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# STRUCTURAL STUDIES OF $La_{2-x}Ba_xCuO_4$ BETWEEN 11-293 K

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## ABSTRACT

Neutron powder diffraction data have been collected from samples of $La_{1.9}Ba_{0.1}CuO_4$ and $La_{1.85}Ba_{0.15}CuO_4$ in the temperature range 11-293 K. The first material undergoes a phase transition from the tetragonal $K_2NiF_4$-type structure (space group I4/mmm) to the orthorhombic $La_2CuO_4$-type structure (space group Bmab) at about 280 K, and then a second transition to another type of tetragonal (or near-tetragonal) structure with probable space group $P4_2/ncm$. The latter transition occurs predominantly between 50-40 K, but about 10% of the orthorhombic phase persists down to 15 K. Rietveld refinement was carried out at selected temperatures in the different structural regions. The differences among the low temperature structures can be characterized by tilting of the $CuO_6$ octahedra about different rotation axes on the basis of the simple X-Y model previously proposed by Axe and coworkers. The tilt angle, which is a measure of the long-range order parameter, is about 3.5° at 15 K.

Data sets were also collected from $La_{1.85}Ba_{0.15}CuO_4$ at 293, 90 and 11K. At the two latter temperatures there was some peak broadening consistent with the distortions observed in previous high resolution neutron [Paul and co-workers] and x-ray [Axe and co-workers] powder studies. Rietveld analysis of the data indicated the presence of local octahedral displacements, but it was not possible to determine the nature of the correlations.

## INTRODUCTION

Following the discovery of high temperature superconductivity in Sr- and Ba-doped $La_2CuO_4$ by Bednorz and Muller [1], some interesting structural anomalies were found in the Ba-substituted system. A high resolution synchrotron x-ray powder diffraction study of $La_{1.8}Ba_{0.2}CuO_4$ revealed a small distortion from the tetragonal $K_2NiF_4$-type structure to an apparently monoclinic structure at about 150 K [2], while a high resolution neutron investigation of $La_{1.85}Ba_{0.15}CuO_4$ showed a tetragonal-to-orthorhombic transition at about 180 K, followed by a fairly abrupt reduction in the orthorhombic strain between 70-60 K [3]. The first transition from the $K_2NiF_4$-type structure to one of $La_2CuO_4$-type is a well-known feature of these substituted materials and is driven by a soft-mode phonon instability [4,5].

Subsequent x-ray and neutron diffraction measurements on $La_{1.9}Ba_{0.1}CuO_4$ and other members of this system have led to the conclusion that the reduction in strain corresponds to a structural transition to a new tetragonal phase with probable symmetry $P4_2/ncm$ [6,7]. This interpretation is supported by a simple Landau-type theoretical analysis. The tetragonal phase can be regarded as a coherent superposition of two orthorhombic twin-related structures of $La_2CuO_4$ type resulting from a second instability in the two-fold degenerate soft mode of the high temperature tetragonal structure. Although the differences between the two structures are quite small, they appear to have large effects on the superconducting properties [8,9,10].

The present paper gives a detailed account of the neutron powder diffraction studies which have been only briefly summarized in the previous work [6,7,11].

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## EXPERIMENTAL DETAILS

Approximately 5g samples of $La_{2-x}Ba_xCuO_4$ with x = 0.1 and 0.15 were prepared from $La_2O_3$, $BaCO_3$ and CuO by a process described in detail previously [8] which has been found to give reproducible results for the superconducting properties. In particular, there are two maxima in $T_c$ at about 25K close to these compositions, and a local minimum at about 5K for x near to 0.12 a feature which has recently been verified independently [10].

Neutron powder diffraction measurememts were made on a triple-axis diffractometer at the Brookhaven High Flux Beam Reactor equipped with pyrolytic graphite monochromator and analyzer crystals. Most of the data were collected with the monochromator and analyzer in the (002) and (004) settings respectively, with collimation 20' in-pile, 40' monochromator- sample, 40' sample-analyzer and 10' analyzer-detector. Some earlier data were obtained with the analyzer in the (002) setting and 20' analyzer- detector collimation. The neutron wavelength was 2.372A, with higher order harmonics suppressed by a pyrolytic graphite filter. The sample was placed in an aluminum holder and loaded into a closed-cycle He cryostat for temperature dependence measurements. In the case of $La_{1.9}Ba_{0.1}CuO_4$ extended data sets for Rietveld refinement were collected at several temperatures over the angular range 18-138°, and shorter scans were made over selected regions at other temperatures to investigate the symmetry changes. For $La_{1.85}Ba_{0.15}CuO_4$ full data sets were collected at 293, 90 and 11 K over the angular range 10-117° with the second of the two diffractometer configurations described above.

