoulders on more than half the lines, as illustrated in Fig. 1 for the 200 and 211 reflections. Attempts to fit these peaks with a single symmetric function, which has been found previously to give very satisfactory results on a variety of powder samples,[9] gave poor agreement. However, the asymmetric peak shapes can be satisfactorily fitted, as shown in Fig. 1, with use of *two* such peaks of identical shape. It was further possible by least-squares fitting to account with high accuracy for the resulting positions of the strong and weak components by indexing them on tetragonal lattices of slightly different size. Table I gives the results of the fits to all of the observed peaks. The amount of second phase as determined by I_2/I_1, is 12 (± 4) %. Judging from the nearly identical lattice parameters, the two phases must have very similar composition (although small compositional differences may be important with respect to superconductivity). In Table I, for several unresolved peaks which could not be fit by independent adjustment of two peaks, the peak positions for the minor phase were set at

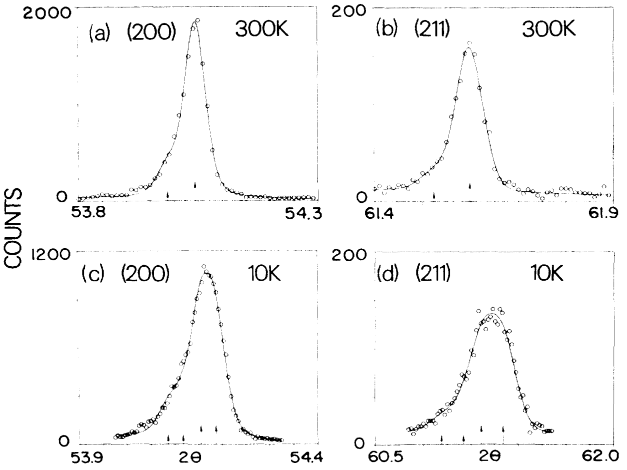

FIG. 1. Least-squares-fitted profiles of the 200 and 211 peaks at 300 and 10 K. Vertical arrows indicate the positions of the major phase and minor phase components. (a) and (b) have single peaks of (assumed) identical shape for the two phases. (c) and (d) are fit with split peaks for both phases with a shape given by the fits in (a) and (b).

TABLE I. Observed and calculated 2θ positions for the major (1) and minor (2) phases at 300 K, the Lorentzian fraction (η) of Lorentzian/Gaussian line shapes found in the fit, and the integrated intensity ratios I_2/I_1.

	Major phase (1)		Minor phase (2)			
hkl	$2\theta_{\rm obs}$	$2\theta_{\rm calc}$ [a]	$2\theta_{\rm obs}$	$2\theta_{\rm calc}$ [b]	η	I_2/I_1
103	34.736	34.738	(34.703)[c]	34.703	1.0	(0.05)
110	37.442	37.441	37.481	37.479	0.57	0.15
112	40.516	40.515	40.472	40.473	0.49	0.10
006	45.576	45.576	(45.530)[c]	45.530	1.0	(0.03)
105	46.493	46.493	(46.446)[c]	46.446	1.0	(0.02)
114	48.680	48.681	(48.631)[c]	48.631	1.0	(0.05)
200	54.043	54.042	53.986	53.985	0.44	0.16
202	56.369	56.368	(Too weak)			
116	60.421	60.423	60.358	60.359	0.62	0.11
107	60.757	60.761	(60.698)[c]	60.698	1.0	(0.07)
211	61.598	61.597	61.523	61.530	0.21	0.12
008	62.189	62.183	(62.118)[c]	62.118	1.0	(0.01)
204	63.007	63.007	62.942	62.940	0.64	0.09
213	65.856	65.857	65.791	65.785	0.48	0.11

[a] Major-phase least-squares fit: $a_1=3.784$ Å, $c_1=13.316$ Å.

[b] Minor-phase least-squares fit: $a_2=3.788$ Å, $c_2=13.329$ Å.

