Evidence for monoclinic distortion in the ground state phase of underdoped $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$: A single crystal neutron diffraction study

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The existing controversy about the symmetry of the crystal structure of the ground state of the critical doped $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ has been resolved by analyzing the single crystal neutron diffraction data collected between 5 and 730 K. We observed small but significant intensities for “forbidden” reflections given by extinction rules of the orthorhombic Bmab space group at low temperatures. A careful investigation of neutron diffraction data reveals that the crystal structure of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ at 5 K is monoclinic with B2/m (2/m 1 1) space group. The monoclinic structure emerges from the orthorhombic structure in a continuous way; however, the structure is stable below ~ 120 K which agrees with other observed phenomena. Our results on symmetry changes are crucial for the interpretation of physical properties also in other high temperature superconductors with similar structures. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4944797>]

I. INTRODUCTION

Since the initial discovery of high temperature (high- T_C) superconductivity in the 214-family of cuprates, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) has got enormous attention and has been a topic of great current interest in condensed matter physics.^{1–3} The mother compound of this family, La_2CuO_4 (LCO), is a heterostructure at the atomic level made of stacks of CuO_2 planes separated by La_2O_2 block layers.⁴ Undoped LCO is a Mott insulator which exhibits a three dimensional (commensurate) antiferromagnetic (AFM) ground state with a Néel temperature (T_N) ~ 325 K.^{4,5} Notably, the AFM ground state of LCO is less sensitive to the presence of doped mobile electrons and is comparatively more sensitive to the presence of doped mobile holes.⁶ For hole doping, relevant to Sr-doping in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the long-range ordered AFM ground state is replaced by a short-range ordered spin-glass state for a strontium (Sr) doping of $x \gtrsim 0.02$.^{7–9} Upon further introduction of holes, a superconducting ground state is achieved with a hole concentration of $x > 0.055$.^{10,11} Upon further increasing doping concentration of Sr (x), T_C of LSCO increases with an optimum peak value in the x versus T_C phase diagram of LSCO for $x \sim 0.17$.^{12–14} In the underdoped regime where the charge carrier (holes/electrons) concentration is lower than the optimum value, several competing phenomena and coexistence of order parameters, such as incommensurate spin and charge stripe ordering,^{15,16} circulating orbital currents,^{17–19} and recently, charge density

wave order,²⁰ have been reported. For the critical doping $x = 0.05$, data on these competing phenomena are scarce. Xu *et al.*²¹ reported the observation of vortex like excitations around 150 K and correlated those to the temperature (T^*) where the pseudogap opens. The occurrence of these excitations also coincides with a minimum in the electrical resistivity.²²

The crystallographic structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, for Sr doping concentration up to $x \sim 0.20$, has been extensively studied by X-ray and neutron diffraction studies.^{4–7} Two modifications are known to exist: the high-temperature tetragonal (HTT) phase (space group $I4/mmm$) and the low temperature orthorhombic (LTO) phase (space group Bmab). In the latter, the CuO_6 octahedra are tilted around [100] resulting in a buckling pattern of the CuO_2 plane. However, the nature of the structural phase transition from HTT to LTO has been an unsettled issue. The existing literature suggests the possibility of (i) first order²³ or second order²⁴ and (ii) displacive^{23,25–27} or order-disorder^{28–31} phase transition. The transition temperature ($T_S \sim 533$ K for $x = 0$) of LSCO from HTT to LTO strongly depends on doping and decreases with increasing x .⁴ Despite of the vast amounts of structural studies on LCO and LSCO using various diffraction techniques, there is unanimity in the literature about the structure of the LTO phase. Furthermore, there have been indications that another structural transition occurs at low temperature. The finding of a symmetry lowering structural transition would present a new angle in the interpretation of the various phenomena observed. The question about the low temperature structure of LCO was first raised by Kasowski, Hsu, and Herman (1987)³² on the basis of first principle pseudopotential band calculations and group theoretical analysis. They have suggested that the conduction and valence bands of

