Anomalous Structural Behavior of the Superconducting Compound $La_{1.85}Ba_{0.15}CuO_4$

D. McK. Paul and G. Balakrishnan
Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom

N. R. Bernhoeft
Department of Physics, University of Durham, Durham DH1 3AP, United Kingdom

and

W. I. F. David and W. T. A. Harrison
Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom
(Received 23 March 1987)

High-resolution neutron powder diffraction experiments on the superconducting compound $La_{1.85}Ba_{0.15}CuO_4$ have revealed the presence of a tetragonal-to-orthorhombic phase transition at 180 K, together with subtle, anomalous structural instabilities at lower temperatures. These experiments demonstrate a correlation between the structural anomalies and changes in the electrical resistivity.

PACS numbers: 74.70.Ya, 61.60.+m, 64.70.Kb

The initial success of the studies by Bednorz and Muller,[1] who observed the onset of superconductivity at 35 K in a mixed-phase sample of lanthanum barium copper oxides, has provoked an intense effort in several laboratories to produce single-phase and related materials with superconducting transitions at these and higher temperatures. Despite a frantic search for the most appropriate composition there have been few experimental studies reported which might relate to the underlying mechanism for this type of high-temperature superconductivity. Experimental and theoretical results aimed at an understanding of the pairing mechanism, the superconducting ground state, and thermal excitations in these materials are of fundamental importance and will do much to stimulate further progress in this field.

Compounds which exhibit superconductivity are often prone to structural instabilities.[2] The structural phase transitions which occur may or may not be directly associated with the superconducting phase transition. Similar reasoning leads one to consider the anomalous behavior of certain vibrational modes of the lattice potentially coupled to the onset of superconductivity through an enhanced electron-phonon interaction. In view of the possible interdependence of crystallographic and electronic (superconducting) phase transitions it is clear that a detailed and accurate knowledge of structural instabilities may clarify the origin of superconductivity in such materials. Furthermore, any relatistic model of the high-temperature superconducting phase will have to satisfy the observed structural constraints.

Recent medium-resolution neutron diffraction experiments reported that $La_{1.85}Ba_{0.15}CuO_4$ adopts the tetragonal $I4/mmm$ structure (similar to K_2NiF_{34}) at various temperatures between 10 and 295 K.[3] In this Letter we report the results of high-resolution neutron diffraction experiments on the same compound, performed by using the high-resolution powder diffractometer on the ISIS neutron spallation source at the Rutherford Appleton Laboratory. Our measurements clearly show that a tetragonal-to-orthorhombic transition occurs at 180 K, together with further structural anomalies on approach of the onset of the superconducting phase transition at 35 K.

The materials used in these experiments were prepared by reaction of La_2O_3, $BaCo_3$, and CuO in the appropriate cation ratios at 1100 K for 24 h; the reacted mixture was then ground, pressed into pellets, and sintered at 1100 K for an additional 12 h. The samples exhibited a sharp superconducting transition with no low-temperature resistivity tail (Fig. 1); further, no evidence could be obtained for a deterioration of these properties with time, as reported by other authors.[4]

First, we give a brief overview of the observed

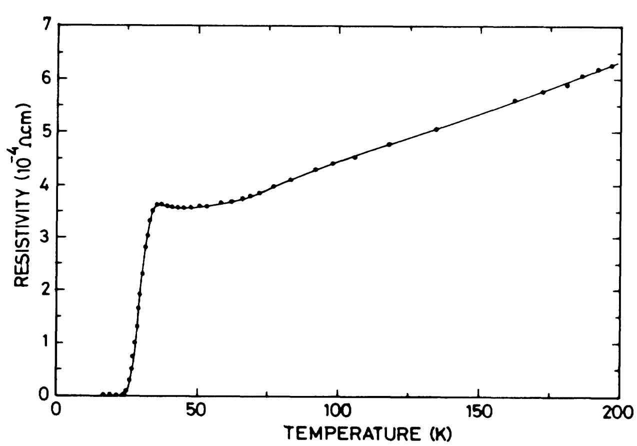

FIG. 1. Temperature dependence of resistivity for $La_{1.85}Ba_{0.15}CuO_4$.

