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EFFECTS OF Ba SUBSTITUTION AND PRESSURE

July 1993

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The crystal structure of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0.03 \leq x \leq 0.24$) have been studied at 115 K and 15 K by high-resolution neutron powder diffraction experiments. The variations in the Cu-O bond lengths refined by profile analysis suggest importance of the apical O(2) as well as that of the planar O(1) for the charge transfer. The compound with $x=0.125$ at 15 K exhibits changes of the Cu-O bonds accompanied by the structural phase transition to the low-temperature tetragonal (LTT) phase. These results are discussed in terms of correlations with the superconducting properties of the system.

Furthermore, to clarify a correlation between structural phase transitions and superconductivity, the crystal structure of the compound with $x=0.125$ has been investigated under pressures up to 0.7 GPa. The transition to the LTT phase, observed at around 80 K at ambient pressure, decreases greatly at the rate of about -135 K/GPa. The bulk superconductivity, on the other hand, enhances under high pressure when the LTT phase disappears. These results show a strong relationship between the crystal structure and superconductivity in this system.

Keywords: Crystal Structure, Superconductivity, Substitution Effects,
Pressure Effects, Oxide Superconductor

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$\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ の結晶構造：Baの置換効果と圧力効果

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$\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0.03 \leq x \leq 0.24$) の結晶構造を高分解能中性子粉末回析法により、115Kと15Kで調べた。プロファイル解析によって得られた銅-酸素ボンドの長さの変化は、電荷の移動に対して、平面内酸素と同様、頂点酸素の重要性を示唆する。 $x=0.125$ の試料の15Kでのデータは銅-酸素ボンドが、低温正方晶(LTT)相への転移によって変化することを示す。これらの結果を系の超伝導特性との関連で議論する。

さらに、構造相転移と超伝導との関連を明らかにするため、 $x=0.125$ の試料の結晶構造を0.7GPaまでの高圧下で調べた。LTT相への転移は圧力とともに-135K/GPaと非常に大きな割合で減少した。バルクの超伝導はこのLTT相が消えると、大きく増大する。この結果は系の結晶構造と超伝導との強い相関を示している。

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1. INTRODUCTION

$\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (M=Ba, Sr, etc) has been studied extensively as a model system of the Cu-based high- T_c oxide superconductors. These investigations showed that the physical properties of the system are strongly changed by the hole doping due to the Ba or Sr substitution for La. Antiferromagnetic ordering observed in the parent compound La_2CuO_4 is suppressed dramatically by the hole doping. With increasing concentration x , the system becomes metallic, and the superconductivity appears abruptly at x around 0.05. The superconducting transition temperature T_c increases on further doping and attains broad maximum (~ 30 to 40 K) at about $x=0.15$. With increasing x further, T_c begins to decrease and the superconductivity finally disappears at x around 0.25. Structural studies of this system showed that the phase transition from the high-temperature tetragonal (HTT; space group $I4/mmm$) to the low-temperature orthorhombic (LTO; space group $Bmab$, the non-standard setting of $Cmca$) structure takes place at about 500 K in the undoped compound. The transition temperature decreases greatly with the substitution of La, and this structural phase transition disappears at around $x=0.25$.

The Ba substituted system, which was discovered as a first high- T_c oxide superconductor¹, has recently attracted renewed interest because it became clear that the bulk superconductivity is suppressed greatly in a narrow range of x around 0.125². The resistivity, Seebeck and Hall coefficients of this compound

exhibit large anomalies around 60 K, which suggests that the electronic structure changes significantly at this temperature.³ Subsequent structural studies clarified that the compound undergoes the successive phase transitions from the HTT phase to the LTO one at around 200 K, and further to the low-temperature tetragonal (LTT; space group $P4_2/nm$) phase at around 80 K upon cooling. Although there is persistence of the LTO phase in the LTT phase, the fraction of the transformed LTT phase seems to be maximum at this concentration.⁴ Thus the anomalous suppression of the superconductivity has been related to changes in the electronic state accompanied with the structural transition from the LTO to the LTT phase. Figure 1 displays the crystal structure in the HTT phase schematically. In the figure a CuO_6 octahedron is shown. The transition from the HTT to the LTO phase is accompanied by staggered rotation of these octahedra about the HTT (1 1 0) axis. The second transition to the LTT phase is caused by the rotations of them both about the HTT (1 1 0) and about (1 $\bar{1}$ 0) axis. Figure 2 shows the phase diagram of the system obtained in the present experiment. The data will be referred later.

These results indicate that the crystal structure closely correlates with the superconductivity of the system. Structural studies on various high- T_c compounds have actually indicated that some particular bond lengths are important to determine the hole density in the CuO_2 planes and thus the superconducting transition temperature T_c . For example, in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ system the

lengths between Cu and apical O decreases greatly with increasing oxygen concentration, indicating that holes are transferred from the CuO chains to the CuO₂ planes.⁵ In the present system also there may be characteristic variations of particular atomic bonds that can be correlated with the concentration dependence of T_C . In order to study changes in structural parameters including bond lengths and angles systematically, and to examine their relationship with the complex superconducting properties of the system, high-resolution neutron diffraction experiments and magnetic susceptibility measurements have been performed on carefully prepared La_{2-x}Ba_xCuO₄ compounds.

As mentioned above, the structural transition to the LTT phase appears near the Ba concentration where the dip in the T_C -x phase diagram occurs; therefore, it has been suggested that there is a correlation between the appearance of the LTT phase and the suppression of the superconductivity.⁴ Various efforts have been made to elucidate this relationship between the suppression of T_C and the onset of structural transitions. The substitution of Th⁴⁺ for La³⁺ indicated that the anomalous behavior in T_C is characterized by the hole density of 1/8 per Cu atom which is coupled with the LTT phase.⁶ Other study showed that the Nd³⁺ substitution for La³⁺ in La_{2-x}Sr_xCuO₄ induces another orthorhombic phase (LTO2; space group *Pccn*), and that the superconductivity is modified by this new structural transition.⁷ Experiments on the effects of pressure on the superconductivity of La_{2-x}Ba_xCuO₄ suggested that T_C in this system is restored when

the LTT phase is suppressed under high pressure.⁸ In this study, however, the suppression of the LTT phase was suggested from the observation of anomalies in the resistivity, and this suppression has not been observed directly. The direct observation of the structural phase transitions can be achieved using diffraction techniques.

In order to clarify the effects of pressure on the structural transitions and superconductivity of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ further and, in particular, to explore the suggestion that the superconductivity in this system is recovered by the suppression of the LTT phase,⁸ we have performed neutron diffraction experiments and ac susceptibility measurements under high pressure on powder specimens with $x=0.125$. The neutron diffraction measurements have been made at ambient pressure, and at 0.35 and 0.7 GPa. The magnetic susceptibility have been measured in detail up to 2.5 GPa. These results directly show that when the LTT phase is suppressed under high pressure, the superconducting transition temperature T_c is recovered; that is, there is a strong correlation between the structural phase transitions and the superconductivity in this system.

2. EXPERIMENTAL

The $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.03, 0.08, 0.125, 0.17$ and 0.24) samples were prepared by solid-state reaction method of a mixture of predried La_2O_3 , BaCO_3 and CuO . The powders were pressed into a

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pellet, calcined at 900°C for 24 h and then sintered at 1050°C in air for several days with frequent grindings. The samples were finally annealed at 500°C for 24 h in flowing O₂ gas.

The superconducting transition temperature T_c for these compounds were examined at temperatures down to 1.8 K by ac induction method. For $x=0.125$ dc susceptibility was measured at temperatures down to 4.2 K using a magnetic balance.

Neutron diffraction experiments to study the crystal structure were made with the high-resolution powder diffractometer installed at the High Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory. The (1 1 5) reflection of Ge was used as the monochromator. The neutron wavelength was 1.4000 Å. The data were collected with a 12' inpile collimator, a 10' monochromatic beam collimator and a 6' diffracted beam collimator. The samples were placed in a cylindrical vanadium cell of thickness 0.05mm and enclosed in an aluminum can filled with helium exchange gas. Measurements were carried out at temperatures down to 15 K using a standard closed-cycle refrigerator. The data obtained were analyzed by a Rietveld refinement program.⁹

Neutron diffraction experiments under high-pressure were made with a clamp-type cell assembly, specially designed for neutron scattering experiments,¹⁰ using a sapphire piston-cylinder. The pressure in the experiments was determined by the calibration curve shown in Ref. 10. As the pressure transmitting medium, 3M Fluorinert liquid was used. The diffraction experiments under pressures were performed at 0.35 and 0.7 GPa. These measurements

were carried out at temperatures down to 15 K using a standard closed-cycle refrigerator. The amount of the powder specimen was limited by the size of the pressure cell, and thus the effective volume of the sample in the measurements was about 0.35 cm^3 . This limitation compounded with the high background scattering from the pressure cell made the diffraction measurements at high-pressures very difficult.