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orthorhombic phase (Bmab) of La_2CuO_4 cannot have a gap and therefore La_2CuO_4 would remain metallic at all temperatures. However, the electrical resistivity measurement on LCO at low temperatures reveals a sharp transition from metallic to a semiconducting behavior below 30 K.³³ In order to explain this phenomenon, they have proposed another structural transition from LTO to a most likely monoclinic phase in B2/m space group around this temperature.³² In a low temperature x-ray powder diffraction study, Skelton *et al.*³³ found a structural phase transition to a lower monoclinic symmetry in the temperature range of 15–30 K with significant change in the diffraction pattern. However, other low-temperature structural investigations of this material have not seen such a transition.^{34–36} A recent neutron diffraction study on an untwinned LCO and partially twinned LSCO ($x = 0.01, 0.03$) single crystals³⁷ has reported a monoclinic distortion in all investigated compounds. For the undoped LCO, they proposed a non-centrosymmetric space group Bm (B m 1 1), whereas their refinement used some highly correlated parameters. It was mentioned further that evidence for a monoclinic distortion has been found also for the Sr-doped samples ($x = 0.01, 0.03$), although no refinement data are provided. The reported monoclinic distortion is so small that it cannot be detected in high resolution x-ray diffraction. The existence of such a small monoclinic distortion would have major impact on the discussion of the various electronic phenomena observed in LSCO. It could, for instance, be seen as evidence for the predicted Jahn-Teller polaron formation.³⁸ Here, the focus had been on the LSCO compound with the critical doping of $x = 0.05$, on the border between insulator and superconductor.

In this paper, we seek to resolve the existing controversies regarding the crystal structure of the ground state phase of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ by analyzing the single crystal neutron diffraction data at low temperature (5 K) and comparing them with the results obtained at room temperature and 730 K. We present unambiguous experimental evidence for the monoclinic distortion (with space group B2/m) in $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ at low temperatures. We show that the monoclinic structure emerges continuously from the orthorhombic structure and becomes stable around 120 K. The observed transition is correlated with the phenomenon of formation of Jahn-Teller polarons reported in the literature using temperature dependent specific heat and dc magnetic susceptibility measurements. In addition, the nature of phase transition from the HTT to the LTO phase in $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ is analyzed.

II. EXPERIMENTAL

A high quality single crystal of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ has been grown from high purity starting reactants of Aldrich chemicals La_2O_3 , SrCO_3 , and CuO with a minimum purity of 99.99%, 99.99%, and 99.98%, respectively, using the travelling-solvent floating zone technique, achieved with an optical mirror furnace. The details of the sample preparation are described in the supplementary material.³⁹ This technique allowed us to grow a large crystal of several centimeters length under accurately well-regulated stable conditions, e.g., flux composition, temperature, and oxygen partial vapor pressure, which are

essential for the growth of homogeneous crystals. In order to check the phase purity, a piece of as-grown $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.05$) single crystal has been finely crushed into powder and X-ray diffraction measurement was carried out using D8 X-ray diffractometer (LDM@ Paul Scherrer Institute (PSI)) operating in the Bragg- Brentano geometry. The data were collected in the 2Θ range of $10^\circ < 2\Theta < 120^\circ$ with a step size of 0.00916° . We used X-rays emitted from Cu target ($K_{\alpha 1} = 1.54056(2) \text{ \AA}$ and $K_{\alpha 2} = 1.54439(2) \text{ \AA}$ with intensity ratio of 0.5). LeBail fit was performed⁴⁰ on collected powder diffraction data to confirm the phase purity of as-grown single crystals. All reflections of experimental data can be refined with a single orthorhombic phase of Bmab space group. The obtained unit cell parameters are “a” = $5.3518(8) \text{ \AA}$, “b” = $3.3824(8) \text{ \AA}$, and “c” = $13.183(1) \text{ \AA}$, in a good agreement with those reported in literature.^{41,42} The profile matching between observed and calculated data obtained after LeBail fit is shown in Fig. 1.