## RESULTS

### $La_{1.9}Ba_{0.1}CuO_4$

The general features of the temperature dependence studies can be summarized as follows. At 285 K, all of the peaks in the pattern could be indexed on the basis of a body-centered tetragonal unit cell, space group I4/mmm, with a = 3.793 Å and c = 13.276 Å. As the temperature was lowered, a transition to orthorhombic symmetry was observed below about 280 K, as revealed by broadening and eventual splitting of the tetragonal (220) peak, and the appearance of several weak superlattice peaks. At 91 K, all peaks were consistent with an orthorhombic cell similar to that of $La_2CuO_4$, space group Bmab, with a = 5.344 Å, b = 5.377 Å and c = 13.239 Å. This setting is used instead of the standard Cmca setting in order to facilitate comparison with the tetragonal cell, and means that the (220) reflection from the latter splits into orthorhombic (040) and (400) peaks.

Over a fairly wide temperature range below 60 K, a third structural modification transition was observed corresponding to transformation of the orthorhombic phase into another type of tetragonal (or near-tetragonal) phase. However, there was little apparent change in the intensities of the weak superlattice peaks. At 15 K, the tetragonal lattice parameters were a = 5.360 Å and c = 13.236 Å.

Least-squares fits of a Gaussian function to the tetragonal (220) peak at 284 K and the orthorhombic (040,400) pair at 91 K are shown in Figures 1a and 1b. The two orthorhombic peaks were assumed to have the same peakwidths (full-width at half-maximum). There is a slight increase in peakwidth to 0.70° at 91 K, compared to 0.61° at 284 K, which is the instrumental resolution for this experimental configuration.

In order to satisfactorily fit the data below 70 K, it was necessary to use a three peak model, as illustrated for the 45 K scan in Figure 1c. By comparison with Figure 1b, it is clear that the two outer peaks are the orthorhombic (040) and (400) reflections, while the central peak is the (400) reflection from the new tetragonal phase, which continues to grow at the expense of the orthorhombic phase as the temperature is lowered further.

