

Structural instability in single crystals of the high- T_c superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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Single crystals of superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x \sim 0.08$) have been investigated in the temperature range 15–298 K and are found to undergo a structural phase transition below room temperature, but above 180 K. Detailed analysis of the diffraction-peak profiles obtained below the transition temperature indicates a breakup of the macroscopic crystals into multiple domains of different orientations. Several cooling and warming cycles always reverse the samples into one-domain crystals at room temperature. Complicated peak profiles prevent the determination of the exact symmetry and structure below the phase transition.

INTRODUCTION

The mixed oxides $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ ($A = \text{Ba}, \text{Sr}$, $x < 0.3$, y unknown but presumed small) have recently been observed to be superconducting with record high-transition temperatures (T_c). The original report¹ noted T_c values around 30 K in a multiphase system with $A = \text{Ba}$. The superconducting component was identified to be the double perovskite phase $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ ($x \sim 0.15$).^{2,3} Depending on the exact composition, purity, and sample history, transition temperatures of 40.2 (Ref. 4) to 52.5 K (Ref. 5) (under applied pressure of ca. 12 kbar), and even 70 K under metastable conditions,⁶ have been reported. The strontium doped derivative has T_c 's of 36 to 40 K.^{7,8} We have recently published the single crystal structure of superconducting ($T_c \sim 8.5$ –9 K) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x \sim 0.08$) at room temperature by means of x-ray diffraction.⁹ In this paper we report single crystal x-ray diffraction results obtained at temperatures down to 15 K, where we establish the existence of a low-symmetry crystalline phase.

EXPERIMENTAL PROCEDURES

$\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ was prepared by carbonate-hydroxide co-precipitation and subsequent firing as described earlier.⁹ The strontium content of this raw material was verified by chemical analysis. Small black crystals in the shape of square platelets (the normal to the plane of the plate was later found to be parallel to the crystallographic c axis) were grown by a high-temperature flux method.⁹ Since insufficient crystalline material for chemical analysis was available, the strontium content of the resulting crystals was estimated by use of the correlation of room-temperature lattice constants with the strontium doping level.¹⁰ The ratio c/a appears to be a particularly reliable indicator because it is independent of systematic instrument errors. In agreement with our observations, Kanbe *et al.*¹⁰ observe a monotonic increase of $c/a = 3.45$ at $x = 0.0$ to 3.515 at $x = 0.23$, followed by a constant value of ca. 3.515 at higher doping levels. Our samples were found to have $c/a = 3.47$, or $x \sim 0.08$, thus much

smaller than expected from the amount of strontium introduced during the crystal growth, but sufficient to produce the superconducting tetragonal phase with T_c (~ 8.5 –9 K) in agreement with the c/a vs T_c correlation.¹⁰

The x-ray diffraction experiments were carried out on several four-circle diffractometers, depending on the desired sample temperature. The majority of the results were obtained on a Syntex P2₁ instrument equipped with a cold nitrogen-gas flow cooling system for the temperature range 95–176 K, as well as for room-temperature measurements. The temperature measurement was estimated to be accurate to within 2 K at temperatures below ca. 130 K. At higher temperatures the nitrogen flow rate was insufficient to maintain laminar flow in the sample region, resulting in increasingly larger uncertainties with higher temperatures. The temperature range between ca. 180 and 295 K was inaccessible with this apparatus. Further room-temperature measurements were carried out on a Nicolet P3/F diffractometer. The experiments at 15 K were carried out on a Huber four-circle goniostat, which has an Air Products Displex[®] closed-cycle helium refrigerator, capable of rotating about the ϕ axis, mounted on the χ circle. All diffractometers were equipped with molybdenum x-ray tubes and incident-beam graphite monochromators ($\text{Mo } K\alpha$, $\lambda = 0.71073 \text{ \AA}$). Lattice constants and crystal orientation were obtained through a least-squares procedure from the carefully centered setting angles of 10–30 reflections, with Bragg angles $20^\circ < 2\theta < 35^\circ$ whenever the temperature was changed. The standard deviations of the lattice parameters are those obtained from the least-squares procedure. All scans shown in this article were recorded with the receiving slits closed to less than $\frac{1}{2}^\circ$.