Single crystal neutron diffraction experiments were carried out on the thermal-neutron four-circle diffractometer TriCS⁴³ at SINQ, PSI, Switzerland. The measured single crystal has dimensions of $3.5 \times 4 \times 3.5 \text{ mm}^3$. For temperatures between 5 K and room temperature, the sample was mounted in a closed cycle refrigerator inside a small aluminum (Al) can filled with helium exchange gas, allowing it to reach a base temperature of 4.5 K while not being exposed to vacuum. The following high temperature measurements up to 750 K were carried out using a small furnace where the sample is directly connected to the heating element. An additional heat shield is also connected to the heater to ensure a uniform temperature on the sample position. A Ge_{311} -monochromator was chosen to produce a monochromatic neutron beam with a wavelength (λ) of $1.1767(1) \text{ \AA}$ (higher harmonics contamination: $\lambda/2 < 0.005\%$, $\lambda/3 < 0.03\%$). The diffracted reflections have been collected with a non-position sensitive ^3He detector tube up to $2\Theta = 115^\circ$ ($\sin \Theta/\lambda = 715 \text{ \AA}^{-1}$). The crystal was aligned with the c-axis vertically (max deviation: $\pm 1.6^\circ$) to allow ω -scans collecting the satellites from both twins. Refinements of single crystal neutron diffraction data were carried out using JANA2006 program package.⁴⁴ For the

FIG. 1. Observed (solid circles), calculated (solid line), and difference (bottom line) patterns obtained from the LeBail analysis of the room temperature x-ray powder diffraction data of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ using Bmab space group. The vertical tick marks above the difference pattern stand for the Bragg peak positions.

extinction correction, isotropic type-I Zacharias formalism with a Lorentzian mosaic distribution has been applied to all the refinements by using the exact shape of the crystal⁴⁵ in relation to the incoming and scattered beams. Neutron scattering lengths of $b_{\text{La}} = 8.240$ fm, $b_{\text{Sr}} = 7.020$ fm, $b_{\text{Cu}} = 7.718$ fm, and $b_{\text{O}} = 5.803$ fm were used⁴⁶ in the refinements.

Heat capacity measurements of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ were carried out on a single crystal of 8.97 mg using a Physical Property Measurement System (PPMS[®]) from Quantum Design and have been corrected by a reference measurement. The dc magnetic susceptibility ($\chi \approx M/H$) was calculated from the magnetization (M) of a 55.40 mg sample measured in a 1000 Oe magnetic field (H), using a Magnetic Property Measurement System (MPMS[®]) from Quantum Design.

III. RESULTS AND DISCUSSION

A. Room temperature crystal structure study

We first investigated the crystalline quality including possible twinning for $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$. For this, we present a qualitative interpretation of single crystal neutron diffraction profiles for characteristic reflections such as $0h0$, $00h$, $hh0$, $h\bar{h}0$, $\bar{h}h0$, and $\bar{h}\bar{h}0$. Fig. 2 depicts the transverse scan (ω -scan about the c -axis) for the 020 , 002 , 220 , $2\bar{2}0$, $\bar{2}20$, and $2\bar{2}0$ reflections. The sharp profiles of all the reflections indicate a homogenous stoichiometry all over the crystal, as any inhomogeneity is supposed to result in a significant profile broadening. The full width at half maximum (FWHM) for all the reflections is within or close to the respective instrumental resolution. It is evident from this figure that the

FIG. 2. Profiles (ω -scan) of the selected reflections of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ obtained by single crystal neutron diffraction at room temperature.