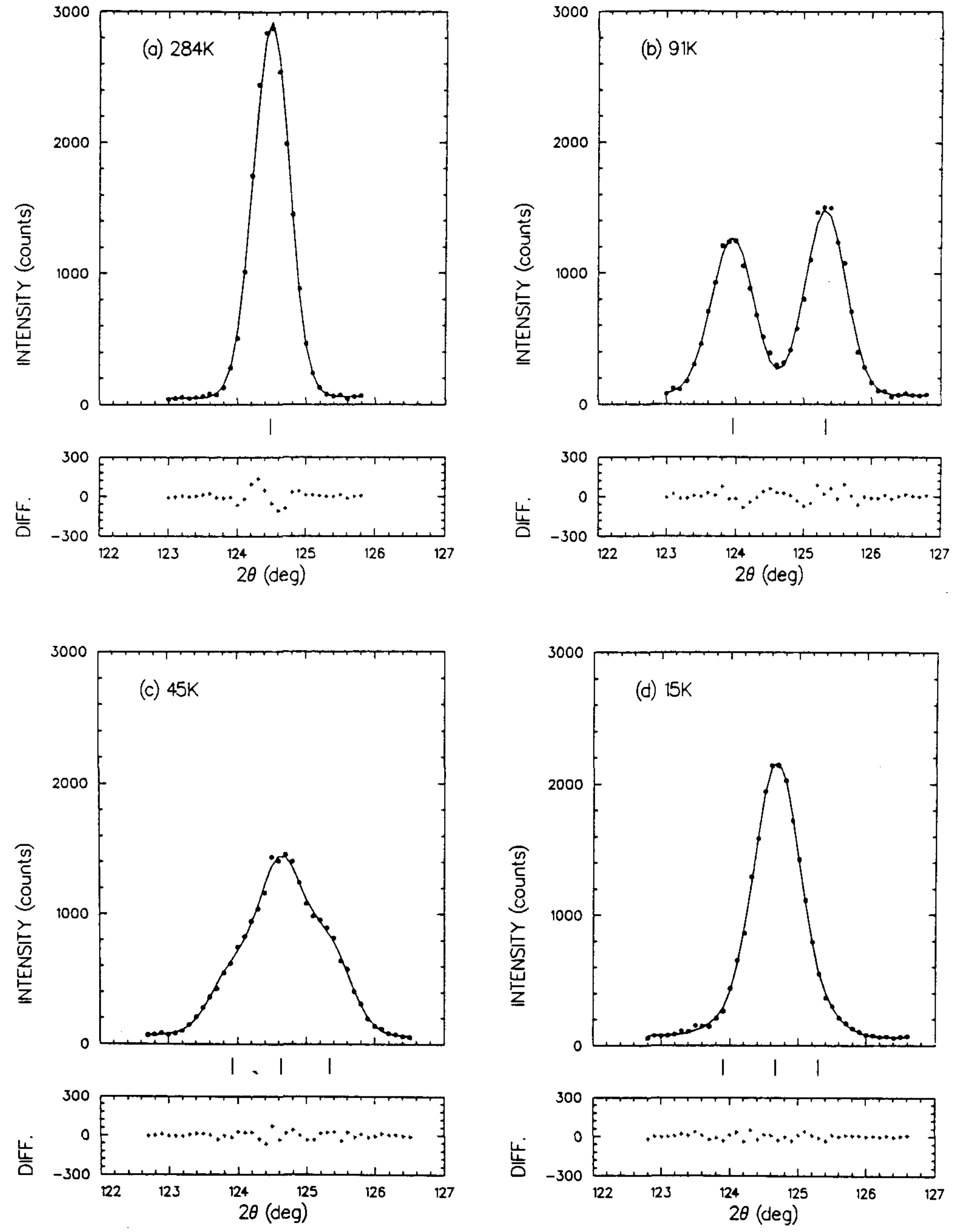

Figure 1. Gaussian fits to (a) tetragonal (220) peak (b) orthorhombic (040) and (400) peaks (c) and (d) orthorhombic (040), (400) and tetragonal $P4_2/ncm$ (400) peaks in two-phase region. Short vertical markers denote peak positions.

However, the latter does not disappear entirely, as even at 15 K a three peak model gave a significantly better fit, which is shown in Figure 1d. From 45-10 K there is a further increase in the peak-width to about 0.8°.

The fractional amount of orthorhombic phase may be estimated from the ratio of the (040)+(400) intensities to the tetragonal (400) intensity, and is shown as a function of temperature in Figure 2. Most of the change occurs in the region between 40-55 K, but there is still about 10% residual orthorhombic material present at 15 K. Hysteresis effects are estimated to be no more than 1-2 K, at least on the time scale needed to achieve thermal equilibrium of the sample, about 20 minutes.

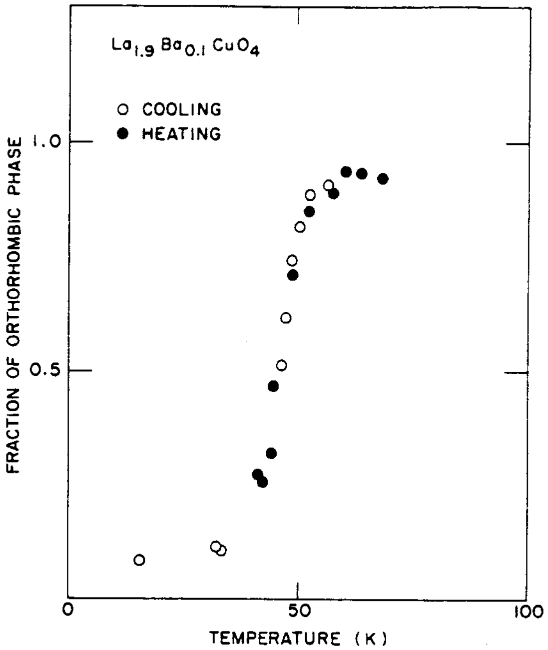

Figure 2. Fractional amount of orthorhombic phase determined from the relative intensities of the Bmab (040),(400) and $P4_2/ncm$ (400) peaks as a function of temperature.

The variation of the lattice parameters with temperature is shown in Figure 3. The points depicted by open squares represent an "equivalent" tetragonal parameter, $a'_T$, derived from fits to the orthorhombic (220) reflection, and the broken line through these points connects the high and low temperature tetragonal regions with no discernible discontinuity. The points for the c parameter were determined from fits to the (008) peak, and likewise show no anomaly at the 50 K transition.

The variation in intensity of the (014) superlattice peak with temperature is plotted in Figure 4. In this case, there is an indication of a small discontinuity between 40-50 K.

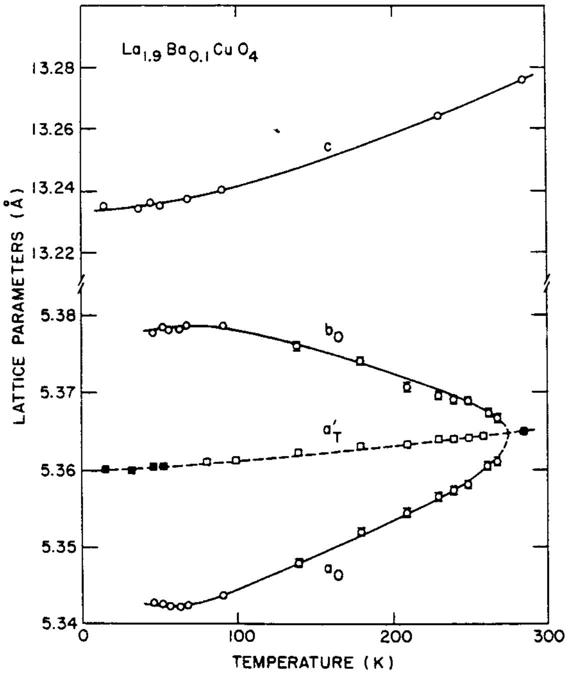

Figure 3. Lattice parameters as a function of temperature. a and b refer to the orthorhombic phase, and $a'_T$ is the "equivalent" tetragonal value desribed in text. The lines are guides to the eye.