Three separate crystals were investigated. Sample A is the same crystal whose room-temperature structure we have reported previously.⁹ It was mounted with the ϕ -rotation axis perpendicular to the b crystal axis, and tilted ca. 7° away from the a axis to avoid multiple diffraction effects. Crystal B was similarly mounted, but with the ϕ axis near the ab plane, and with larger tilting (ca. 20°). Crystal C was mounted with the tetragonal c axis parallel to ϕ in order to examine peak profiles along directions of reciprocal space different from samples A and B.

RESULTS

At room temperature, all crystals were observed to be tetragonal (space group $I4/mmm$) with a small variation of the lattice constants: $a=3.7966(7)$, $3.8067(6)$, $3.7987(7)$ Å, $c=13.186(4)$, $13.208(3)$, $13.213(7)$ Å, $V=190.1(1)$, $191.4(1)$, $190.7(1)$ Å³, and $c/a=3.473(1)$, $3.470(1)$, and $3.478(2)$ for the three crystals, A, B, and C, respectively. The lattice constants of crystal B at various temperatures are shown in Fig. 1. The in-plane lengths a and b , as well as the out-of-plane angles α and β , show no significant deviations from their corresponding room-temperature values. However, c shows a marked reduction of 0.30% upon cooling to 95 K. The data point at 176 K suggests, although not with high certainty due to the estimated error margin, that this decrease may not be smooth in nature, and that there may be a temperature region with an abrupt drop of the c lattice parameter. The in-plane angle γ shows significant and reproducible deviations from 90° below at least 150 K. Since the tetragonal crystal system requires all cell angles to be 90°, a change of γ must be accompanied by a decrease in crystal symmetry. However, the deviation of γ from 90° does not necessarily imply monoclinic symmetry, since the ab diagonals, due to the equal lengths of a and b , still intersect at right angles. Furthermore, the peak centering procedure is only reliable on single, symmetrical peaks which, as described below, is not the case at temperatures far below room temperature and, therefore, the lattice constants presented

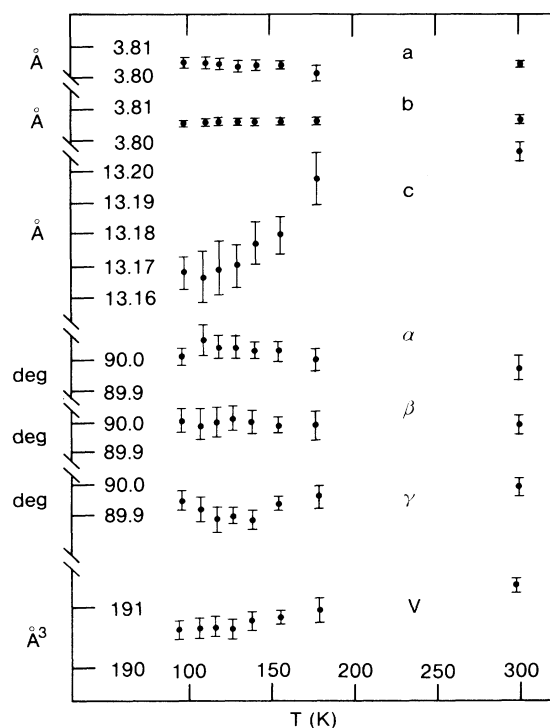


FIG. 1. Variation of lattice parameters in single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x \sim 0.08$) with temperature. The parameters at low temperatures are inaccurate due to the composite peak profiles which prohibit exact peak centering.

in Fig. 1 may not reflect the true values at low temperature.

We have examined the peak profiles upon rocking of the sample through a 2° range about the most sensitive diffractometer angle (ω axis) for a large number of Bragg peaks of crystal B at seven temperatures in the range 95 to 176 K, and at room temperature. From the sample mount, the rocking about ω (at constant scattering angle θ) covers reciprocal space along a direction perpendicular to the scattering vector in the b^*c^* plane for reflections near zero χ angle, i.e., reflections near the $0kl$ zone, and more general directions otherwise.