The superconducting transition temperature T_c for this compound was examined under pressures of up to 2.5 GPa by the ac induction method. The sample used for these measurements was not the same one used in the neutron diffraction experiments but was taken from the same batch. The ac measuring frequency was 353 Hz and driving field was 0.83 Oe. The pressure was generated by a clamp-type piston cylinder apparatus with a Teflon cell. 3M Flourinert liquid was also used as the pressure transmitting medium. In these measurements the sample was cooled down to 2 K by pumping liquid ^4He . The temperature was measured using a C.G.R. (Carbon glass resistance) thermometer.

3. RESULTS AND DISCUSSION

3.1 *Ba substitution effects*

The superconducting transition temperature T_c were determined by the onset of the diamagnetic susceptibility. For $x=0.03$ and 0.24 the superconducting transition was not observed down to

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3. RESULTS AND DISCUSSION

3.1 *Ba substitution effects*

The superconducting transition temperature T_c were determined by the onset of the diamagnetic susceptibility. For $x=0.03$ and 0.24 the superconducting transition was not observed down to

1.8 K. The transition temperatures T_C for the compounds with $x=0.08$ and 0.17 were observed at 25 K and 26 K, respectively. In the insert of Fig. 3, the temperature dependence of the susceptibility is shown for the sample with $x=0.125$. As reported in previous investigations², the susceptibility shows that the superconducting transition of this compound is fairly suppressed, and that there exists a two-step superconducting transition. The first component is quite small, but it can be observed at around 30 K. This component may be a trace of superconductivity which is due to the presence of a very small fraction of the LTO phase. Upon cooling the second component appears at about 4 K. This seems to be bulk transition, but the volume fraction of the superconductivity is still only a few percent. For this sample the *dc* susceptibility was measured to see the superconducting and other physical properties more precisely. As displayed in Fig. 3, the susceptibility decreases abruptly at around 30 K, indicating the trace of the superconductivity mentioned above. This *dc* susceptibility shows several other anomalies. These anomalies can be related with the structural phase transitions, and will be discussed later. The transition temperatures T_C observed are plotted by triangles in Fig. 2 together with those of the structural transitions as a function of the Ba concentration. The concentration dependence of T_C shows two maxima, and is consistent with earlier experiments.^{2,3}

The neutron diffraction data obtained at 115 K were analyzed in the orthorhombic *Bmab* space group for $x=0.03$, 0.08 and 0.125

(low-temperature orthorhombic: LTO), and in the tetragonal $I4/mmm$ space group for $x=0.17$ and 0.24 (high-temperature tetragonal: HTT). As an example, Fig. 4 shows a Rietveld refinement profile for the sample with $x=0.125$ at 115 K. The structural parameters at 115 K determined are summarized in Table I. In the early stage of the refinements, the deficiency at the oxygen sites was found to be quite small for all samples. The occupation factors of oxygens were, thus, set at 1.0 for the final refinements. Isotropic thermal factors B were used for the refinements. As seen in the table, however, the thermal factor for the apical O(2) is considerably larger than that for the other atoms. This may be due to a large thermal vibration of this oxygen atom, or to a static disorder in the position of this atom. Supposing the former possibility, anisotropic thermal factors of this apical oxygen atom were refined. The results showed that the thermal vibrations of O(2) in the horizontal directions are two or three times larger than that in the vertical direction. In the refinements, the La and Ba atoms were assumed to occupy the same position. This might be right since the thermal parameters for these atoms are relatively small. The crystal parameters change subtly with increasing the Ba concentration x , corresponding with a reduction of the orthorhombicity. The positional parameter z of the La/Ba atoms and the apical O atoms decrease with the Ba concentration. The change in z of the apical O is rather large.

The data at 15 K for $x=0.03$, 0.08 and 0.17 were analyzed in the orthorhombic symmetry (LTO) and those for $x=0.24$ were refined

in the tetragonal one (HTT). The parameters refined for these compounds exhibits no significant change compared with those at 115 K. On the other hand, the diffraction pattern for $x=0.125$ shows a change to the different crystal structure, as was reported previously. Figure 5 displays the temperature dependence of the tetragonal (2 2 0) reflection of this compound. As the temperature is lowered the single peak of this HTT phase splits continuously below about 202 K, exhibiting the transition to the LTO structure. Below around 78 K a central component appears, and this indicates a transition to another low temperature phase. At 70 K this peak becomes fairly sharp, and at 15 K it can be regarded almost as a single peak. Thus the sample in the present experiment shows an almost complete transition to the low-temperature structure; that is, the fraction of the low-temperature structure is much larger than that reported previously⁴. The anomalies which correspond with these structural transitions can be seen clearly in the *dc* susceptibility displayed in the insert of Fig. 3. The anomaly at around 200 K indicates the transition between the HTT and LTO phase, and that at around 80 K does that between the LTO and another low-temperature phase. In the sample with $x=0.08$, the low-temperature phase appears around 40 K; however, the fraction of this phase is below 15 % at the lowest temperature 15 K. The transition to that low-temperature phase in the compound with $x=0.17$ is not observed evidently. Thus the low-temperature phase appears more sharply in the phase diagram than the previous report.⁴

For the low temperature phase the symmetry of $P4/ncm$ (low-temperature tetragonal: LTT) and $Pccn$ (orthorhombic) are proposed. However, the electron diffraction experiments on the compound with $x=0.125$ indicated that the tetragonal phase exists actually and they coexists with the orthorhombic phase whose orthorhombicity is quite small.¹¹ Accordingly, even if our sample contains such a pseudo orthorhombic phase, these two symmetry types cannot be distinguished within the experimental accuracy. Hence the data were analyzed in the tetragonal $P4/ncm$ symmetry (LTT). The result of the refinement is shown in Fig. 6. The crystal parameters determined are displayed in Table II. Compared with the parameters of this compound at 115 K, the changes accompanied by the phase transition are fairly small.

The lattice parameters a , b and c were plotted as a function of the Ba concentration x in Fig. 7. The parameters a for the tetragonal phase were multiplied by the factor $\sqrt{2}$ for a purpose of comparison. With increasing x the parameter b decreases greatly with the reduction of the orthorhombicity. The lattice parameter c , in contrast, shows a large increase. There is no evident anomalous behavior in these parameters with increasing the Ba concentration x .

As shown in Fig. 1, the Cu atoms are bonded to four planar O(1) atoms and to two apical O(2) atoms. These bonds, thus, form CuO_6 octahedra. The bond length of Cu-O(1) ($\sim 1.90 \text{ \AA}$) is much shorter than that of Cu-O(2) ($\sim 2.42 \text{ \AA}$), which shows that the overlap of Cu-O(1) orbital is quite strong and the octahedron is

fairly distorted. Changes in these Cu-O bond lengths are plotted in Fig. 8 as a function of x . As seen in the figure these Cu-O bond lengths decrease almost linearly with x , indicating that the overlap of Cu-O orbital increases. The decreasing rate in the lengths between Cu and planar O(1) is about -0.008 \AA per $x=0.1$. It is particularly noted that the length of Cu-apical O(2) decreases also at the rate of half as large as that of Cu-O(1) bond ($\sim -0.004 \text{ \AA}$ per $x=0.1$). This shows that the distortion of the CuO_6 octahedron increases with the Ba concentration x . In the compounds with $x=0.125$ at 15 K there exist two different bond lengths for Cu-planar O in the sample with $x=0.125$, corresponding with the transition to the LTT phase. The changes in these Cu-O(1) bond lengths accompanied with this structural transition are, however, fairly small.

The changes in the structure between the tetragonal and orthorhombic phase transition involves the buckling of CuO_2 planes associated with the tilting of the CuO_6 octahedron. The bond angle between Cu-O(1)-Cu which characterizes this buckling is plotted in Fig. 9. The angle increases on the whole with increasing x . This also indicates the increase in the overlap of planar Cu-O orbital. For the compound with $x=0.125$ at 15 K, two different angles appear, corresponding with the change in the form of the buckling in the LTT structure. As seen in the figure, the change in the angle is comparatively large. One of these angles becomes smaller than that for $x=0.08$.