reflections 220 and $\bar{2}20$ are singlets, whereas reflections $2\bar{2}0$ and 220 clearly split into two peaks with intensity ratio of $\sim 48(2)/52(2)$ as consequence of the twinning along $\langle 110 \rangle$. The schematic representation of twinning with two domain states is shown in Fig. 3. The reflection 020 is also doublet but the splitting is less due to partial overlapping of the two reflections. These observations reveal that the crystal is twinned and has two domain states sharing a common $(1\bar{1}0)$ plane which results in the angular separations of “ Δ ” between $h00$ and $0h0$ reflections and 2Δ for $h\bar{h}0$ reflections with $\Delta = \arctan(a/b) - \arctan(b/a)$, where “ a ” and “ b ” are the orthorhombic unit cell parameters. Reflections 002 and $00\bar{2}$ are singlets because they are not sensitive to this twinning. The angular separation between the peaks of different reflections, namely, 2Δ for $h\bar{h}0$ independent of Miller indices and wavelength, is proportional to orthorhombicity and can be directly calculated from the unit cell parameters “ a ” and “ b ” using above relations. The angular separation for reflection 020 is nearly half of the angular separation for reflection 220 , which are $0.29(1)$ and $0.54(1)$, respectively, as can be seen from Fig. 2.

For the room temperature investigation of the crystal structure of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$, a data set with a total number of 712 reflections has been collected with hkl values in range $-6 \leq h \leq 6$, $-3 \leq k \leq 7$, and $-4 \leq l \leq 17$. Structural refinements were carried using the orthorhombic Bmab ($B2/m$ $2_1/a$ $2/b$) space group. Except for the occupancy parameters of the La/Sr atoms, which were fixed at the nominal composition, all other parameters, such as the scale factor, positional coordinates, isotropic extinction parameter, twin fractions, and anisotropic thermal displacement parameters (ADP’s), were varied in the course of the refinement. For the absorption correction in the refinement, we have used a calculated absorption coefficient $\mu = 0.0147 \text{ mm}^{-1}$. The extinction correction parameter (g) which is related to the mosaic distribution resulted in the refinement to be $g = 178(3) \text{ rad}^{-1}$. The volume fractions of the two twins obtained from the refinement are $48(2)$ and $52(2)$. This is in excellent agreement with the value $(46(2)/54(2))$ obtained from the ratio of integrated intensities of the splitted $\bar{2}20$ reflection. The fit between observed (F_{obs}) and calculated (F_{cal}) structure factors is distinguished as shown by the ratio of

FIG. 3. Schematic representation of the reciprocal lattice for stoichiometric twinned $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ crystal with two possible domain states in the orthorhombic phase. The two domain states share a common (-110) plane which results in an angular splitting Δ between $h00$ and $0h0$ reflections and 2Δ in $h\bar{h}0$ reflection.

$F_{\text{obs}}/F_{\text{cal}}$ shown in Fig. 4. The crystal structure of LSCO at room temperature is illustrated in Fig. 5 and detailed results of the refinement are listed in Table S1 of supplementary material.³⁹ The occupancies of all the atoms in the asymmetric unit obtained after the refinement are close to the stoichiometric ratio of the composition $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$. The ADP's were considered during the refinements for all the atoms in asymmetric unit. The structural parameters of LSCO for $x = 0.05$ at room temperature are comparable to the structural parameters reported for the orthorhombic phase of LCO near room temperature.³⁷ The ADP's of oxygen in LSCO are considerably high at room temperature which may be a signature of local oxygen disorder as a consequence of additional octahedral distortion present at room temperature. Alternatively, the high ADP values can be interpreted as the formation of dynamic Jahn-Teller polarons.³⁸ The additional tilting of oxygen octahedral may stabilize (or become significant) at low temperature which results otherwise in a change of the crystal structure from Bmab to another lower symmetry phase.

