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TEMPERATURE DEPENDENT SINGLE CRYSTAL X-RAY DIFFRACTION STUDY
OF THE T* PHASE COMPOUND $(\text{La}_{1.20}\text{Tb}_{0.72}\text{Pb}_{0.08})\text{CuO}_4$

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1. INTRODUCTION

The 2:1:4 cuprate superconductors are known to crystallize with three structures, the K_2NiF_4 -type, the Nd_2CuO_4 -type and the more recently discovered (Nd, Sr, Ce)₂CuO₄-type¹. For brevity they will be referred to as the T, T' and T* phases, respectively. In the T structure the A cations are surrounded by 9 oxygen neighbors forming cuboctahedra in which the top four or bottom four anions have been replaced by one. The B cations are surrounded by apically elongated octahedra. In the T' structure the A' cations are surrounded by 8 oxygen atoms arranged as a square prism, while the B cations are surrounded by four oxygen atoms arranged as a square. Since these squares are the remnants of octahedra, they form corner-sharing layers.

In the T* structure the sequence of (AO) and (BO₂) layers is such that it comprises alternately one half the T' unit cell and one half the T unit cell. There are two sites for the large cations, one 9-coordinated A inside the T/2 cell, and one 8-coordinated A' inside the T'/2 cell. The B cations are surrounded by square pyramids forming corner-sharing pyramidal layers. These layers are one of the common features for most of the cuprate high T_c superconductors.

The compound (Nd, Sr, Ce)₂CuO_{4-y} having the T* structure was reported to become superconducting by Akimitsu et al.². The structural arrangement of the T* phase was determined by the combined use of X-ray and neutron powder diffraction, and high resolution electron microscopy¹. It was found to be tetragonal, space group P4/nmm with lattice parameters, $a \approx 3.86 \text{ \AA}$ and $c \approx 12.5 \text{ \AA}$. From neutron powder data, Izumi et al.³ refined the structure of a Nd_{1.32}Sr_{0.41}Ce_{0.27}CuO_{4-y} sample which had been fully oxidized and found superconducting. These authors carried out as well the structural refinement of a deoxidized, non superconducting sample. However, no appreciable differences were found between the two structures. The O₂ atoms of the [(Nd,Sr) O] layers which are apexes of the CuO₅ pyramids had a large thermal factor

indicating static displacements attributed to partial ordering of the Nd^{3+} and Sr^{2+} cations on the A sites. To justify the superconducting properties of the oxidized sample the authors suggested that the samples have inhomogeneous domain structures in which oxygen-rich superconducting regions coexist with oxygen-poor non superconducting regions.

We report the results of X-ray diffraction studies of $(\text{La}, \text{Sr}, \text{Tb})_2\text{CuO}_4$ single crystals which exhibit the T^* structure. This compound was found to be orthorhombic at room temperature and to undergo a phase transition where its symmetry becomes tetragonal at about 150°C .

2. SAMPLE PREPARATION

Single crystals of $\text{La}_{2-x}\text{Tb}_x\text{CuO}_4$ were grown from a CuO/PbO flux. La_2O_3 , Tb_4O_7 , CuO and PbO powders were mixed in the weight ratio of 1.29 : 0.71 : 0.4 : 2.8. This mixture was heated to 1250°C for 4 hours, slowly cooled to 800°C during 100 hours period and then furnace-cooled to room temperature. Small single crystals, platelet-like, ($\approx 0.5 \times 0.5 \times 0.1 \text{ mm}^3$) were removed mechanically from the flux. They were examined by energy dispersive microanalysis using a JEOL 840A SEM and a Kevex delta class system. The presence of a small quantity of lead coming from the flux was detected in all of them. The single crystal used in the X-ray diffraction analysis yielded the following composition : $(\text{La}_{1.13} \text{Tb}_{0.81} \text{Pb}_{0.06})\text{Cu}_{1.00}\text{O}_x$.