La and Ba atoms are nine-fold coordinated by oxygens - one

apical O(2) in the plane of the other La/Ba atom, four O(2) in its own La/Ba plane, and four planar O(1) in the plane of Cu. These La/Ba-O bond lengths were averaged in each group, and they are plotted in Fig. 10. The shortest La/Ba-apical O(2) bond ($\sim 2.37 \text{ \AA}$) increases with x at the fairly large rate of $\sim 0.018 \text{ \AA}$ per $x=0.1$. The bond length between La/Ba and O(2) in its own La/Ba plane, which length is rather long ($\sim 2.74 \text{ \AA}$), decreases with the Ba concentration ($\sim -0.014 \text{ \AA}$ per $x=0.1$). Then, the bond length between O(1) in the Cu plane ($\sim 2.64 \text{ \AA}$) increases at the rate of about 0.006 \AA per $x=0.1$. Owing to the elongation of the shorter bonds the lattice parameter c increases greatly. The decrease in the length of the longest (the weakest) La/Ba-O(2) bond would be a result of the movement of atoms accompanied with the elongation of the shorter La/Sr bonds.

The results obtained can be related with the variation of the hole concentration in the system since the interatomic distances are sensitive measures of the amount of charge in the bonds. As was indicated experimentally,¹² the undoped compound La_2CuO_4 has the charge-transfer gap which is produced by strong electron correlation. By the Ba substitution the number of valence electrons decreases, and hence holes will be doped in the system. These hole states would be developed in the charge-transfer gap, and may form the Fermi surface, as was observed clearly for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ in the inverse photoemission study.¹³ The predominant orbitals of these in-gap states will be strongly antibonding Cu $3d(x^2-y^2)$ and O $2p(x,y)$ states; thus the bonds

between Cu and O(1) in the CuO_2 plane would be primarily important in this system. Those bonds with antibonding character become strengthened when electrons are removed, i.e. with increasing the hole density. (The orbital overlap in these bonds increases with the hole concentration.) Thus, the shortening in the bond length Cu-O(1) and the increase in the bond angle between these atoms can be directly correlated with the increase in the hole concentration in the CuO_2 plane.

The decrease in the length between Cu and apical O(2), which was observed clearly in the present experiment, also suggests the increase of holes in this bond. These holes would occupy the planar Cu $3d(3z^2-r^2)$ or O $2p(z)$ states. On this point, recent experiments on the Sr substituted system indicated that doped holes have a substantial out-of-plane O $2p(z)$ character.¹⁴ If so, a significant amount of holes induced in this bond would occupy the apical O orbitals. The increase of such holes with the Ba concentration x suggests that the apical O might play some important role for the superconductivity of the system.

On the other hand, the bond lengths increase with decreasing in valence of atoms. The elongation in the La/Ba-O bonds, hence, corresponds with the decrease in the average valence of La/Ba atoms by the substitution. Since the decrease in the valence means the increase of hole concentration, the La/Ba-O bond lengths increase in correlation with the increase in the hole concentration of the system.

These changes in the bonds could be further related with the

concentration dependence of T_C according to an empirical relationship between hole concentration and T_C . Since the results at 115 K show that the Cu-O bond lengths and the tilt angle of the CuO_6 octahedron decrease almost linearly and that no appreciable anomaly is observed as a function of x , the hole density would increase monotonously with x ; therefore, it is expected that T_C will increase first with x , then exhibit a broad maximum, and finally decrease in the overdoped region, as was observed in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. In the present system, as has been mentioned, the variation of T_C shows a sharp minimum around $x=0.125$, corresponding with the structural phase transition at low temperatures. Changes in the Cu-O(1) bond lengths accompanied with the structural transition to LTT, however, are rather small. The bond angles exhibit somewhat large changes on the phase transition. Although these changes are generally small, such distortions of the Cu-O₂ plane could be one of the parameters which can be correlated with the sharp suppression of T_C . In recent electronic structural consideration on this system, it is indicated that the density of states near E_F lowers somewhat in the LTT phase, corresponding with the existence of two different sites for the planar O(1).¹⁵ This result suggests that an additional gap will be produced in the states in the charge-transfer gap and may lead to the suppression of T_C . Such an electronic transition would cause anomalies in transport phenomena, and so forth. The anomaly observed at around 80 K in the *dc* susceptibility (Fig. 3) could be related with this electronic instability. Another

anomaly at about 55 K in the magnetic susceptibility seems to correspond with anomalies observed at around 60 K in various transport phenomena.³ If this is the case, it is suggested that the temperature where anomalies in the transport phenomena appear might not be the same temperature where the structural phase transition occurs. Furthermore, the experiments on $\text{La}_{2-x}(\text{Ba},\text{Sr})_x\text{CuO}_4$ indicated that the electronic instability monitored by the resistivity anomaly is not always accompanied by the structural phase transition to LTT.¹⁶ However, to make clear the suggestion pointed out here, more detailed and systematic studies will be required, including the sample characterization.

The results obtained here are somewhat different from those for $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. In this compound, the bond length between planar Cu and apical O decreases greatly with the hole doping by increasing oxygen content.⁵ This feature might originate from the uniqueness of the crystal structure in which the apical O bridges the CuO_2 plane and the CuO chain. Electronic structural studies of this system indicate that the bonding of the Cu and apical O are significant to determine the electronic states near E_F , as well as the Cu-O bonding in the plane and in the chain.¹⁷ Thus the Cu-apical O bonding might play an important role to change the hole density in the CuO_2 plane of this system. On the other hand, the Cu-O bonds in the plane do not change appreciably, and the puckering of Cu and O of the plane increases with increasing the oxygen content. These features are probably due to a result that the planar Cu atoms move towards the

apical O.

3.2 Pressure effects

Figure 11 shows again the neutron diffraction data of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.125$) at ambient pressure for the (2 2 0) reflection of the high-temperature tetragonal phase (HTT; $I4/mmm$). As the temperature is lowered from room temperature, this single peak starts to split below about 202 K, indicating the transition to the low-temperature orthorhombic structure (LTO; $Cmca$). These diffraction peaks are indexed as (0 0 4) and (4 0 0) of the LTO structure. This splitting becomes larger when the temperature is decreased. Below around 78 K, a central component appears, which indicates the transition to another low-temperature phase. At 70 K this peak becomes fairly sharp, and at 15 K it can be regarded almost as a single peak (within the instrumental resolution of 0.2 degrees). Thus the sample in the present experiment shows an almost complete transition to a low-temperature phase, which is tetragonal (LTT; $P4_2/ncm$) within the experimental accuracy. This diffraction peak can be indexed as (4 0 0) of the LTT structure. (This low-temperature phase could also be, at least partially, orthorhombic $Pccn$. However, if this is the case, the orthorhombicity is at least an order of magnitude smaller than that of the LTO structure.¹¹⁾)

Figure 12 displays the temperature dependence of the same reflection under 0.35 GPa. The broadening of this peak, which

shows the transition from the HTT to the LTO phase, starts at around 190 K and it continues down to around 30 K. Below this temperature a central component appears but, unlike the ambient pressure case, this peak remains broad even at 15 K. This result indicates that although the transition to the LTT phase takes place at around 30 K, the phase transition may not be complete even at 15 K, and the sample perhaps contains a small fraction of the LTO phase.

Diffraction data of the same reflection under 0.7 GPa are shown in Fig. 13. In this case the transition temperature to the LTO phase, as estimated by the broadening of the HTT (2 0 0) reflection, is about 183 K. When the temperature is lowered, the split of the peak becomes clearer. Under this pressure, however, the appearance of a central component is not evident down to 15 K. The transition to the LTT phase, thus, seems to have disappeared under the pressure of 0.7 GPa.