We found that some peaks showed no change in shape, others developed shoulders, and approximately one-half are clearly split into multiple parts. Typical examples of the latter are shown in Fig. 2. Reflection $(-3,0,3)$ is an example of a peak splitting into at least three unequal components, whereas $(-2,1,-3)$ exhibits a symmetrical doublet. There was no systematic pattern as to which reflections were split at low temperatures. Furthermore, a similar ω -scan data collection at 103 K on sample C (with the c axis along the diffractometer ϕ axis) showed in some instances splittings where crystal B did not, and vice versa, in addition to reflections with multiple components in both samples. Up to four components could be distinguished in some scans from crystal C [for reflections $(-1,0,3)$, $(0,0,4)$, and $(1,0,3)$]. The onset of the change in peak shape was above the highest cryogenic temperature investigated.

Sample C was mounted ideally for rotation about the diffraction vector for $(0,0,l)$ Bragg peaks ($\chi = -89.67^\circ$ at 101 K, -89.71° at 295 K). We have measured ω scans at every 10° rotation about the c^* reciprocal axis for the $(0,0,6)$ reflection at 295 and 101 K. These scans cover a circular area on the surface of a sphere in reciprocal space whose radius is given by the Bragg angle, perpendicular to the c^* axis. Neglecting the slight deviations of the unit cell angles from 90° at low temperatures and the curvature of the sphere within the section formed by the 2° rocking range (0.056 sterad solid angle), these scans probe reciprocal space in the a^*b^* plane at $l=6$. Surface plots of the intensity within this plane, at room temperature and at 101 K, are shown in Fig. 3. At room

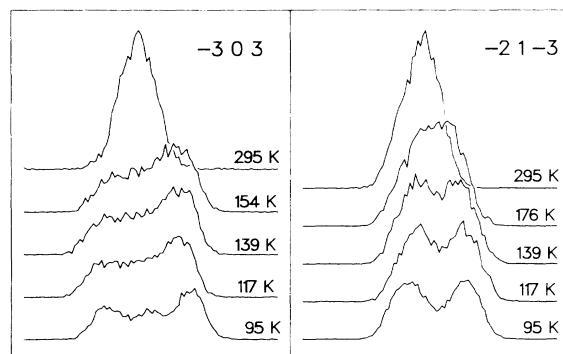


FIG. 2. Intensity profiles along the rocking angle (diffractometer ω axis) of two representative Bragg reflections at various temperatures. The scans are 2° wide.

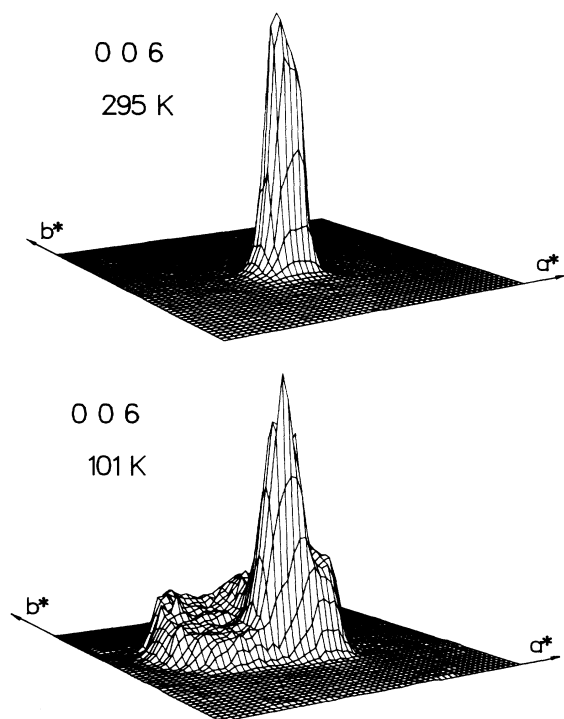


FIG. 3. Intensity distribution of the (0,0,6) Bragg reflection of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ within a cross section parallel to the a^*b^* plane at 295 and 101 K. The total width of the graph corresponds to 2° angular spread, or $0.060a^*$. The intensities of the two plots are not on the same scale.

temperature, only one narrow, symmetrical peak is observed. At 101 K, the diffracted intensity is spread over a larger area. It is dominated by a large peak which is surrounded on three sides by at least three side peaks and an extended plateau area. It should be noted that upon warming to room temperature, the crystals again yield sharp, single Bragg peaks. In fact, the 295-K data of Fig. 3 were measured after the 101-K data, and the scans of Fig. 2 were obtained during several cooling cycles, with reproducible results.