3. PRECESSION CAMERA STUDIES

Single crystal platelets were characterized by X-ray diffraction using a precession camera and Zr filtered MoK α radiation. All reflections corresponded to the $P4/nmm$ space group of the T^* phase with cell parameters $a_p = b_p \approx 3.86\text{\AA}$ and $c \approx 12.46\text{\AA}$. However, longer exposures of the $(hk0)$ and $(hk1)$ reciprocal planes revealed the presence of weak superstructure spots which could not be indexed on the above cell but were indexable on the diagonal unit cell $a_p\sqrt{2} \times a_p\sqrt{2} \times c$. With this cell, the detected systematic absences among the $(hk0)$ reflections occur when h and k are both odd. Such an extinction rule does not correspond to any translation symmetry element. It can be explained by assuming that the crystal is twinned by the (110) plane and the extra spots occur only along one direction. The symmetry then becomes orthorhombic, the symmetry absence $(hk0)$ for $h = 2n + 1$, and the space group $Pmma$ or one of its subgroups. In that case, the observed (hkl) reflections contain the intensity of the (hkl) reflection of the I twin individual plus the intensity of the (khl) reflection of the II twin individual. In the $(hk0)$ plane, the reflections with h and k even follow this rule, while those with h and k of different parity contain the contribution from only one domain. When both h and k are odd the reflections are absent because of the glide mirror. No reflection splitting due to twinning was observed on the precession photographs. The same superstructure pattern was observed for all crystals tested.

In order to determine the behavior of the superstructure with temperature, the precession photographs containing the extra spots were taken as a function of temperature. Temperatures higher than room temperature were attained by the use of a high temperature gas blower with which temperatures can be regulated within ± 0.1 K. The superstructure spots disappeared between 150 and 200 °C above which the precession patterns correspond to the T^* phase with $P4/nmm$ symmetry. The transition from $Pmma$ to $P4/nmm$ is still reversible after several heating and cooling cycles.

4. 4-CIRCLE DIFFRACTOMETER EXPERIMENT

A single crystal platelet ($0.32 \times 0.32 \times 0.04$ mm³) was mounted on a CAD4 diffractometer installed on a NONIUS FR 571 rotating anode generator operated at 57 kV and 60 mA. Graphite monochromatized $AgK\alpha$ radiation was used. High temperature cement was used to glue the crystal to the quartz fiber. The high temperatures were achieved by the same apparatus mentioned above, while for the low temperatures a modified Leybold nitrogen gas blower with a $\pm 1^\circ\text{C}$ temperature stability was used. The room temperature data collection was carried out first, then the temperature was gradually increased in 5 K steps up to 520 K. The cell parameters and several sub- and superstructure reflection profiles were measured at each temperature. Once at 520 K a second intensity data collection was carried out on the $P4/nmm$ space group. Subsequently the temperature was decreased stepwise to room temperature and then to 150 K. The lattice parameters and reflection profiles were measured again at each temperature.

The room- and high temperature data collections were carried out using the ω -scan technique with a 1.4° scan width and 3 mm horizontal and vertical detector slits. The intensities of the reflections included in the reciprocal sphere of radius $\theta = 30^\circ$ were measured in both experiments, plus a half reciprocal sphere between 30° and 35° in θ for the room temperature experiment.

The cell parameters were obtained by refining the absolute θ values of 12 reflections with θ varying between 18° and 27° . The room temperature values are $a = b = 5.451(2)$ Å, $c = 12.426(6)$ Å. One should note that at every temperatures the a and b parameters were observed to be equal within the experimental precision and no reflection splitting due to the orthorhombic distortion could be detected. The variation of the cell parameter and cell volume with temperature exhibit a Debye-like behavior without any transition in the temperature range investigated.

The superstructure reflections begin to exhibit a detectable intensity for $T < 470$ K, which increases slightly as the temperature is lowered to ≈ 380 K. By further lowering the temperature, the superstructure intensities increase strongly and begin to saturate at temperatures around 150 K. This means that the transition width is extremely large, at least 300 K. Thus, the room temperature intensity data, taken in the middle of the

transition, would not yield the complete distortion of the structure. An intensity data collection at 50 K has been carried out, and the refinements are in progress.