These results show that the effect of pressure on the LTO=LTT transition is quite observable and that the orthorhombic phase is stabilized under high pressure. Furthermore, the results indicate that the temperature where the resistivity anomaly or other transport anomalies take place (~ 60 K at ambient pressure and dependent on pressure rather moderately)^{8,18} may not be the same temperature where the structural phase transition occurs. The anomalies in the transport phenomena might be caused by some other electronic instability. As mentioned before, a similar decoupling of the resistivity anomaly and the structure

change has been reported in the experiments on the $(\text{La}_{1-x}\text{Ba}_x\text{Sr}_y)_2\text{CuO}_4$ system.¹⁶

Although neutron diffraction measurements have been performed at only three pressures (0, 0.35 and 0.7 GPa), the temperature-pressure phase diagram on the crystal structure of the present system can be sketched as shown in Fig. 14. The pressure coefficient of the transition temperature for the HTT-LTO phase transition dT_1/dP is $-28 \text{ K}(\pm 6 \text{ K})/\text{GPa}$, and that of the LTO-LTT transition dT_2/dP is $-135 \text{ K}(\pm 10 \text{ K})/\text{GPa}$. The value dT_1/dP is rather small, and is just about 1/4 of that of the $(\text{La},\text{Sr})_2\text{CuO}_4$ system obtained from X-ray diffraction experiments.¹⁹ The value of dT_2/dP , on the other hand, is rather large. From this figure the pressure that causes the LTT phase to disappear can be extrapolated to about 0.6 GPa.

Figure 15 shows the magnetic susceptibility of the sample for several pressures as a function of temperature. As reported in previous investigations,² the diamagnetic susceptibility shows a two-step superconducting transition. The first component is quite small at ambient pressure, but it can be observed at about 30 K. (In the resistivity measurements, on the other hand, two anomalies which correspond with the two-step transition are clear.^{2,8}) This component may be a trace of superconductivity which is due to the presence of a very small fraction of the LTO phase. The volume of this phase at ambient pressure would be too small to be observed in the diffraction data at low-temperatures (Fig. 11). With increasing pressure, this transition temperature

increases and the volume fraction of this superconductivity also increases slightly. The second component is a bulk transition observed at about 4 K. As the magnetic susceptibility shows, however, the volume fraction of this bulk superconductivity is also small - a few percent - at ambient pressure. Under pressures up to 0.5 GPa, the behavior of this susceptibility does not significantly change: the superconducting transition temperature remains almost constant. However, above 0.6 GPa the bulk superconductivity is greatly enhanced. Both T_C and the volume fraction of the superconductivity increase significantly with pressure up to about 1.5 GPa, the pressure at which these characteristic values seem to saturate.

The pressure dependence of these superconducting transition temperatures is shown in Fig. 16. Here, the higher transition temperature is defined as the temperature where the signal deviates from the normal-state value, and the bulk T_C at lower temperatures is defined by the temperature at which the susceptibility deviates from the signal of the superconducting state at the higher temperatures. The transition temperature for the trace of the superconductivity at higher temperatures increases at the rate of $7 (\pm 2)$ K/GPa, and saturates at around 2 GPa. On the other hand, the transition to the bulk superconductivity does not change up to 0.5 GPa; above this pressure T_C increases significantly. The pressure coefficient dT_C/dP is $10 (\pm 2)$ K/GPa. At around 1.5 GPa the transition temperature seems to saturate, and then decreases somewhat. In the figure the LTO-LTT transi-

tion temperature is shown as a broken line. From this figure, it is apparent that the bulk T_c is greatly enhanced when the LTT phase disappears under high pressure. These results clearly show a correlation between the suppression of the bulk superconductivity and the structural phase transition to the LTT phase. The pressure derivatives of T_c mentioned above are two or three times larger than those for the Sr substituted system.²⁰ Since the Sr substitution does not induce the transition to the LTT phase, there should be no suppression of T_c . Thus, the large pressure derivatives in the present system may arise from the restoration of the superconductivity due to the depression of the LTT phase under pressure. The value of 10 K/GPa is somewhat larger than that in other experiments on this system.²¹ This difference would be due to the fact that the pressure effects on T_c appear only above 0.5 GPa as clarified in our detailed study.

As mentioned above, the superconducting transition at higher temperatures saturates at high pressures above around 1.5 GPa. This behavior, which has also been observed in other oxide superconductors,²² might suggest a saturation of the hole density under high pressure. The bulk superconductivity, moreover, remains around 15 K even at the highest pressure applied in this experiment (2.5 GPa). That is, the bulk T_c under pressure does not reach 30 K (T_c in the LTO phase of the 30 K class superconductors). This observation suggests that the electronic structure of the orthorhombic (LTO) phase stabilized under high pressure is still complicated in this particular compound with the

hole density of $1/8$. Possibly the density of states at the Fermi level (i.e. the density of holes which are responsible for the superconductivity) may be lower than that of the LTO phase in the 30 K class superconductors. The saturation of T_c in this system under high pressure has also been reported.⁸ Recently the same group suggested that impurity scattering may be the origin of the relatively low T_c under pressure in this system.²³

Another possibility for the saturation of the bulk T_c under high pressure is as follows. In the experiments for the $\text{La}_{1.88-x}\text{Nd}_x\text{Sr}_{0.12}\text{CuO}_4$ system,⁷ the Nd substitution induces the structural change from the LTO to another orthorhombic $Pccn$, and then to the LTT phase. Furthermore, in this structure sequence T_c decreases systematically. The transition temperature of around 15 K, observed in the orthorhombic $Pccn$ phase of that system, is close to the T_c obtained under high pressure in the present experiment. Hence, if the same relation between the structure and T_c exists in the present system, it is possible that the structure induced under high pressure may be $Pccn$. Although the transition to the orthorhombic $Pccn$ under pressure is not clear in the data under 0.7 GPa within experimental uncertainty, it might be possible that pressure induces such an intermediate orthorhombic structure rather than it changes the structure to the LTO ($Cmca$) phase directly. To make clear whether the $Pccn$ structure is induced or not, more detailed experiments under high pressures will be necessary.

The pressure effects on the crystal structure would be

related to the contraction of the lattice. As was observed in the experiments on $(\text{La},\text{Ba})_2\text{CuO}_4$, the substitution of La with larger Ba expands the LaO/BaO polyhedra and contracts the CuO_6 octahedra. With these changes, the compressive stress exerted on the CuO_6 octahedra is reduced, and hence the crystal structure changes from LTO toward HTT.²⁴ Between these phases LTT appears sharply at around $x=0.125$. Under high pressure the whole crystal is contracted; accordingly, the correspondence with the case of the Ba substitution is not straightforward. However, if the effects of the contraction of the CuO_6 octahedra is dominant in the LTO phase, the stress on these octahedra is reduced, and the HTT phase may be stabilized. That is, the temperature for the HTT-LTO transition T_1 decreases under high pressure. The effect of pressure on the LTT phase might be explained similarly. If the CuO_6 octahedra is contracted effectively and the stress on them is decreased in the LTT phase also, the LTT structure may be unstabilized and consequently the orthorhombic structure would be stabilized. A similar effect of the lattice contraction on the LTT structure was observed in the Sr substituted $(\text{La},\text{Ba})_2\text{CuO}_4$ system.¹⁶ By the substitution of smaller Sr ions for Ba, the lattice is contracted, and the structural change to the LTO phase is induced. Furthermore, T_c increases also in this system.

4. SUMMARY

The crystal structure of the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ system ($x=0.03$,

related to the contraction of the lattice. As was observed in the experiments on $(\text{La},\text{Ba})_2\text{CuO}_4$, the substitution of La with larger Ba expands the LaO/BaO polyhedra and contracts the CuO_6 octahedra. With these changes, the compressive stress exerted on the CuO_6 octahedra is reduced, and hence the crystal structure changes from LTO toward HTT.²⁴ Between these phases LTT appears sharply at around $x=0.125$. Under high pressure the whole crystal is contracted; accordingly, the correspondence with the case of the Ba substitution is not straightforward. However, if the effects of the contraction of the CuO_6 octahedra is dominant in the LTO phase, the stress on these octahedra is reduced, and the HTT phase may be stabilized. That is, the temperature for the HTT-LTO transition T_1 decreases under high pressure. The effect of pressure on the LTT phase might be explained similarly. If the CuO_6 octahedra is contracted effectively and the stress on them is decreased in the LTT phase also, the LTT structure may be unstabilized and consequently the orthorhombic structure would be stabilized. A similar effect of the lattice contraction on the LTT structure was observed in the Sr substituted $(\text{La},\text{Ba})_2\text{CuO}_4$ system.¹⁶ By the substitution of smaller Sr ions for Ba, the lattice is contracted, and the structural change to the LTO phase is induced. Furthermore, T_c increases also in this system.