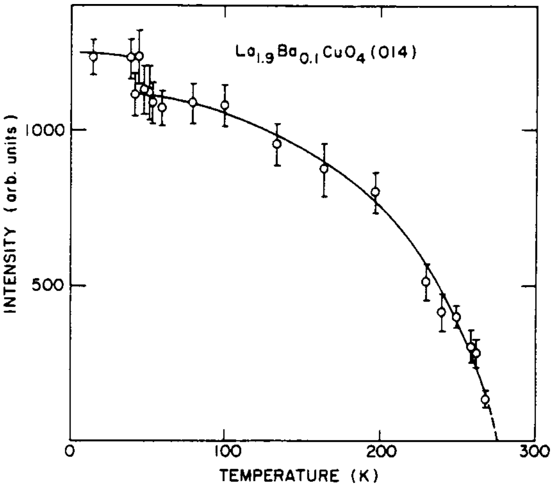

Figure 4. Intensity of the (014) superlattice peak as a function of temperature. The line is a guide to the eye.

$La_{1.85}Ba_{0.15}CuO_4$

The 293 K pattern showed a body-centered tetragonal phase with a = 3.784Å and c = 13.284Å, and also one weak impurity peak with a d-spacing of 2.58 Å and an intensity about 0.5 % of that of the strongest peak. At 90 and 11 K the tetragonal (110) peak was seen to be broadened, consistent with the distortions noted previously (3,6,7). However, no intensity could be detected at the superlattice peak positions within the uncertainty of the counting statistics.

## STRUCTURE REFINEMENT

$La_{1.9}Ba_{0.1}CuO_4$

Rietveld profile analysis of the extended data sets was carried out with the program GSAS [12], which makes provision for refinement of multiple phases. The low temperature space group was assumed to be $P4_2/ncm$, which is the highest symmetry tetragonal sub-group of I4/mmm with this kind of enlarged cell. However, because of the observed broadening of the (400) peak in the low temperature region, we cannot exclude the possibility that the true space group is orthorhombic Pccn. It may be noted that Bmab is also a sub-group of I4/mmm, but not of $P4_2/ncm$; however, it is possible in principle to have a continuous transformation from Bmab to $P4_2/ncm$ symmetry via Pccn. This can be seen from the respective coordinates listed in Table I and is

Table I. Relationships among atomic coordinates and reflection conditions for the various space groups discussed in text.

| | I4/mmm | Bmab | Pccn | $P4_2/ncm$ |
|---|---|---|---|---|
| Cu | 2(a): 0 0 0 | 4(a): 0 0 0 | 4(a): 0 0 0 | 4(d): 0 0 0 |
| 01 | 4(c): 0 1/2 0 | 8(e): 1/4 1/4 z | 4(c): 1/4 1/4 z<br>4(d): 1/4 3/4 z | 4(e): 1/4 1/4 z<br>4(a): 1/4 3/4 0 |
| La,Ba<br>02 | 4(e): 0 0 z | 8(f): 0 y z | 8(e): x y z | 8(i): x x z |
| | hkl: h+k+l=2n | hkl: h+l=2n<br>hk0: h,k=2n<br>0kl: l=2n | hk0: h+k=2n<br>0kl: l=2n | hk0: h+k=2n<br>0kl, h0l: l=2n |

predicted theoretically [6]. A further point to note is that the systematic reflection absences are not so restrictive in $P4_2/ncm$ (or Pccn) as in Bmab, and thus additional weak peaks not allowed by a B-centered lattice (such as (110) and (211))could appear. A careful examination of the 15 K data did not reveal any such peaks at an intensity level above the detectable threshold of about 0.3% of the strongest fundamental peaks.

A satisfactory refinement of both structures was obtained from the 45 K data set for which the two components are present in roughly equal proportions. Refinement at 15 K was accomplished with the atomic coordinates and temperature factors of the minority orthorhombic phase fixed at their 45 K values, and vice versa for the tetragonal phase at 60 K. Significantly better profile fits were obtained for refinements in the two-phase region when the a and b parameters of the tetragonal component were not constrained to be equal, which is not too surprising in view of the previously mentioned broadening of the (400) peak. However, no further improvement in the fit was obtained when refinement was attempted in space group Pccn. The results are summarized in Table II, and some profile fits and difference plots are reproduced in Figure 5.