structural instabilities of the parent compound La_2CuO_4. At high temperatures the material displays the tetragonal symmetry of the *I*4/*mmm* space group before distorting to a lower-symmetry orthorhombic state below 500 K.[5,6] We have taken neutron diffraction data at a temperature of 295 K on samples of La_2CuO_4 prepared by a route similar to that used for the barium-doped superconductors. Structural analysis in both the (*Abma*) and (*Fmmm*), space groups by the Rietveld profile refinement technique enables us to assign the (*Abma*) structure as being preferred, and also allows us to define an orthorhombic splitting ratio between the (a,b) basal-plane lattice vectors equal to $(b-a)/(b+a)$ and of magnitude 3.98×10^{-3} at room temperature.

In contrast, our high-resolution neutron diffraction data indicate the following anomalous behavior in the barium-doped compound $La_{1.85}Ba_{0.15}CuO_4$. At temperatures greater than 180 K we observe the tetragonal *I*4/*mmm* structure (as in the parent compound above 500 K). Below this temperature a symmetry-breaking orthorhombic transition occurs with a splitting ratio which increases monotonically with decreasing temperature, reaching a maximum value at 75 K. Below 75 K a highly unusual and unexpected *decrease* in lattice distortion is observed which saturates at 35 K coincident with the onset of superconductivity in this sample. Direct evidence for this orthorhombic distortion is presented in Fig. 2 which clearly indicates the development of the splitting between the (400) and (040) Bragg reflections on entering the orthorhombic phase and its subsequent collapse with further lowering of temperature.

All data, taken in 5-K steps between 10 and 185 K, have been refined in both the (*Abma*) and (*Fmmm*) space groups. The preferred structure in the orthorhombic phase is found to be (*Abma*), as in the parent compound, and allows us to calculate the orthorhombic splitting ratio as a function of temperature. The temperature dependence of this ratio, the spontaneous strain, is presented graphically in Fig. 3.

For the lanthanum site the positional parameters derived in the (*Abma*) refinement are very similar in both the barium-doped superconductor and the parent compound but the oxygen parameters are anomalous. The oxygen atoms have positional parameters with large estimated standard deviations (2 or 3 times that of the oxygen in the parent compound) together with large thermal parameters. This suggests that the effective potential localizing the oxygen atoms is rather flat and that abnormalities in both the electronic and the vibrational responses may be correlated with this fact.

In addition to the site positional anomalies the Bragg (h00)-type reflections are noticably wider than their (0h0) counterparts. This broadening, which is well described by a Lorentzian line shape, is consistent with the existence of stacking faults taking the structure locally from the (*Abma*) into the (*Fmmm*) sequence. The presence of such stacking faults may be anticipated in this weakly split orthorhombic state since the required energy to shift between the (*Abma*) and (*Fmmm*) space groups is small. We note that such effects may actually be