[c] Distinct shoulder not visible; minor peak was fixed at $2\theta_{\rm calc}$ and its intensity was adjusted to give the fit.

their calculated values and the optimized I_2/I_1 ratios are noted in parentheses.

Figure 2(a) presents the fitted peak widths, $\Delta 2\theta$, at 300 and 10 K. At 300 K, the peak widths increase nearly linearly with 2θ, with the exception of the 006 and 008 reflections, which show significant additional broadening, as also noted by Jorgensen *et al.*[8] All of the peak widths are also significantly broadened with respect to the instrumental resolution.

Significant *further* broadening occurs on cooling the sample to 10 K, which we interpret as resulting from a distortion of (at least) the major tetragonal phase to a symmetry lower than orthorhombic. [An La_2CuO_4-type orthorhombic distortion for example, would split $(110)_T$ into $(200)_O$ and $(020)_O$; but $(200)_T$ would not split.] The simplest assumption is monoclinic symmetry,[7] in which case the $\{h0l\}$ and $\{hhl\}$ peaks are split into two components, while $\{hkl\}$, $h\neq k$, are split into four. The 10-K data were analyzed with use of the following approximation for the shift of a monoclinic peak $(hkl)_M$ from its *tetragonal* $(hkl)_T$ parent:

$$\delta(2\theta)=2\theta(hkl)_M-2\theta(hkl)_T$$

$$\approx\frac{\lambda^2}{a_T^2\sin(2\theta)}\left[\frac{\Delta}{a_T}(k^2-h^2)-\alpha hk\right],$$

where $a_M=a_T+\Delta$, $b_M=a_T-\Delta$, and $\gamma=90-\alpha$. $\Delta s(2\theta)$ is then the difference in $\delta(2\theta)$ for any two split members of an original $(hkl)_T$ set, e.g., $(200)_T\rightarrow(200)_M+(020)_M$. The additional assumption was made that the peak shapes and widths were unchanged from 300 K. The results for six reflections are listed in Table II. Although, in the case of the 211 and 213 reflections, it was not practical to refine four separate peak positions, the overall agreement is satisfactory, but the possibility of a lower triclinic distortion cannot be ruled out.

The variation of the widths of the (110) and (200) peaks with temperature is shown in Fig. 2(b). The lines, drawn as a guide, suggest the onset of a phase transformation at a temperature roughly between 130 and 150 K. This transition is reversible (with some possible hys-

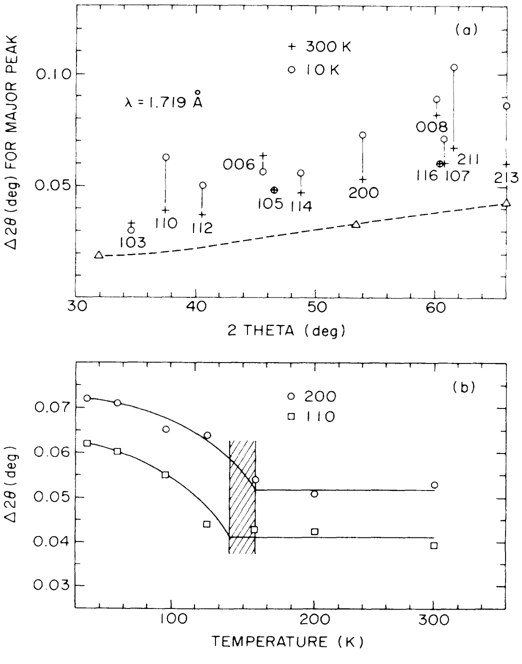

FIG. 2. (a) A display of the FWHM ($\Delta 2\theta$) of all the measured Bragg peaks at 300 and 10 K; the major phase width is used except where there is only a single, nominally symmetrical, peak. The dashed curve is the measured instrumental width. (b) The widths of the 200 and 110 peaks vs temperature revealing a "transition region" at about 130–150 K. Uncertainties in $\Delta 2\theta$ are about ±0.005° for (a) and (b).