Table II. Results of Rietveld refinement for $La_{1.9}Ba_{0.1}CuO_4$ at different temperatures. Scattering amplitudes for La, Ba, Cu and O 0.827, 0.525, 0.7718 and 0.5805 X $10^{-12}$cm respectively [13]. Numbers in parentheses are esd's referred to the least significant digit(s). f is the fractional amount of orthorhombic phase. $R_I$ and $S_p$ are the weighted profile R-factor and goodness-of-fit index respectively as defined in Ref. [14].

| | 15K | ----- 45K ----- | | 60K | 91K | 285K |
|---|---|---|---|---|---|---|
| | $P4_2/ncm$ | $P4_2/ncm$ | Bmab | Bmab | Bmab | I4/mmm |
| Cu:B($Å^2$) | 0.0(1) | -0.2(2) | -0.2(5) | -0.7(1) | -0.1(1) | 0.2(1) |
| La:x | 0.0042(2) | 0.0039(4) | - | - | - | - |
| y | 0.0042 | 0.0039 | 0.0089(10) | 0.0062(7) | 0.0056(4) | - |
| z | 0.3612(1) | 0.3619(4) | 0.3590(8) | 0.3608(1) | 0.3609(1) | 0.3607(1) |
| B($Å^2$) | 0.0(1) | 0.1(2) | -0.5(4) | -0.7(1) | 0.1(1) | 0.3(1) |
| O1:z | 0.0081(4) | 0.0102(9) | 0.0052(10) | 0.0047(4) | 0.0054(2) | - |
| B($Å^2$) | -0.1(3) | 0.3(6) | 0.0(4) | -0.4(1) | 0.3(1) | 0.7(1) |
| O2:x | -0.0213(3) | -0.0198(6) | - | - | - | - |
| y | -0.0213 | -0.0198 | -0.0298(15) | -0.0313(11) | -0.0279(5) | - |
| z | 0.1824(2) | 0.1822(7) | 0.1829(12) | 0.1828(2) | 0.1825(2) | 0.1824(1) |
| B($Å^2$) | 0.6(1) | 0.6(2) | 0.1(3) | -0.3(1) | 0.7(1) | 1.5(1) |
| $a_T$(Å) | 5.3548(1) | 5.3541(3) | | 5.3546(40) | - | 3.7931(1) |
| $b_T$(Å) | 5.3643(1) | 5.3649(3) | | 5.3670(39) | - | 3.7931 |
| $c_T$(Å) | 13.2356(3) | 13.2379(8) | | 13.2272(29) | - | 13.2755(2) |
| $a_0$(Å) | 5.3393(7) | 5.3404(3) | | 5.3415(5) | 5.3436(1) | - |
| $b_0$(Å) | 5.3853(7) | 5.3801(3) | | 5.3805(5) | 5.3773(1) | - |
| $c_0$(Å) | 13.2092(37) | 13.2273(15) | | 13.2409(8) | 13.2386(2) | - |
| f | 0.08(1) | 0.32(4) | | 0.76(9) | 1.0 | 0.0 |
| $R_I$ | 0.079 | 0.082 | | 0.061 | 0.085 | 0.091 |
| $S_p$ | 1.15 | 1.16 | | 1.45 | 1.19 | 1.24 |