B. Low temperature study

1. Evidence for ground state monoclinic phase

In order to determine the crystallographic ground state of LSCO for $x = 0.05$, we measured a data set with a total number of 2756 reflections ($-7 \leq h \leq 7$, $-7 \leq k \leq 7$, and $-10 \leq l \leq 15$) at 5 K, including 843 reflections which are forbidden in the Bmab space group. A careful examination of these “forbidden” reflections suggests that the intensities of some reflections are considerably higher than the background intensity (see Fig. 6 for reflections 309, 450, and 070) but much lower in comparison to the reflections allowed in Bmab space group. This indicates that the structure of LSCO at 5 K is marginally deviated from the orthorhombic Bmab space group. The peak shape of these reflections is well defined and FWHM is comparable to the instrumental broadening, which suggests that these reflections are not spurious but characteristic features of the low temperature phase of LSCO ($x = 0.05$). The observations of significant intensities for these “forbidden” reflections reveal that the ground state

FIG. 4. Ratio of observed (F_{obs}) and calculated (F_{cal}) structure factor obtained from refinement of single crystal neutron diffraction data of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ at room temperature.

FIG. 5. Crystal structure of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ at room temperature. Schematic views of thermal vibrations of atoms are plotted as thermal ellipsoid (90% probability).

phase of LSCO ($x = 0.05$) belongs to a lower symmetry with respect to room temperature Bmab phase. These reflections are restricted by the condition $h + l = 2n$, which suggests that the ground state phase of LSCO is a B-centered lattice.

We assume that the structural distortion has to obey a group/subgroup related ordering as laid-out below. The Jana 2006 package has been used to perform a group analysis. The maximal non-isomorphic subgroups of Bmab are B2ab (B 2 a b), B2am (B 2 a m), Bb21m (B b 2₁ m), B2212 (B 2 2₁ 2), B2/b (B 2/b 1 1), P2₁/c (P 2₁/c 1 1), and B2/m (B 2/m 1 1). However, in addition to the condition $h + l = 2n$, reflections are systematically present for $h k 0$ with $h = \text{even}$, $k = \text{odd}$, $0 k 0$ with $k = \text{odd}$, and $h 0 l$ with $h, l = \text{odd}$. These conditions suggest that there is loss of both “a” and “b” glide planes in the ground state phase of LSCO. This implies that the translation symmetry of the atoms along the “a” and “b” axes is no longer necessarily $t = a/2$ and $t = b/2$. Following these conditions of reflections, we can conclude that the possible ground state of LSCO ($x = 0.05$) is most likely monoclinic in the B2/m space group.

Following these preliminary considerations, we carried out a full refinement of our single crystal neutron diffraction data set using both, Bmab and B2/m space group. For a comparison, the structural parameters and agreement R-factors obtained are listed in Table I. Despite of rejecting 159 reflections due to systematic extinction conditions in Bmab, the reliability factors for Bmab (g.o.f. = 4.47, $R_F = 5.75\%$, $wR_F = 7.31\%$) are

FIG. 6. Profiles (ω -scans) of the selected reflections of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ obtained by single crystal neutron diffraction at 5 K.

significantly higher than the reliability factors ($\text{g.o.f.} = 3.26$, $R_F = 4.41\%$, $\text{w}R_F = 5.42\%$) for B2/m. This model also fails to explain the intensities of the “forbidden” reflections. Therefore, out of the two models described above, the intensities observed for the “forbidden” reflections can be explained B2/m space group for which agreement factors are also lower. Table II lists the observed and calculated structure factors of selected reflections which are forbidden by extinction rules in the Bmab space group, obtained after the structural refinement of neutron diffraction data using B2/m space group. The values of F_{obs} and F_{cal} is in good agreement for all reflections. Thus, we conclude that the B2/m model not only gives a better satisfactory fit for the observed intensities but also fully explains all of them. To be more confident, we further checked the reflections which are forbidden by the extinction conditions of B2/m space group symmetry. The observed intensities for these reflections are almost in the background level and can be ignored without any further consideration (see Fig. 6(d) for reflection 0 0 11). Our results are in agreement with the finding of Reehuis *et al.*³⁷ in terms of the existence of monoclinic distortion in LCO and lightly doped LSCO. Our refinement yields a “monoclinic” angle of 90° and no evidence of line broadening or even for the splitting of reflections was found. Considering the small intensities of the observed “forbidden” reflections (0.4% of the

normal reflections), it is hard to detect such a small monoclinic distortion directly from any powder diffraction method.