4. SUMMARY

The crystal structure of the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ system ($x=0.03$,

0.08, 0.125, 0.17 and 0.24) has been investigated systematically using a high-resolution neutron powder diffractometer. The decrease in bond lengths of Cu-O and in the tilt angle of the CuO_6 octahedron may be relevant parameters to measure the change in the hole density and hence to determine T_C of the system. It is particularly noted that the bond length of Cu-apical O decreases with increasing x at the rate of about half as large as that of Cu-planar O, which suggests that the apical O also plays some important role for the superconductivity of the system. The bond changes accompanied with the phase transition to LTT in the compound with $x=0.125$ are generally small; however, these changes representing the distortion of the Cu-O plane could be a parameter to characterize the suppression of T_C in this system.

To clarify a correlation between the structural phase transitions and the superconductivity of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with $x=0.125$, experiments on the effects of pressure have been performed. Neutron diffraction experiments directly show that the structural transition temperatures, both HTT-LTO and LTO-LTT, decrease with pressure. The suppression of the LTT phase under a pressure of about 0.6 GPa is particularly noted. The pressure effects on the superconductivity are rather complicated, and a two-step transition to the superconducting states exists even under high pressures. The bulk superconductivity is greatly enhanced when the LTT phase disappears under high pressure. These results support earlier suggestions that there exists a strong correlation between T_C and the crystal structure and that the LTT phase is

detrimental to the superconductivity in this system.

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The authors are grateful to Prof. A. Onodera who provided the sapphire cylinder for neutron diffraction experiments under high pressure. They also wish to thank J.R. Weir III for the technical assistance in neutron diffraction experiments, and M. Takai and A. Tomioka in measuring *ac* susceptibility. The neutron diffraction experiments were carried out at the Oak Ridge National Laboratory under the U.S.-Japan Cooperative Program on Neutron Scattering. The Oak Ridge National Laboratory is managed by Martin Marietta Energy Systems, Inc. for the Division of Materials Science of the U.S. Department of Energy under Contract No. DE-AC05-84OR21400.

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Table I Structural parameters for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ at 115 K. Space group: the orthorhombic $Bmab$ (the non-standard setting of $Cmca$) for $x=0.03$, 0.08 and 0.125, and the tetragonal $I4/mmm$ for $x=0.17$ and 0.24. Atom positions are La/Ba: $8f(0,y,z)$, Cu: $4a(0,0,0)$, $O(1)$: $8e(1/4,1/4,z)$, $O(2)$: $8f(0,y,z)$ in the $Bmab$ space group, and are La/Ba: $4e(0,0,z)$, Cu: $2a(0,0,0)$, $O(1)$: $4c(0,1/2,0)$ and $O(2)$: $4e(0,0,z)$ in the $I4/mmm$ space group.

$x=$	0.03	0.08	0.125	0.17	0.24
La/Ba					
x	0	0	0	0	0
y	-0.0077(3)	-0.0063(3)	-0.0047(4)	0	0
z	0.36112(10)	0.3610(9)	0.36086(8)	0.36071(10)	0.36026(12)
$B(\text{\AA}^2)$	0.13(2)	0.13(2)	0.14(2)	0.15(2)	0.13(3)
Cu					
$B(\text{\AA}^2)$	0.12(3)	0.10(2)	0.17(2)	0.23(3)	0.12(3)
$O(1)$					
x	1/4	1.4	1/4	0	0
y	1/4	1/4	1/4	1/2	1/2
z	0.0077(2)	0.0064(2)	0.0051(2)	0	0
$B(\text{\AA}^2)$	0.28(3)	0.33(3)	0.39(3)	0.45(3)	0.41(4)
$O(2)$					
x	0	0	0	0	0
y	0.0366(3)	0.0301(4)	0.0222(5)	0	0
z	0.1834(2)	0.1828(1)	0.1822(2)	0.1817(2)	0.1811(2)
$B(\text{\AA}^2)$	0.67(7)	0.76(6)	0.89(6)	1.02(4)	1.12(5)

Table I (continued)

$a(\text{\AA})$	5.34070(13)	5.34141(9)	5.33915(9)	3.77993(6)	3.77866(7)
$b(\text{\AA})$	5.40540(13)	5.38390(9)	5.35882(9)		
$c(\text{\AA})$	13.1554(3)	13.2060(2)	13.2414(2)	13.2885(2)	13.3235(3)
R_{WP}	7.70	7.49	7.22	8.50	10.48
R_{P}	6.09	6.09	5.66	6.77	8.14
χ^2	1.19	1.31	1.25	1.18	2.25

Table II Structural parameters for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with $x=0.125$ at 15 K. Rietveld refinements were done in the tetragonal $P4_2/nm$ space group. Atom positions are La/Ba: $8i(x,x,z)$, Cu: $4d(0,0,0)$, $0(1)$: $4e(1/4,1/4,z)$, $0(1')$: $4a(3/4,1/4,0)$ and $0(2)$: $8i(x,x,z)$.

Atom	x	y	z	$B(\text{\AA}^2)$
La/Ba	0.0053(4)	0.0053(4)	0.36059(12)	0.25(2)
Cu	0	0	0	0.18(3)
$0(1)$	1/4	1/4	0.0074(5)	0.28(3)
$0(1')$	3/4	1/4	0	0.50(2)
$0(2)$	-0.0163(6)	-0.0163(6)	0.1821(2)	0.99(7)
$a(\text{\AA})$	5.34837(9)			
$c(\text{\AA})$	13.2352(3)			
R_{WP}	10.25			
R_{p}	7.70			
χ^2	2.04			

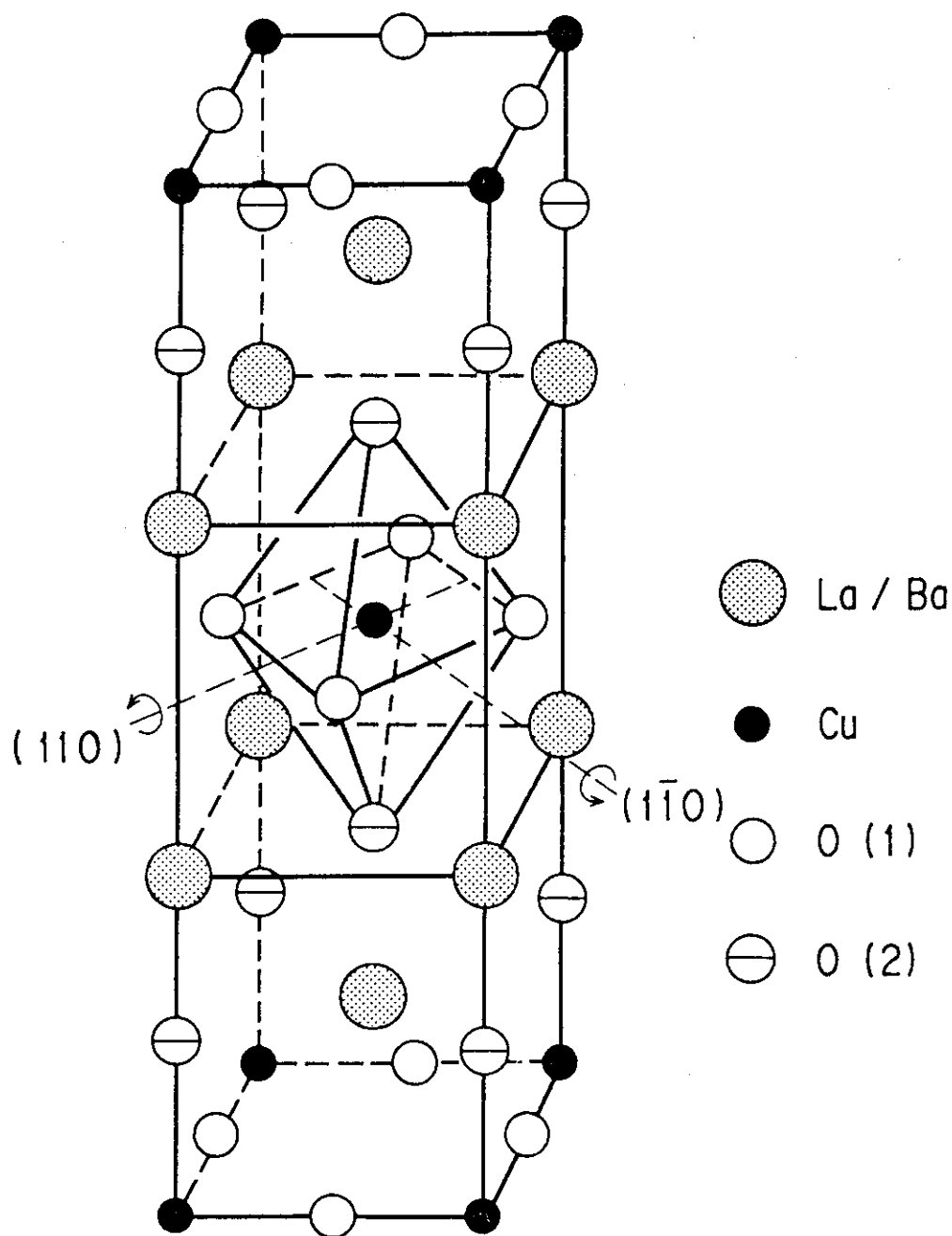


Fig. 1 Schematic diagram of the crystal structure of the tetragonal $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. The structural phase transitions are caused by cooperative rotations of the CuO_6 octahedra around $(1\ 1\ 0)$ and $(1\ \bar{1}\ 0)$ axes.