A comparison between the profile of (410) superstructure reflection and that of (401) structure reflection at room temperature shows that the superstructure reflection is broader. This indicates that the superstructure correlation length is small. The same comparison at 273 K (after the high temperature data collection, i.e. after a heat treatment at 520 K for a few days) shows that both reflections (410) and (401) have become narrower, and the superstructure one has done more so than the structure reflection. This behavior can be better understood by following the evolution of the (410) superstructure profile from room temperature (before the high temperature data collection) to 273 K (after the high temperature data collection) shown in fig. 1.

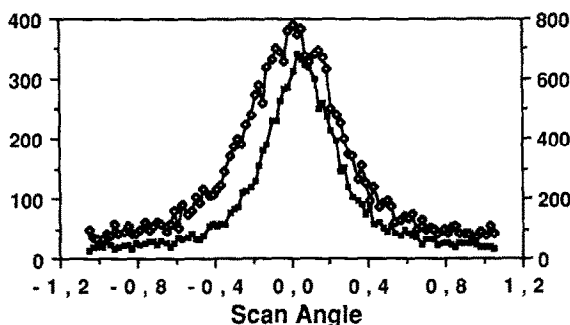


Figure 1

Comparison of the ω -scan profiles of the (4 1 0) superstructure reflection measured at 303 K (empty squares) and 273 K (full squares) i.e. before and after the high temperature data collection, respectively.

It can be seen that the narrowing of the superstructure reflection takes place between room temperature and 273 K measurements. No additional effect is seen on further lowering of the temperature. Thus, it is reasonable to assume that the sharpening of the superstructure reflections is due to the sample annealing during the high temperature data collection. This conclusion is corroborated by the observation of the same effect, although much less pronounced, for the structure reflections.

5. SYNCHROTRON RADIATION EXPERIMENT

As reported above, no reflection splitting or difference between the *a* and *b* parameters could be observed below the transition temperature either by film techniques or by 4-circle diffractometer measurements. The orthorhombic symmetry of the low temperature phase was inferred only from the systematic extinctions. In order to study the shapes of the reflections at very high resolution, we performed X-ray

diffraction experiments on the 6-circle diffractometer installed on the X16B beam line at the NSLS Brookhaven National Laboratory, U.S.A. The experiment was carried out with a vertically focusing mirror, a horizontally focusing Ge(111) monochromator and a Ge(111) analyser at $\lambda = 1.6904 \text{ \AA}$. The same crystal was used for the conventional X-ray source experiments described above. Reciprocal space scans around the principal directions were measured around structure and superstructure reflections.

The most striking result obtained is the observation of two phases with slightly different c parameters inside the crystal. The presence of the second phase is revealed by the existence of a small peak at lower Bragg angle on the scans along the $[00l]$ direction (Fig. 2a). Since the angular differences between the principal and extra peak positions increase with the Bragg angle, the extra peak cannot be attributed to twinning, but to a second phase with a different c parameter. From the peak positions, the c parameters of the two phases are $12.472(1) \text{ \AA}$ and $12.547(3) \text{ \AA}$ for the major and minor phases, respectively. Since no extra peak is observed in the scans measured

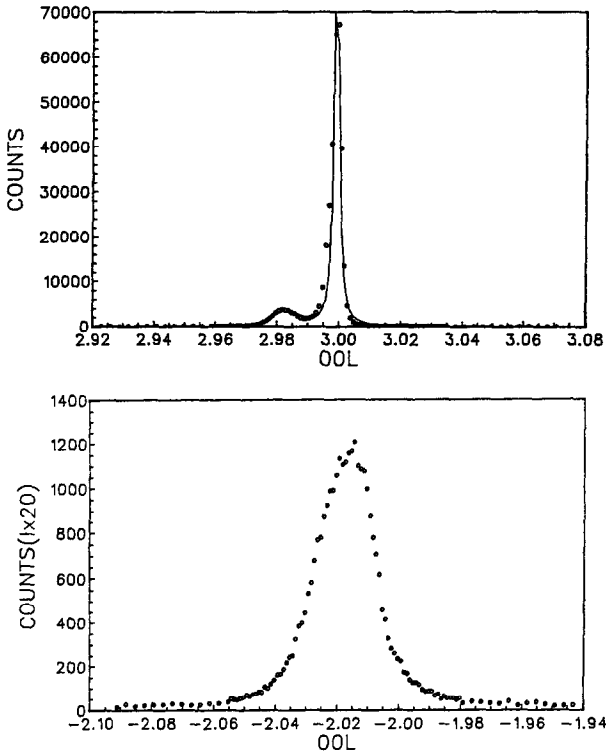


FIGURE 2

Scans along the $[00l]$ direction of the (003) (a) structure and (0-3-2) (b) superstructure reflections. In (a), the small peak is due to a different phase in the crystal.