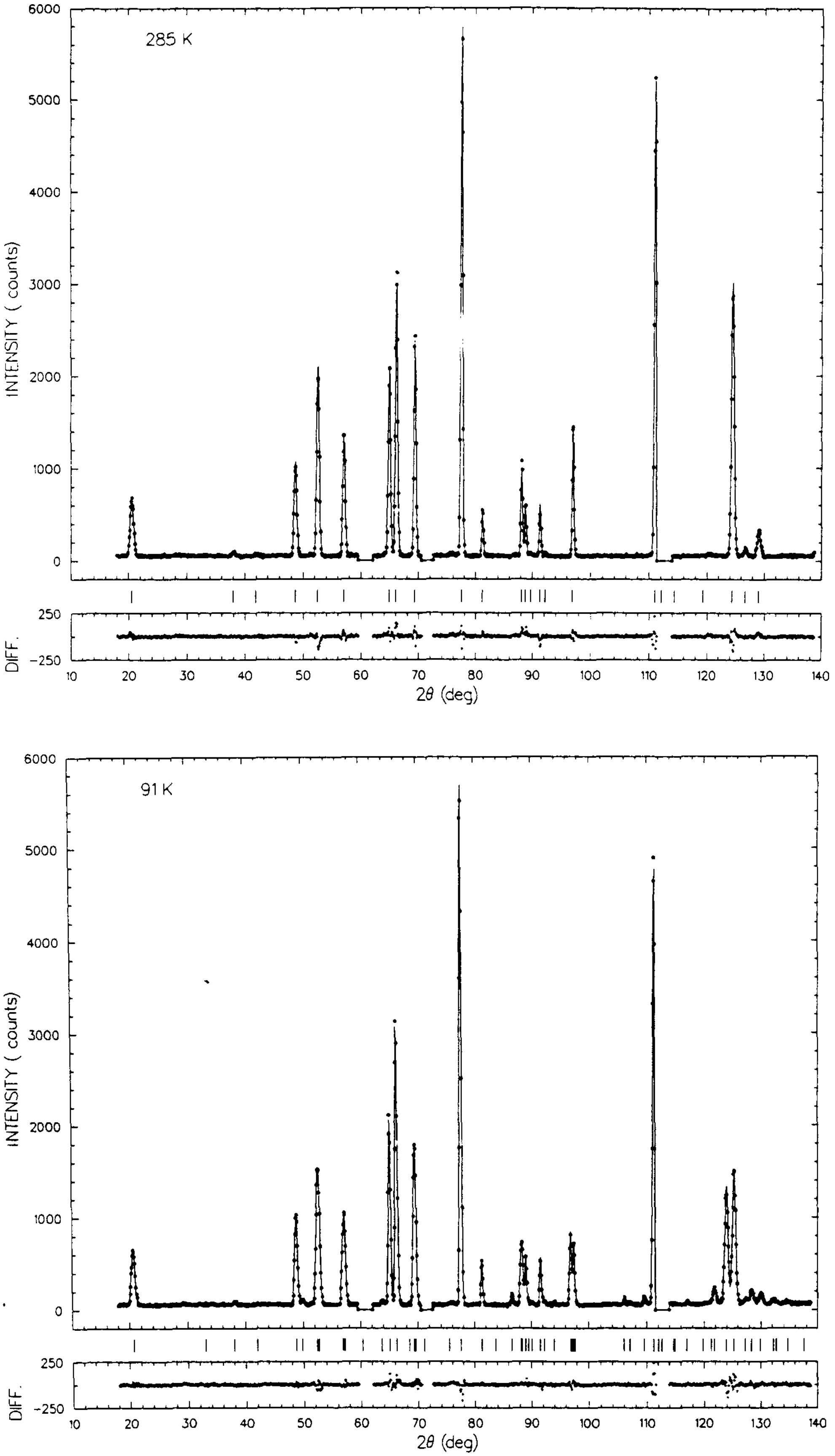

Figure 5. Profile fits and difference plots for $La_{1.9}Ba_{0.1}CuO_4$ at 285 and 91 K in the single phase tetragonal (I4/mmm) and orthorhombic (Bmab) regions. Short vertical markers represent allowed reflections.