2. Temperature dependent study

In order to determine the critical temperature of the monoclinic distortion, the strongest “forbidden” reflection, 309, was measured as a function of temperature with very high statistics. The results are plotted in Fig. 7 along the temperature dependence of an allowed reflection 400. To compare these reflections, they have been normalized to their respective intensity at base temperature. For the 309 reflection, two different regimes can be distinguished. First, the intensity increases with decreasing temperature starting from room temperature. In fact, a small peak is still observed at room temperature, yet only visible in a high statistic experiment. The increase on intensity is approximately linear down to 110 K from where the intensity increases at a much smaller rate or stays nearly constant. This can be understood as a sort of lock-in transition at which the ground state of the crystallographic structure is achieved. Hysteretic behavior is observed between 110 K and room temperature and while the structural transition seems to be continuous the observation of temperature hysteresis indicates a first order transition, thus justifying the assumption of a group/subgroup related ordering. To relate the observed transition to the various reported phenomena in the literature, additional measurements of the specific heat and the magnetic susceptibility were performed using single crystals from the same growth. The specific heat measured from 2 K to room temperature and its derivative are shown in Fig. 8. The specific heat itself seems featureless over the whole temperature range; however, its derivative shows a broad hump centered around 20 K. No additional anomaly is observed around 110 K. In the magnetic susceptibility, as shown in Fig. 9, two points can be identified. First, as shown in the inset, the slope of the inverse susceptibility changes around 20 K. We presume that weak anomalies observed in specific heat and magnetic susceptibility around 20 K are most likely due to the formation of the spin-glass clustering as reported in this system.^{7–9} Second, the magnetic susceptibility is nearly constant at temperatures above 150 K which can be interpreted as a term of the Pauli-paramagnetism, where the only contribution to the susceptibility stems from the conduction electrons. Below this temperature, an additional response from the magnetic moment of the Cu-ions is observable. A possible interpretation might be that at high temperatures the electronic ground state of the Cu-ions is degenerated. Approaching towards lower temperatures, a lattice distortion becomes favorable: A phenomenon which is widely known as Jahn-Teller effect. Here, we follow the interpretation of Keller *et al.*³⁸ who predicted the occurrence of a Jahn-Teller distortion in LSCO and presented a model of the formation of Jahn-Teller polarons, which could be the explanation of observed electronic properties including superconductivity.

C. High temperature phase transition study

For studying the phase transition behaviour of LSCO above the room temperature, we examined the 220 and $\bar{2}20$

TABLE I. Refined structural parameters for $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ at 5 K as obtained from the analysis of neutron diffraction data using Bmab and B2/m (B 2/m 1 1) space groups.