DISCUSSION

At room temperature, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x \sim 0.08$) possesses a well-defined tetragonal structure. However, at a transition temperature above 180 K, which may well depend on the strontium doping level x , the Bragg peaks start to broaden and eventually split into multiple components as the temperature is reduced. There are no special crystallographic zones which do not show peak splitting, which leads us to the conclusion that the crystals break up into domains of slightly different orientation upon going through a *symmetry-lowering* phase transition. At 103 K, an intensity data set collected in the unit cell setting (at room temperature) of orthorhombic La_2CuO_4 (Ref. 11) ($a_o = a_t + b_t$, $b_o = -a_t + b_t$, $c_o = c_t$, where subscripts o and t denote the orthorhombic and tetragonal cells, respectively), without any crystallograph-

ic centering restrictions, showed no indication of Bragg peaks which did not originate from the original I -centered tetragonal cell. The phase transition thus either preserves the size of the room-temperature reduced cell, or the changes in atomic positions are so small as to give only very small structure factor amplitudes for the reflections originating from a possible large supercell. At 15 K, where the same general features are observed as described above, except for more pronounced peak splittings, very faint reflections at a few "forbidden" locations appear most notably in the $\{0,2,1\}$ class.

Recently, $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{4-y}$ have been studied by means of neutron¹² and synchrotron x-ray¹³ powder diffraction, respectively. The former was found to undergo a distortion to orthorhombic symmetry (with the same space group as La_2CuO_4 at room temperature¹¹) near 200 K,¹² whereas the latter has a phase transition near 150 K, leading to monoclinic symmetry.¹³ We have calculated x-ray diffraction intensities based on the structural parameters of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ at 60 K, as given by Cava, Santoro, Johnson, and Rhodes,¹² and found that the intensity of the strongest peak not attributable to the room-temperature unit cell is only 0.4% of the overall strongest peak. Therefore, we would not expect to observe such a superstructure within the limits of an acceptable signal-to-noise ratio by means of x-ray diffraction.

Clearly, the transition temperature in $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ is above 176 K, in a region which is inaccessible with our current cooling equipment. A rough estimate of the transition temperature may be made from the linear extrapolation of the peak splittings towards zero. For the $(-2,1,-3)$ reflection (Fig. 2) the decrease in the splitting leads to a zero intercept at about 207 K. However, this number is only an estimate (a) due to the inaccurate thermometry at the high end of the cooled temperature range, and (b) because the splitting may vary in a non-linear fashion near the phase-transition temperature.

As to the detailed crystal structure of the low-temperature modification of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, its determination is not practical from the large, multidomain crystals which form below the phase transition because (i) the complicated reflection profiles render the accurate peak centering and thus the determination of reliable lattice constants, as well as the metric symmetry of the unit cell, impossible; and (ii) symmetry lowering, especially if the atomic displacements are small, will most likely lead to some kind of internal twinning, in addition to the breakup into domains as described above. Therefore, the intensity distribution of the diffraction pattern may show more symmetry than that of a true single crystal, further complicating the structure determination, and (iii) if the low-temperature modification involves the formation of a supercell, as suggested by our 15-K experiments and the neutron-diffraction results,¹² the intensities of the extra reflections will be extremely weak at best, and the superstructure difficult to determine.

In summary, single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ undergo a symmetry-lowering phase transition below room temperature, but above 180 K. The diffraction patterns of the low-temperature phase are typical of multiple domains

with no discernible twinning law. It is, at present, not possible to determine the structure of the low-temperature modification from these multiple domain crystals.

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