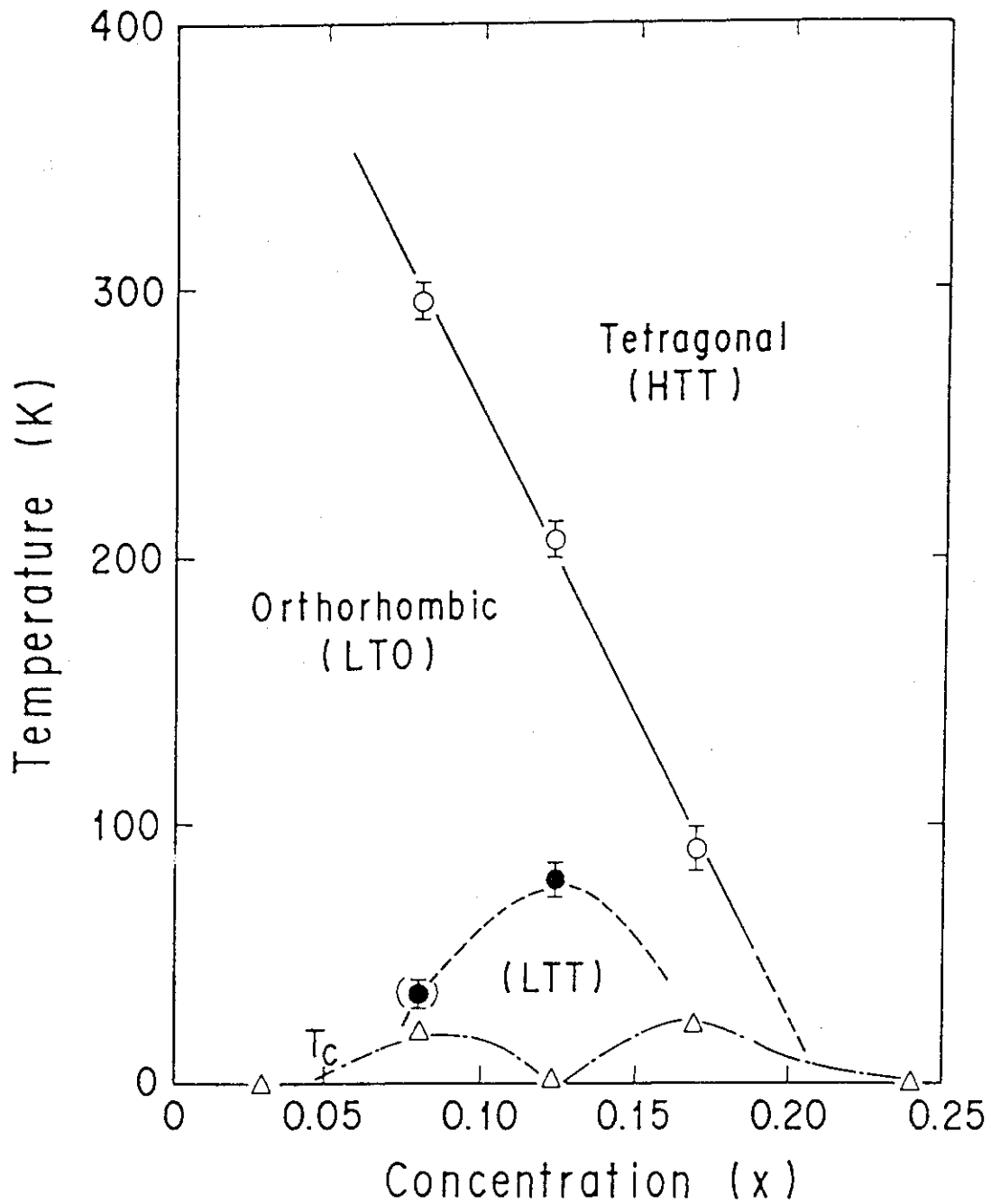


Fig. 2 Phase diagram of the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ system. T_c : the superconducting transition temperature, HTT: the high-temperature tetragonal, LTO: the low-temperature orthorhombic and LTT: the low-temperature tetragonal. For $x=0.08$ the fraction of the LTT phase is estimated to be only 15% at 15 K.

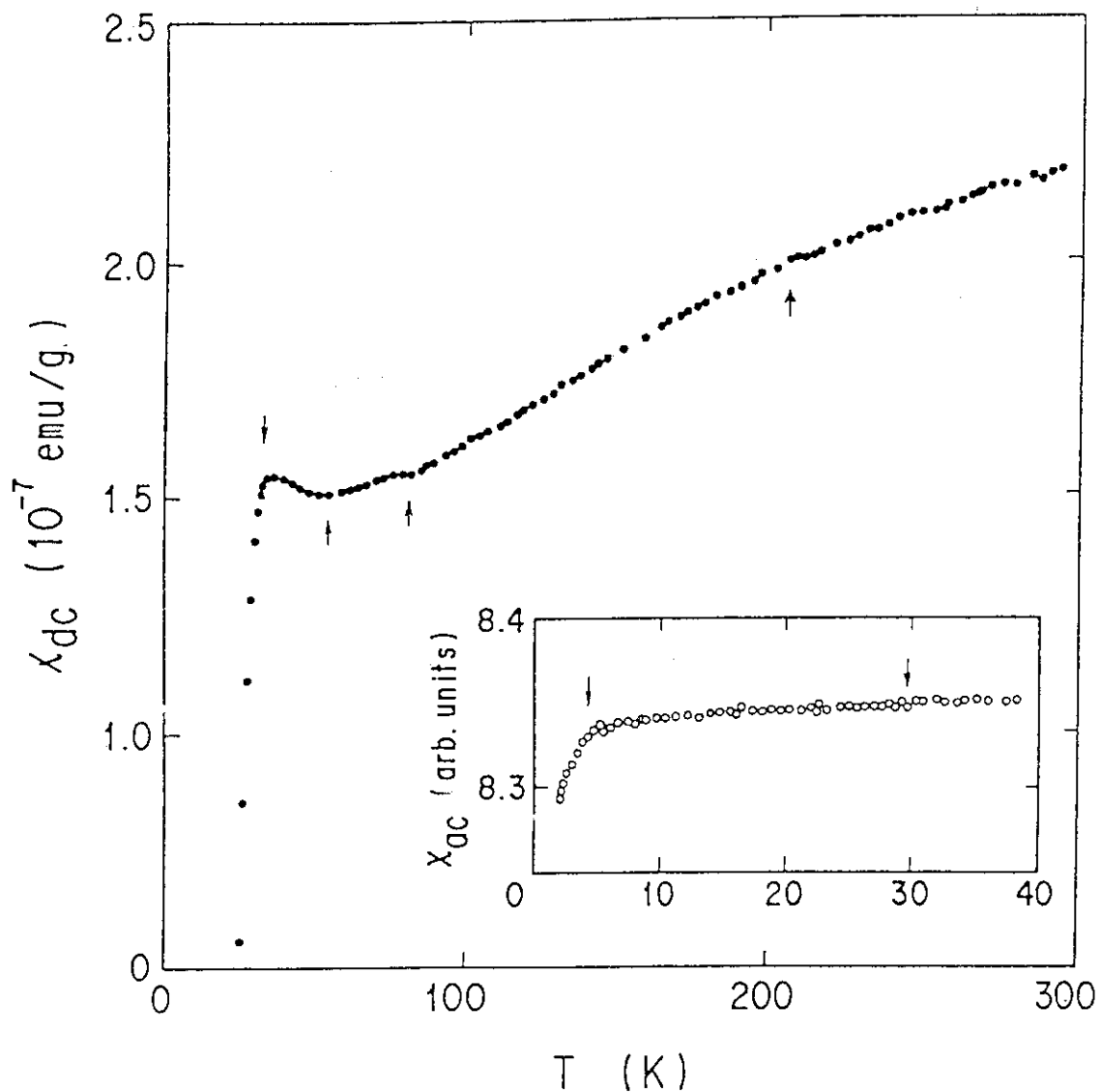


Fig. 3 The temperature dependence of the *dc* magnetic susceptibility of the compound with $x=0.125$. The insert shows the temperature dependence of the *ac* susceptibility signals of the sample. The arrows indicate anomalies in the susceptibility curve. Details are described in the text.