Atom	WS	Occ	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}
Bmab: $a = 5.3799 \text{ \AA}$, $b = 5.3799 \text{ \AA}$, $c = 13.1756 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $R_F (\%) = 5.75$, $wR_F (\%) = 7.31$, $g.o.f = 4.47$												
La	8f	0.975	0	-0.00746(8)	0.36094(5)	0.34(4)	0.34(4)	0.27(4)	0	0	-0.03(1)	0.32(2)
Sr	8f	0.025	0	-0.00746(8)	0.36094(5)	0.34(4)	0.34(4)	0.27(4)	0	0	-0.03(1)	0.32(2)
Cu	4a	1.032(6)	0	0	0	...	...	...	...	...	...	0.29(2)
O1	8e	0.998(7)	$1/4$	$1/4$	-0.00780(2)	0.08(6)	0.80(7)	0.62(5)	-0.18(2)	0	0	0.50(3)
O2	8f	1.024(8)	0	0.0375(2)	0.18343(7)	0.71(5)	1.19(4)	1.08(6)	0	0	0.07(3)	0.99(7)
B2/m: $a = 5.3799 \text{ \AA}$, $b = 5.3799 \text{ \AA}$, $c = 13.1756 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $R_F (\%) = 4.41$, $wR_F (\%) = 5.42$, $g.o.f = 3.26$												
La1	4i	0.975	0	0.0010(3)	0.3613(1)	0.81(6)	0.81(6)	0.74(5)	0	0	0.15(3)	0.79(3)
Sr1	4i	0.025	0	0.0010(3)	0.3613(1)	0.81(6)	0.81(6)	0.74(5)	0	0	0.15(3)	0.79(3)
La2	4i	0.975	0	0.5126(3)	0.1392(1)	...	...	...	...	...	...	0.17(2)
Sr2	4i	0.025	0	0.5126(3)	0.1392(1)	...	...	...	...	...	...	0.17(2)
Cu1	2a	1.01(1)	0	0	0	...	...	...	...	...	...	0.17(5)
Cu2	2d	1.01(1)	$1/2$	$1/2$	0	0.73(9)	0.6(1)	1.2(1)	0	0	-0.21(5)	0.88(6)
O1	8j	0.994(6)	0.2506(2)	0.2504(3)	0.00766(6)	0.53(6)	0.68(5)	0.82(4)	-0.06(2)	0.22(6)	-0.45(8)	0.67(3)
O2	4i	0.99(1)	0	-0.0444(3)	0.1851(2)	1.38(8)	0.71(5)	1.63(9)	0	0	-0.28(8)	1.24(5)
O3	4i	1.03(1)	0	0.4696(3)	0.3177(2)	0.34(7)	1.33(8)	0.6(1)	0	0	-0.48(6)	0.76(5)

^aAveraged values used in the data collection due to the twinning as shown in Fig. 3.

reflections as function of temperature in the temperature range from 298 to 730 K. Fig. 10 depicts the evolution of $\bar{2}20$ reflections measured by neutron diffraction as a function of temperature in the range between 298 and 650 K while ramping up. As we have discussed, the $\bar{2}20$ reflection is a doublet due to twinning in the orthorhombic phase of LSCO ($x = 0.05$) at room temperature. It is evident from this figure that the splitting of reflection decreases with increasing temperature and vanishes around 375 K. We do not observe any other changes in the profiles of $\bar{2}20$ reflection while ramping up to 730 K. The high temperature tetragonal phase (space group $I4/mmm$) has been confirmed by analyzing a set of neutron diffraction data of 712 reflections collected at 730 K. The refined parameters are shown in Table S2 of the supplementary material.³⁹ In order to get a clear picture about the splitting of the $\bar{2}20$ reflection, a profile deconvolution was attempted as a function of temperature, and the results are shown in Fig. 11. This figure reveals that no phase coexistence region between LTO and HTT phase exists in the whole temperature range. The integrated

intensity (sum of the intensity of two reflections), obtained after the deconvolution of the profile, and the FWHM (obtained by assuming one peak instead of two) are plotted as a function of temperature in Fig. 12. This can be seen by the decrease in the integrated intensity and the FWHM with increasing temperature becomes constant above 375 K. We have confirmed the variation of integrated intensity of $\bar{2}20$ as a function of temperature by plotting the integrated intensity of 220 which is a singlet for the LTO as well the HTT phase. The intensity of the 220 reflection at a given temperature is equal to sum of the intensity of two peaks of the $\bar{2}20$ reflection as can be seen from Fig. 12. A continuous decrease of the FWHM of the $\bar{2}20$ reflection resembles a second order phase transition and might be misleading when experimental probes are used which are sensitive to an orthorhombic splitting as,

TABLE II. Observed and calculated structure factors of the selected reflections at 5 K obtained from the structure refinement in the monoclinic space group (B2/m 1 1). The table lists only the structure of reflections that are systematically absent in orthorhombic space group Bmab.