TABLE II. Comparison of measured and calculated peak separations $\Delta s(2\theta)$ at 10 K assuming a small monoclinic distortion of the tetragonal axes: $a_M - b_M = 2\Delta$, $\gamma = 90 - \alpha$ ($\Delta = 0.00096$ Å; $\alpha = 0.039°$).

hkl set	Δs_{meas} (deg)	Δs_{calc} (deg)
$110\text{-}1\bar{1}0$	0.028	0.027
$200\text{-}020$	0.032	0.032
$112\text{-}1\bar{1}2$	0.022	0.025
$114\text{-}1\bar{1}4$	0.019	0.021
$(1\bar{2}1,2\bar{1}1)\text{-}(121,211)$[a]	0.046	0.037
$(1\bar{2}3,2\bar{1}3)\text{-}(123,213)$[a]	0.030	0.035

[a] The quadruplet was treated as a (+) pair and a (−) pair for fitting the single broad "21*l*" reflection.

teresis) on cycling between 300 and 10 K. It is impossible with the present data to determine whether there is a phase transformation in the minor tetragonal phase. For the major tetragonal phase between 150 and 300 K, $a^{-1} da/dT \approx 9.7 \times 10^{-6}$ K^{-1} and $c^{-1} dc/dT \approx 12.8 \times 10^{-6}$ K^{-1}.

Single-crystal data were also taken to complement the powder results presented above. By setting the diffractometer 2θ (analyzer) arm at a given *hkl* reflection and rocking the sample through a small range, one picks up the occasional strong diffraction from a large single grain. By suitable masking we could effectively isolate individually reflecting small (70–80-μm) crystals. Figure 3(a) shows an example of rocking curves taken with the analyzer removed at two temperatures for the 110 reflection of such a small crystal, clearly showing increased structure at low temperature. These and other scans taken around the 200 and 211 reflections, which also broaden or display incipient splitting at low temperature, are consistent with our interpretation of the powder data. The shape of θ-2θ scans from single-crystal reflections also shows that *major and minor phases can coexist within a single macroscopic crystal of ≈ 70 μm size.*

Additional single-crystal measurements were made using a novel high-resolution Weissenberg photographic technique.[10] A specially designed camera was mounted on the 2θ arm of the diffractometer at a distance of 0.5 m (giving a 2θ resolution of ≈ 0.01° for a 70-μm crystal). As the sample is rocked stepwise through the diffraction condition the film is translated simultaneously in the vertical direction, permitting the three-dimensional (3D) intensity distribution around a reciprocal lattice point to be efficiently mapped on the 2D film with high resolution. Figure 3(b) shows such enlarged photographs of 110 diffraction spots from a single crystallite at 200 and 9 K. Images for two neighboring rotational settings of the crystal are shown for both temperatures. A splitting in the 2θ direction of ≈ 0.02° is clearly observable at 9 K, consistent with the interpretation of the powder pattern. The unequal intensity may simply reflect unequal domain distributions.

The observations of a minor phase in this sample, and also to varying extent at another Ba concentration and in a series of Sr-substituted compounds,[11] suggest phase separation within a nominally single-phase field as a motif in these oxides. The form and extent of this phase separation may depend both upon elastic anisotropy[12,13] and on thermal and/or oxygen treatment.[5,7] The anomalous broadening of the 00*l* reflections may reflect intergrowth faulting along the *c* axis,[7,14] and may also depend sensitively on oxygen content.[5,7]