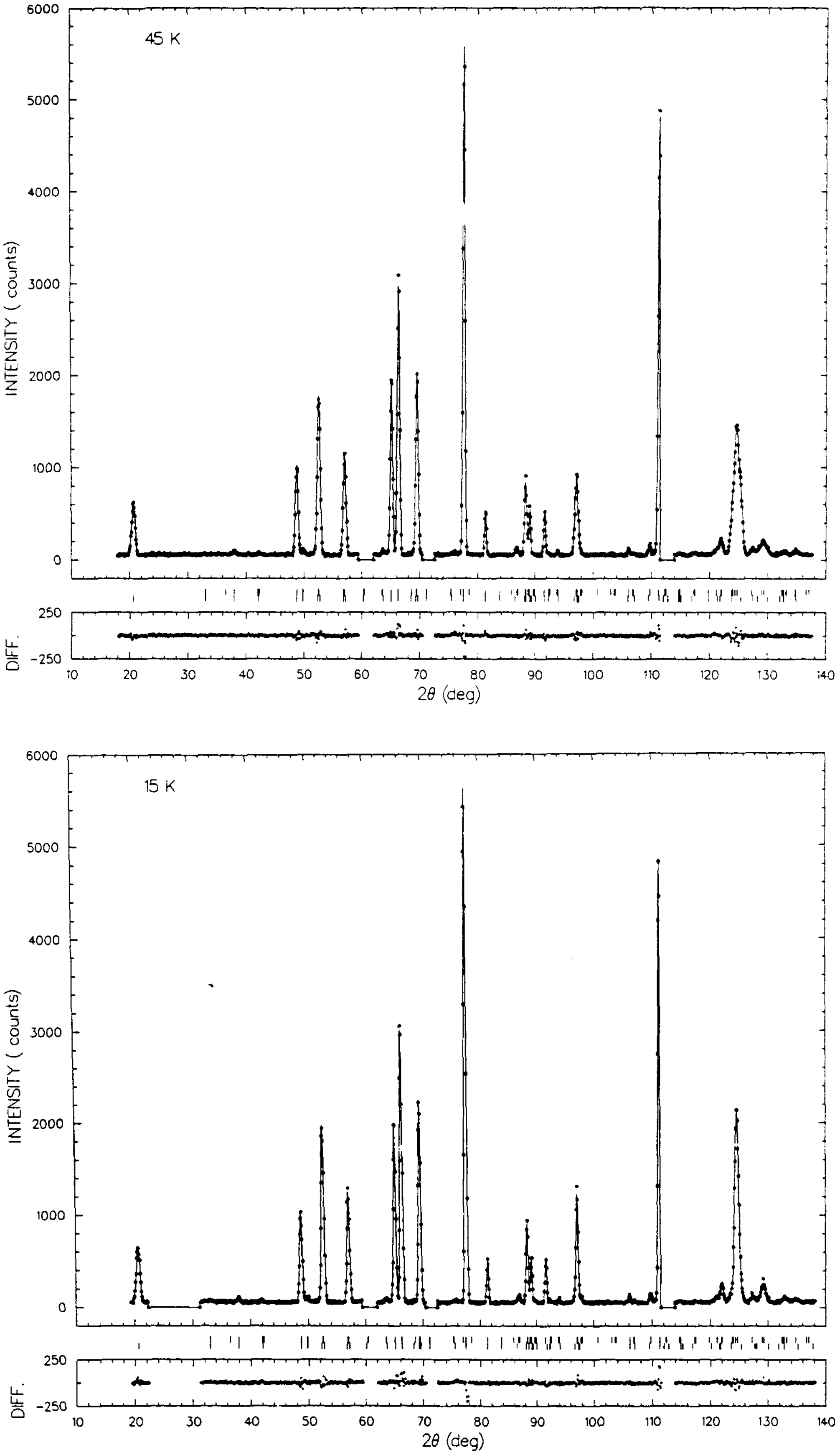

Figure 5. Profile fits and difference plots for $La_{1.9}Ba_{0.1}CuO_4$ at 45 and 15 K in the two phase orthorhombic (Bmab) and tetragonal ($P4_2/ncm$) regions. Short vertical markers represent allowed reflections.

The parameters listed in Table II correspond to Cu-O1 and Cu-O2 bond lengths of about 1.90 and 2.42 Å respectively, very close to those reported for $La_2CuO_4$ [15]. In the $P4_2/ncm$ phase at 15 and 45 K, the oxygen displacements are consistent with near-rigid tilting of the $CuO_6$ octahedra of roughly 3.5° about the <110> axes, compared to 5° in $La_2CuO_4$. In the Bmab region between 45-91 K, the O1 displacements indicate tilting of about 2°, but the O2 shifts are then a factor of two too large for rigid tilting. This may reflect anisotropic thermal effects and/o local uncorrelated displacements which are perhaps a precursor to the low temperature transition.

$La_{1.85}Ba_{0.15}CuO_4$

Because of the absence of any observable superlattice peaks in the 90 and 11 K data sets even though there is broadening of the peaks consistent with the previously reported orthorhombic distortion [3,7], refinement in space group Bmab cannot be expected to yield reliable results for the long-range correlations in the oxygen displacements. Refinement was therefore carried out with the O1 atoms equally distributed between two sets of 8(e) positions at 1/4 1/4 z and 1/4 1/4 -z, and O2 likewise between 8(f) positions at 0 y z and 0 -y z. This allows displacements consistent with local tilting of the oxygen octahedra, but no long-range order. To provide a direct comparison to the high temperature tetragonal structure, an analogous model was used in this case too.

The results are summarized in Table III, and indicate that substantial displacements are indeed present, corresponding to local tilting of about 3-4°. The orthorhombic strain at 90 K (defined as (b-a)/(b+a)) is about 1.5 X $10^{-3}$, close to that reported by Paul et al. [3]. At 11 K the strain is significantly smaller, about 1.1 X $10^{-3}$, but not as small as that observed by the latter workers. The z parameters of the La and O2 atoms are in good agreement with those derived in a previous study based upon the assumption of I4/mmm symmetry at both 295 and 10K [15].

Table III. Results of Rietveld refinement for $La_{1.85}Ba_{0.15}CuO_4$ at different temperatures based on the local displacement model described in text.

| | 11 K | 90 K | 293 K |
|---|---|---|---|
| Cu:B($Å^2$) | 0.8(2) | 0.7(2) | 0.4(2) |
| La:z | 0.3610(2) | 0.3609(2) | 0.3606(2) |
| B($Å^2$) | 0.6(2) | 0.5(2) | 0.3(2) |
| O1:z | 0.0102(10) | 0.0097(10) | 0.0069(15) |
| B($Å^2$) | 0.6(2) | -0.1(2) | 0.4(2) |
| O2:x | -0.0306(31) | -0.0290(30) | -0.0208(44) |
| z | 0.1818(4) | 0.1824(3) | 0.1822(3) |
| B($Å^2$) | 1.0(2) | 0.9(2) | 1.1(20 |
| a (Å) | 5.3381(11) | 5.3349(10) | 3.7840(5) |
| b (Å) | 5.3500(11) | 5.3511(9) | 3.7840 |
| c (Å) | 13.2437(22) | 13.2433(21) | 13.2832(20 |
| $R_I$ | 0.101 | 0.100 | 0.110 |
| $S_p$ | 1.32 | 1.27 | 1.29 |

## DISCUSSION

The results obtained for $La_{1.9}Ba_{0.1}CuO_4$ from the detailed analysis of the evolution of the (040,400) peaks are in good agreement with those obtained in x-ray studies. In particular, the data are consistent with a first-order low temperature orthorhombic-tetragonal transition, although the interpretation is complicated somewhat by the persistence of an appreciable fraction of orthorhombic material well below the transition and the additional broadening of the tetragonal peak. This broadening could possibly be attributed to domain-size effects; alternatively the true symmetry could be Pccn, although this cannot be confirmed from the structure refinements. As pointed out in previous papers [6,7] the essential differences among the low temperature structures are determined by the direction of the axis of rotation of the $CuO_6$ octahedra, and can be discussed in terms of a simple X-Y model.