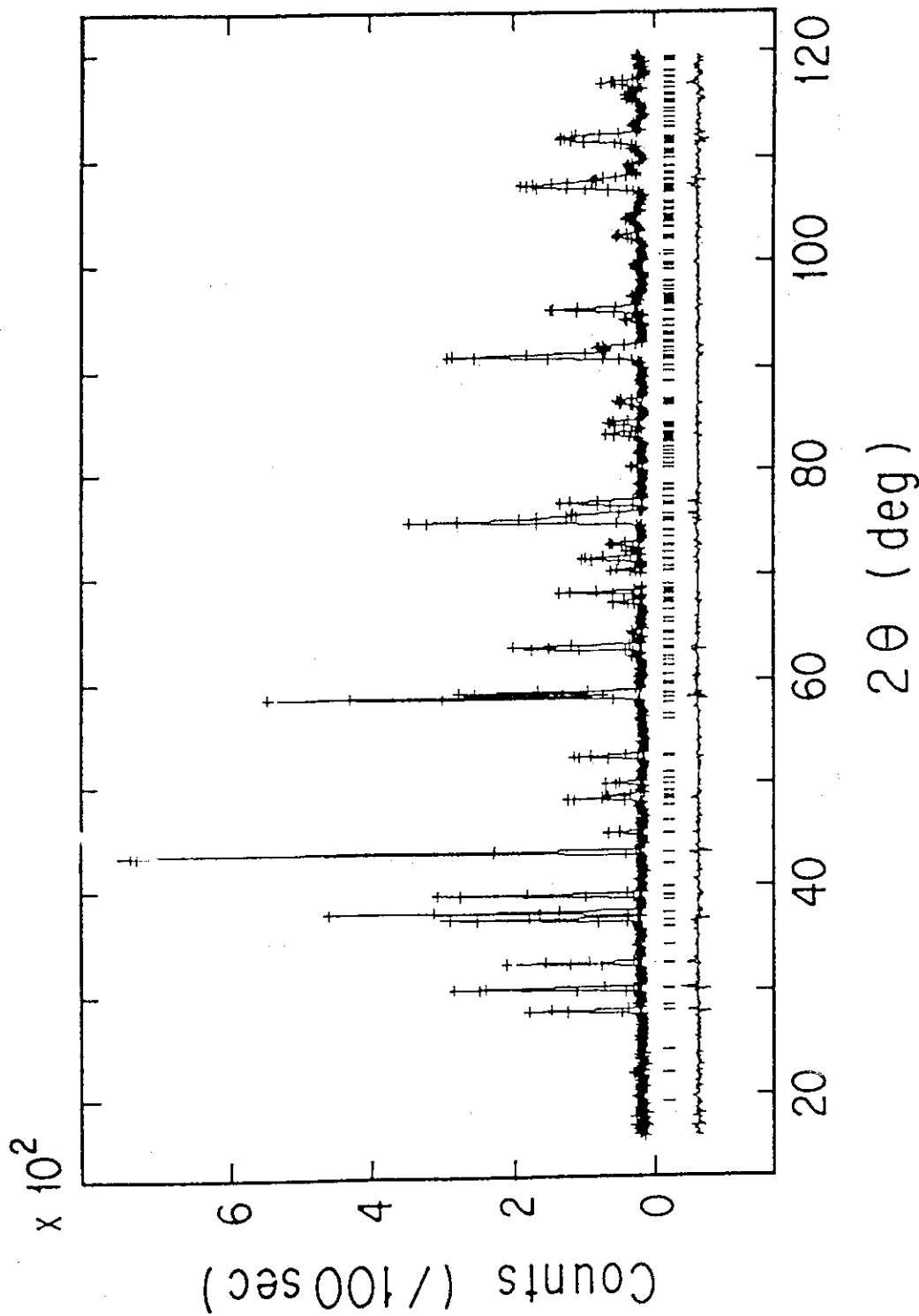


Fig. 4 Rietveld refinement profile for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with $x=0.125$ at 115 K (Space group *Bmab*). The plus signs are the neutron powder diffraction data. The solid line is the calculated profile. Tick marks show the positions of possible Bragg reflections.

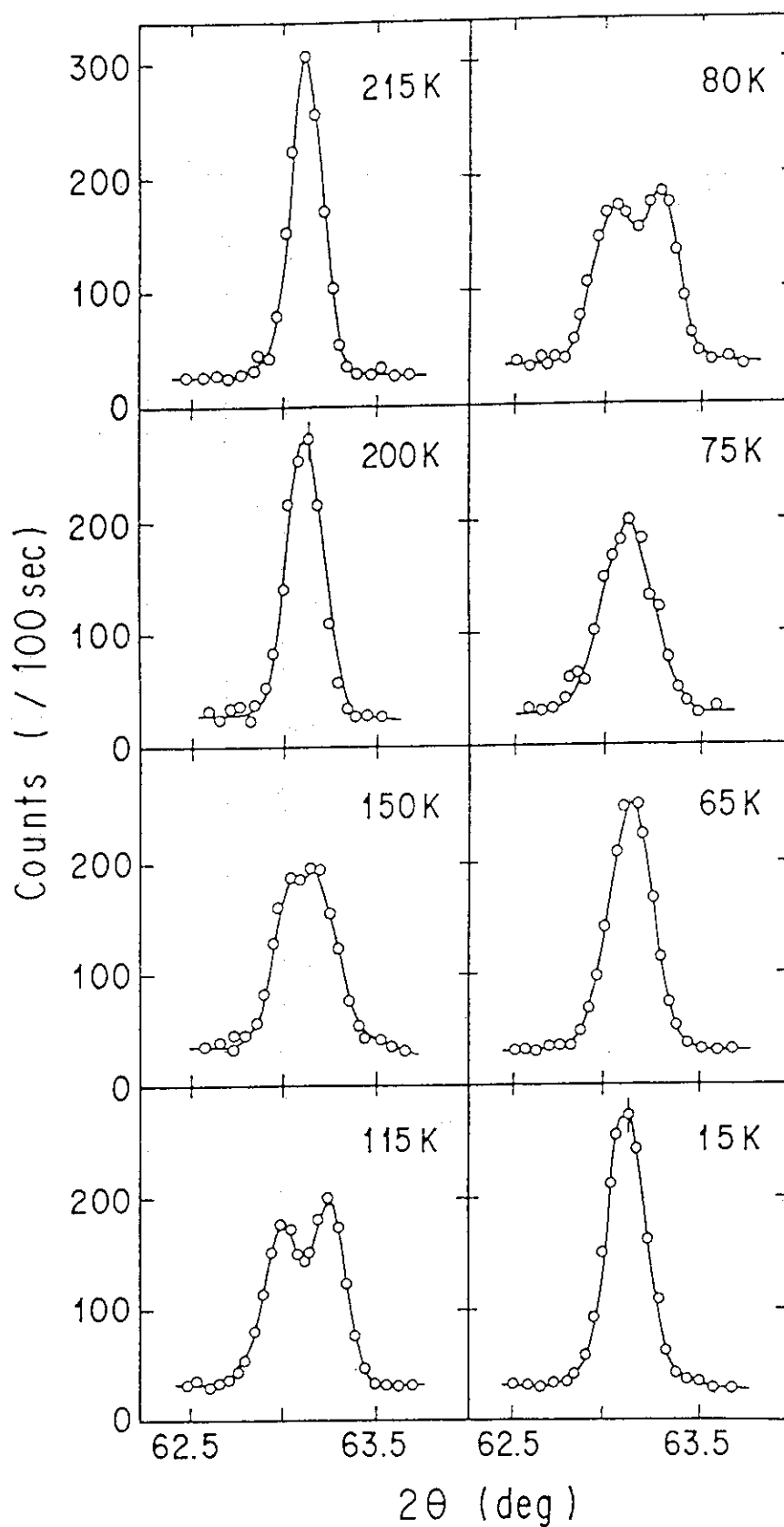


Fig. 5 Temperature dependence of the HTT (2 2 0) reflection of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with $x=0.125$. The data are fitted one or two Gaussians. The bar shows typical errors in the measurements. The instrumental resolution is 0.2 deg.