along the (hk0) plane directions, the a and b parameters of the two phases are equal. As deduced from the diffracted intensity ratios, the minor phase does not represent more than a few percents of the sample volume. The existence of this second phase might be due to the Pb impurities on the La site or to variations of the (Tb/La) composition of the Tb site. It is not of the same nature as the phase separation observed in $\text{La}_2\text{CuO}_{4+\delta}$. A consequence of the existence of the second phase in (La, Tb, Pb) $_2\text{CuO}_4$ crystals is the presence of structural defects in the crystal. These defects are revealed by the observation of broad and structured reflection profiles in the planes perpendicular to the reciprocal vectors originated at the center of the lattice.

No splitting of the reflections due to an orthorhombic distortion could be observed during this experiment. However, the superstructure reflections display considerably broader profiles than the structure ones (Fig. 2b), with asymmetric broadening along the [100], [010] and [001] directions. This broadening is due to short range ordering with a coherence length of ≈ 300 Å as deduced from the reflection widths. The reflection profile asymmetry cannot be accounted for with tetragonal symmetry. It must be attributed to microtwinning of small orthorhombic domains. The small coherence length of these domains is the reason why the a and b parameters appear to be equal in X-ray diffraction experiments. Since no broadening of the structure reflections is observed, the contribution of the structural distortion to these reflections must be very weak.

6. REFINEMENT OF THE TETRAGONAL STRUCTURE AT 520 K

The intensities of 4354 reflections collected at 520 K were corrected for Lorentz-polarization effects, standard-reflection intensity variations and absorption. They were averaged in the 4/mmm point group yielding 475 independent reflections. The structural refinements were based on 406 reflections having $I > 3\sigma(I)$ and $\sin\theta/\lambda > 0.2$. The starting positional parameters were those of Izumi et al. for (Nd, Sr, Ce) $_2\text{CuO}_4$, with La in the 9-fold coordinated site and Tb in the 8-fold one. Low-angle reflections were excluded because, as checked by psi scan measurements, they were affected by multiple diffraction effects. During the final refinement cycles, the occupancy factors of La and Tb were varied and all atoms except O2 had anisotropic thermal vibrations. The O2 atom had to be placed in the 8j (x x z) position because it exhibited an anomalously large thermal factor. This disorder was already observed for (Nd, Sr, Ce) $_2\text{CuO}_4$ by Izumi et al. The final R-factors are $R = 3.5\%$ and $wR = 3.4\%$, the occupancy factors of La and Tb are 1.034(1) and 0.966(1), respectively. If one assumes that the Pb cations are accommodated on the La site and that some of the Tb sites are occupied by La, the above values correspond to a chemical formula such as : (La_{1.198}Tb_{0.724}Pb_{0.078})CuO₄, which is in reasonable agreement with that determined by microanalysis. The A sites are occupied by (La_{0.92}, Pb_{0.08}) whereas the A' sites are occupied by (Tb_{0.72}, La_{0.28}). The crystallographic parameters and relevant interatomic distances are reported in table 1.