It seems likely that the high resolution neutron data reported by Paul and coworkers [3] for $La_{1.85}Ba_{0.15}CuO_4$ can be interpreted in an analogous way, although they make no mention of any coexistence region. Our data for material of similar composition are not sufficiently well-resolved to throw any further light on this point. A very small reduction in orthorhombic strain has also been observed in $La_{1.85}Sr_{0.15}CuO_4$ between 40-20 K [16], and this too could indicate a transition of similar type. Furthermore, evidence for local octahedral tilting modes has been seen in the radial distribution function obtained from neutron data taken on material of comparable composition [17].

Structural modifications have also been found in related transition metal compounds. A recent single crystal study of $La_2CoO_4$ [18] has revealed a discontinuous transformation from the Bmab structure at about 135 K to a tetragonal structure which could well have $P4_2/ncm$ symmetry. A transition has recently been reported to occur in $La_2NiO_4$ at about 80 K [19] in which there is a reduction in the orthorhombic strain. (In this case the results were interpreted in terms of a model in which the symmetry remained unchanged, since refinement in space group Pccn did not improve the fit). The suggestion that the explanation is as discussed here is in better accord with very recent single crystal experiments [20].

## ACKNOWLEDGMENTS

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## REFERENCES

[1]. J. G. Bednorz and K. A. Muller, Z. Phys. B64, 189 (1986).

[2]. S. C. Moss, K. Forster, J. D. Axe, H. You, D. Hohlwein, D. E. Cox, P. H. Hor, R. L. Meng and C. W. Chu, Phys. Rev. B35, 7195 (1987).

[3]. D. Mck. Paul, G. Balakrishnan, N. R. Bernhoeft, W. I. F. David and W. T. A. Harrison, Phys. Rev. Lett. 58, 1976 (1987).

[4]. R. J. Birgeneau, C. Y. Chen, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. Thio, T. R. Thurston, H. L. Tuller, J. D. Axe, P. Boni and G. Shirane, Phys. Rev. Lett. 59, 1329 (1987).

[5]. P. Boni, J. D. Axe, G. Shirane, R. J. Birgeneau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone and T. R. Thurston, Phys. Rev. B38, 185 (1988).

[6]. J. D. Axe, D. E. Cox, K. Mohanty, H. Moudden, A. R. Moodenbaugh, Y. Xu and T. R. Thurston, IBM J. Res. Devel. (in press).

[7] J. D. Axe, A. H. Moudden, D. Hohlwein, D. E. Cox, K. M. Mohanty, A. R. Moodenbaugh and Y. Xu, Phys. Rev. Lett. (submitted).

[8]. A. R. Moodenbaugh, Y. Xu, M. Suenaga, T. J. Folkerts and R. N. Shelton, Phys. Rev. B38, 4596 (1988).

[9]. M. Sera, Y. Ando, S. Kondoh, K. Fukuda, M. Sato, I. Watanabe, S. Nakashima and Y. Kumagai, Solid State Commun. 69, 851 (1989).

[10]. K. Kumagai, Y. Nakamura, I. Watanabe, Y. Nakamichi and H. Nakajima, J. Mag. Magn. Mater. (in press).

[11]. D. E. Cox, J. D. Axe, H. Moudden, K. M. Mohanty and A. R. Moodenbaugh, Amer. Cryst. Assn. Annual Meeting 16, 110 (1988).

[12]. A. C. Larson and R. B. Von Dreele, GSAS, Los Alamos National Laboratory Report LAUR 86-748 (1988).

[13]. L. Koester and W. B. Yelon, "Neutron Cross Section Data", Netherlands Energy Research Foundation, ECN, Petten (1983).

[14]. H. G. Scott, J. Appl. Cryst. 16, 159 (1983).

[15]. J. D. Jorgensen, H.-B. Schuttler, D. G. Hinks, D. W. Capone, K. Zhang, M. B. Brodsky and D. J. Scalapino, Phys. Rev. Lett. 58, 1024 (1987).

[16]. P. Day, M. Rosseinsky, K. Prassides, W. I. F. David, O. Moze and A. Soper, J. Phys. C, 20, 1429 (1987).

[17]. T. Egami, W. Dmowski, J. D. Jorgensen, D. G. Hinks, D. W. Capone, C. U. Segre and K. Zhang, Inter. Conf. on Superconductivity, Drexel University (1987).

[18]. K. Yamada, M. Matsuda, Y. Endoh, B. Keimer, R. J. Birgeneau, S. Onodera, J. Misuzaki, T. Matsuura, and G. Shirane, Phys. Rev. B39, 2336 (1989).

[19]. J. Rodriguez-Carvajal, J. L. Martinez, J. Pannetier and R. Saez-Puche, Phys. Rev. B38, 7148 (1988).

[20]. G. Lander, P. J. Brown, J. M. Honig and J. Spalek (private communication ).