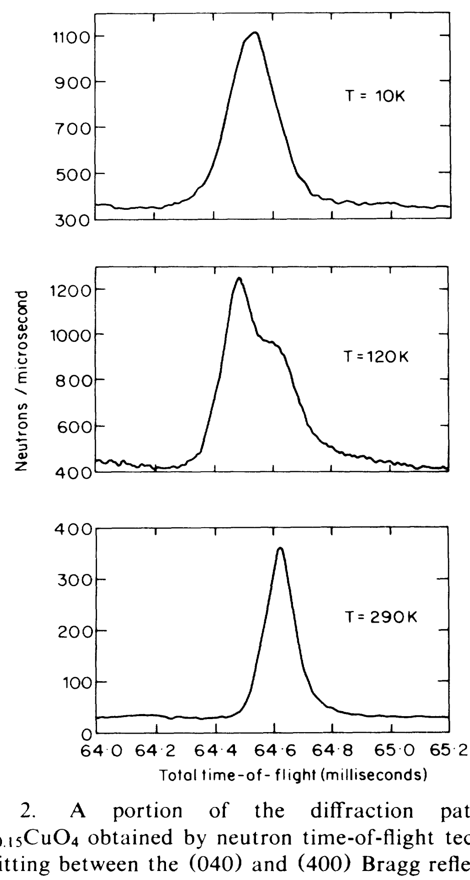

FIG. 2. A portion of the diffraction pattern of $La_{1.85}B_{0.15}CuO_4$ obtained by neutron time-of-flight techniques. The splitting between the (040) and (400) Bragg reflections of the orthorhombic phase is apparent at 120 K. At 10 K the splitting is not resolved because of sample broadening; however, a visual comparison with the equivalent reflection in the tetra- gonal phase, at 290 K, demonstrates that a small orthorhombic distortion is still present.

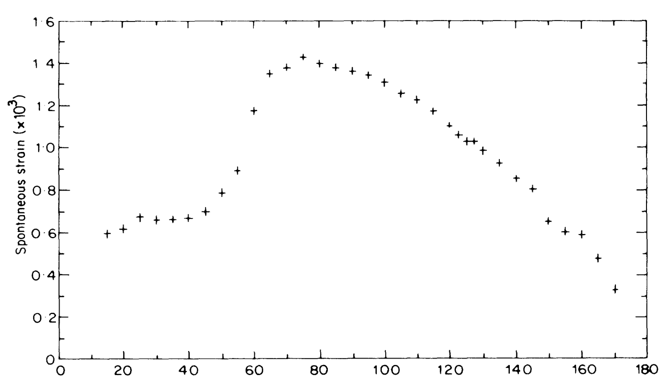

FIG. 3. The temperature dependence of the orthorhombic splitting, defined as spontaneous strain, for $La_{1.85}Ba_{0.15}CuO_4$

enhanced by the presence of the barium "impurity" atoms on the lanthanum sites.

It is of interest to speculate on the correlation apparent between the subtle and anomalous structural features that we observe in the orthorhombic phase and the electrical resistivity.

The dc electrical resistivity of our barium-doped sample, measured by a standard four-terminal method, is similar in form to that published by other groups. The gross features are an approximately linear decrease in resistivity from room to liquid-nitrogen temperatures (metallic behavior), followed by a plateau or gentle rise, before the rapid decrease to zero below the superconductivity transition at 35 K (Fig. 1). We note that the anomalous decrease in orthorhombic splitting correlates with the plateau in resistivity and further that the onset of superconductivity at 35 K corresponds to the saturation of this splitting at a very low level.

Full details of the structural refinements discussed in this text will be published in the near future and correlated with our recent measurements of the phonon density of states.

The authors would like to acknowledge the generous support of Professor A. J. Leadbetter, Dr. W. G. Williams, and the staff of the Neutron Division at the Rutherford Appleton Laboratory. The continuing advice and encouragement supplied by Dr. G. G. Lonzarich and Professor B. D. Rainford have considerably contributed to the success of this work. The funding for this project was supplied by the Science and Engineering Research Council.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2]M. L. Cohen and P. W. Anderson, in *Proceedings of the Conference on Superconductivity in d- and f-Band Metals —1972,* edited by D. H. Douglass, AIP Conference Proceedings No. 4 (American Institute of Physics, New York, 1972).

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

[4]Z. X. Zhao, L. Q. Chen, C. G. Cui, Y. Z. Huang, J. X. Liu, G. H. Chen, S. L. Li, S. Q. Guo, and Y. Y. He, Sci. Rev. (China) (to be published).

[5]Von B. Grande, H. k. Müller-Buschbaum, and M. Schweizer, Z. Anorg. Allg. Chem. **428**, 120 (1977).

[6]J. M. Longo and P. M. Raccah, J. Solid State Chem. **6**, 529 (1973).