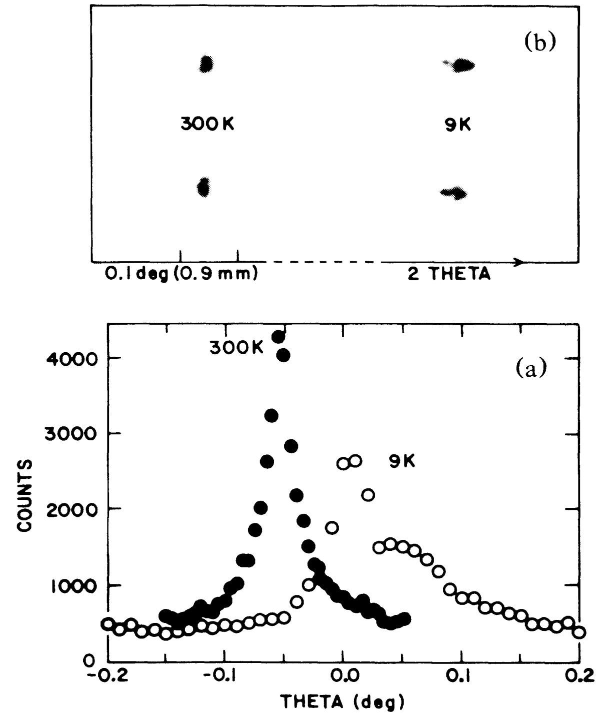

FIG. 3. (a) Variation in diffracted intensity upon sample rotation at the 110 reflection for a single small crystal (≈ 70 μm diameter) at two temperatures. (b) Weissenberg photographs of the same 110 reflection at two temperatures. Horizontal splitting due to *d*-spacing differences are clearly seen at low temperature.

The significance of the weak structural distortion at ≈ 150 K to the low-temperature transport properties is not clear. However, it is believed that the orthorhombic distortion present in pure La_2CuO_4 is unfavorable to superconductivity,[8] while in the related $Ba(Pb,Bi)O_3$ orthorhombic and monoclinic distortions are associated with suppression of superconductivity.[15,16] Since we are unable to determine whether the minor phase also transforms at low temperatures, it is possible that either T_c is only weakly suppressed in the major phase or that the superconductivity is confined to the (possibly still tetragonal) minor phase. The presence of interfaces between the observed phases or intergrowth faulted regions could also contribute to superconductivity in these materials if the electronic structures of the phases are significantly different.[17]

We wish to thank T. Tsakalakos, J. W. Cahn, A. J. Freeman, and C. S. Ting for helpful discussions and R. Gronsky for communication of his electron-microscope results. The work at the University of Houston was supported by National Science Foundation (NSF) Grant No. DMR-86-03662 (S.C.M., K.F.), and by NSF Grant No. DMR-86-16539, U.S. Department of Energy, U.S. National Aeronautics and Space Administration (NASA) Grant No. NAGW-977, and the Energy Laboratory of the University of Houston (P.H., R.L.M., C.W.C.). The work done at Brookhaven National Laboratory was supported by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC02-76CH00016. D. Hohlwein thanks the Deutschen Forschungsgemeinschaft (Bonn, Germany) for support.

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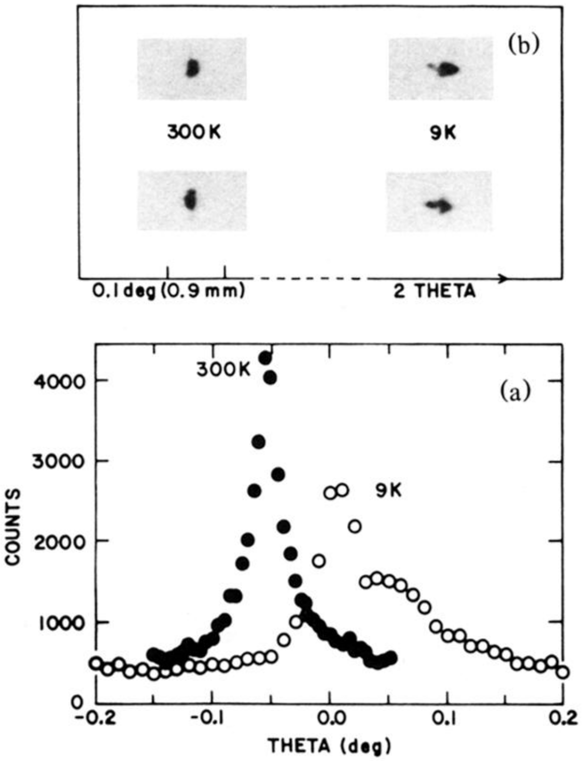

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