h k l	F _{obs}	F _{cal}	h k l	F _{obs}	F _{cal}	h k l	F _{obs}	F _{cal}	h k l	F _{obs}	F _{cal}
2 5 0	16.7	16.6	2 3 0	10.1	9.7	3 0 3	12.8	5.3	7 0 7	19.3	21.7
0 7 0	18.7	17.1	6 3 0	10.3	19.5	3 0 7	14.0	6.6	5 0 9	18.6	17.0
4 3 0	14.0	12.3	7 0 5	14.6	10.5	5 0 11	12.7	17.1	5 0 7	21.1	15.7
4 1 0	12.5	10.3	7 0 3	15.0	10.1	5 0 3	18.3	6.6	5 0 1	17.2	2.3
2 1 0	7.2	4.4	7 0 1	10.7	8.7	3 0 5	11.1	3.4	5 0 13	14.5	22.7
2 7 0	12.1	19.7	1 0 1	8.1	1.1	3 0 9	16.6	12.9	3 0 1	13.1	1.4
0 5 0	17.2	18.4	5 0 5	10.3	9.8	3 0 15	14.8	22.5	1 0 9	7.6	11.6
4 5 0	13.3	17.9	1 0 3	6.1	3.2	3 0 13	13.8	14.2	1 0 13	17.4	16.3
6 1 0	12.2	17.6	1 0 7	11.6	2.9	1 0 11	10.2	11.5	3 0 11	12.0	13.8

FIG. 7. Temperature variation of the intensity of the “forbidden” 309 reflection. We plotted for comparison the allowed 400, which is only influenced by thermal displacement factors.

FIG. 8. Heat capacity measurement (red, left scale) and its first derivative (blue, right scale) of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$.

for instance, neutron spectroscopy.²⁴ However, the integrated intensity abruptly drops near T_S (deviation from linear dependence shown by dotted line in Fig. 12). This indicates that the phase transition from LTO to HTT has the characteristic of first order which is in agreement with the recent nuclear magnetic resonance (NMR) studies.²³ A ^{139}La NMR study on an underdoped $\text{La}_{1.97}\text{Sr}_{0.07}\text{CuO}_4$ has shown that the structural order parameter vanishes discontinuously at T_S , which is a first-order like characteristic. Except in the region of phase transition, the structural order parameter indicates second order-like temperature dependence.²³ Our results further prove the absence of phase coexistence region between the LTO and the HTT phase.

IV. CONCLUSIONS

We have investigated the crystal structure of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ using single crystal neutron diffraction in the temperature range of 5 to 730 K. The considerable intensities observed for the reflections forbidden in the orthorhombic Bmab space group at low temperatures suggest that $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ stabilizes in a lower symmetry phase. The refinement of our

FIG. 9. Inverse susceptibility as function of temperature. Above 120 K, the susceptibility is constant and probably only the free electrons contribute (Pauli para). The inset shows the low temperature part, indicating a change in the magnetic properties around 20 K.

FIG. 10. Thermal evolution of the $\bar{2}20$ reflection of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ obtained by single crystal neutron diffraction (ω -scan, TriCS@SINQ) while ramping up.

neutron diffraction data reveals that the low temperature crystallographic structure of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ can be described in the monoclinic space group B2/m which is in agreement with the prediction of first principle calculations and can be interpreted as an evidence of Jahn-Teller polaron formation. From this study, we could identify a critical temperature of 120 K which correlates to the onset of the formation of magnetic moment in the Cu-ions. With the measurement of the 220 reflection, we were able to characterize the HTT to LTO transition occurring at 375 K. The abrupt change of intensity shows this transition to be a first order transition. The development of the twinning and the

FIG. 11. Thermal evolution of observed and deconvoluted profiles (ω -scan) of the $\bar{2}20$ reflection of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ obtained by single crystal neutron diffraction.

FIG. 12. Temperature dependence of integrated intensities of the 220 and $\bar{2}20$ reflections and the FWHM of 220 reflection of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$.

internal strain resembles a second order transition and could be misleading for experimental probes sensitive enough to this. Our data rule out the possibility of a co-existence of the two phases across the HTT to LTO phase transition.

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