TABLE 1

Positional, thermal parameters and interatomic distances for $(\text{La}, \text{Tb}, \text{Pb})_2\text{CuO}_4$ at 520K

Atome	Position	occup.	x	y	z	U11	U22	U33
La	2c	1.034(1)	1/4	1/4	.38436(3)	.01457(8)	.01457(8)	.0133(1)
Tb	2c	0.966(1)	1/4	1/4	.09683(3)	.00885(6)	.00885(6)	.0133(1)
Cu	2c	1	1/4	1/4	.75594(7)	.0061(2)	.0061(2)	.0180(3)
O1	4f	1	3/4	1/4	.2378(3)	.024(3)	.003(2)	.035(2)
O2	8j	1	.295(1)	.295(1)	.5716(5)	1.1(1)		
O3	2a	1	3/4	1/4	0	.011(1)	.011(1)	.023(2)

 $a = b = 3.870(2)\text{Å}$, $c = 12.504(6)\text{Å}$

La-O1 x4	2.665(3)	Tb-O1 x4	2.618(3)
La-O2 x1	2.354(6) (apical)	Tb-O3 x4	2.283(2)
x2	2.802(4)	Cu-O1 x4	1.937(2)
x1	2.553(4)	Cu-O2 x1	2.318(6)
x1	3.031(4)		

7. DISCUSSION

The more puzzling question concerning the structure of the T^* phase is the origin of the positional disorder observed for the O2 atom. Izumi et al. attributed it to a partial ordering between the Nd and Sr cations on the 9 coordinated site. However, since the differences in size of cations occupying this site vary from one compound to the other while the oxygen displacements are exactly the same, the cation ordering cannot be the cause of this displacement.

These results indicate that the O2 displacement is intrinsic to the T^* structure and is related to the superstructure observed in $(\text{La}, \text{Tb}, \text{Pb})_2\text{CuO}_4$ below 470 K. This superstructure is due to ordered canting of the CuO_5 pyramids and the displacement of the O2 atom at temperatures above the transition indicates a dynamical distortion of these pyramids. In the orthorhombic low temperature phase, this canting generates two inequivalent A sites. For one type of sites there would be four bonds with O1 ($A\text{-O1} = 2.665 \text{Å}$), one with O2 ($A\text{-O2} = 2.354 \text{Å}$) and four bonds with O2 at the same distance ($A\text{-O2} = 2.802 \text{Å}$), with an average A-O distance of 2.691Å . For the other type of sites, the four latter bonds would be replaced by two A-O2 short bonds ($A\text{-O2} = 2.553 \text{Å}$) and two A-O2 long ones ($A\text{-O2} = 3.031 \text{Å}$) yielding an average distance : 2.687Å . The T^* phase should form more easily if there are two types of cations on the A site. This explains why it has not been possible so far to synthesize a T^* compound with only one type of cation on the A site.

The A' sites are also occupied by two different types of cations, however, no ordering is detected as the two types of oxygen atoms forming the 8-fold coordination polyhedra of the A' cations (O1 and O3) have normal temperature factors. The average

A'-O distance is 2.451 Å. It is in good agreement with the average ionic radii calculated from the values tabulated by Shannon⁵ for 8-coordinated cations : 2.454 Å.

The Cu cations occupy pyramidal sites with four short bonds and a longer one. The distance to the apical oxygen of the Cu coordination pyramid is 2.318 Å. It is 0.05 Å shorter for (Nd, Sr, Ce)₂CuO₄ which is superconducting. Thus, as already observed for other high T_c compounds⁶, the positive charges created by the substitution of Nd³⁺ by Sr²⁺ are transferred to the CuO₂ plane via the shortening of the apical oxygen distance. It must be pointed out, though, that this model does not explain why the deoxidized sample of (Nd, Sr, Ce)₂CuO₄ reported by Izumi et al. is non-superconducting. The apical oxygen-planar Cu distance in this sample is exactly the same as that of the oxidized superconducting sample.

In the low temperature orthorhombic phase of (La, Tb, Pb)₂CuO₄, there are two non equivalent Cu sites in the CuO₂ plane. The presence of these two inequivalent sites could favor charge ordering in this plane, which would be detrimental to superconductivity. The superconducting properties would depend not only on the number of charges transferred to the CuO₂ plane, but also on the degree of charge ordering. As shown above a prolonged annealing of the (La, Tb, Pb)₂CuO₄ single crystal induced the superstructure to become more long range. Similarly, the annealing at 500 °C used by Izumi et al. to "deoxidize" their sample could favor the long range ordering of the superstructure and consequently of the charges, leading to the disappearance of the superconducting properties.

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