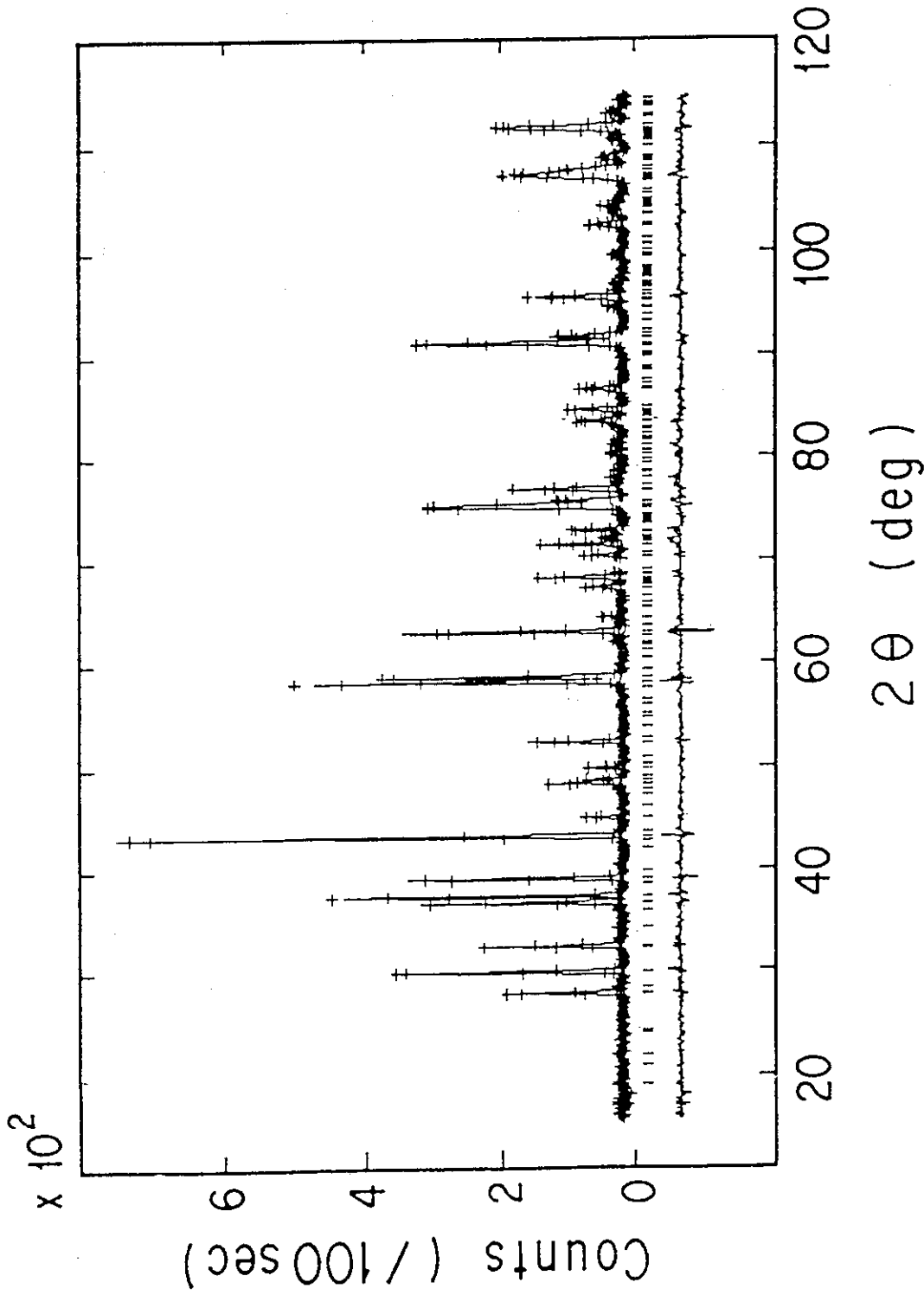


Fig. 6 Rietveld refinement profile for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with $x=0.125$ at 15 K (Space group $P4/n\text{cm}$). The plus signs are the neutron powder diffraction data. The solid line is the calculated profile. Tick marks show the positions of possible Bragg reflections.

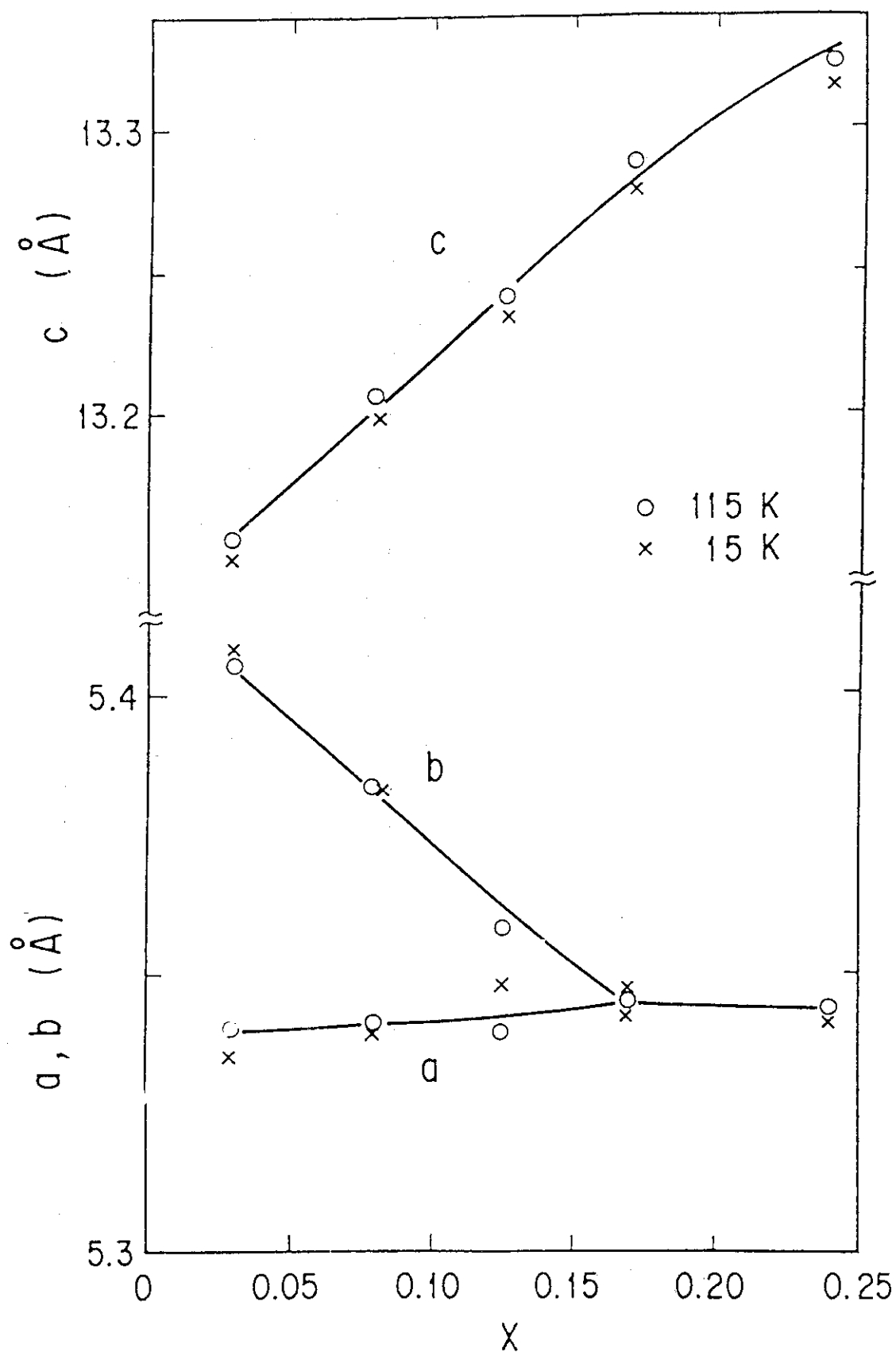


Fig. 7 Lattice parameters a, b and c of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ at 115 K (o) and 15 K (x) as a function of x . For the tetragonal compounds, $\sqrt{2} a$ is plotted.

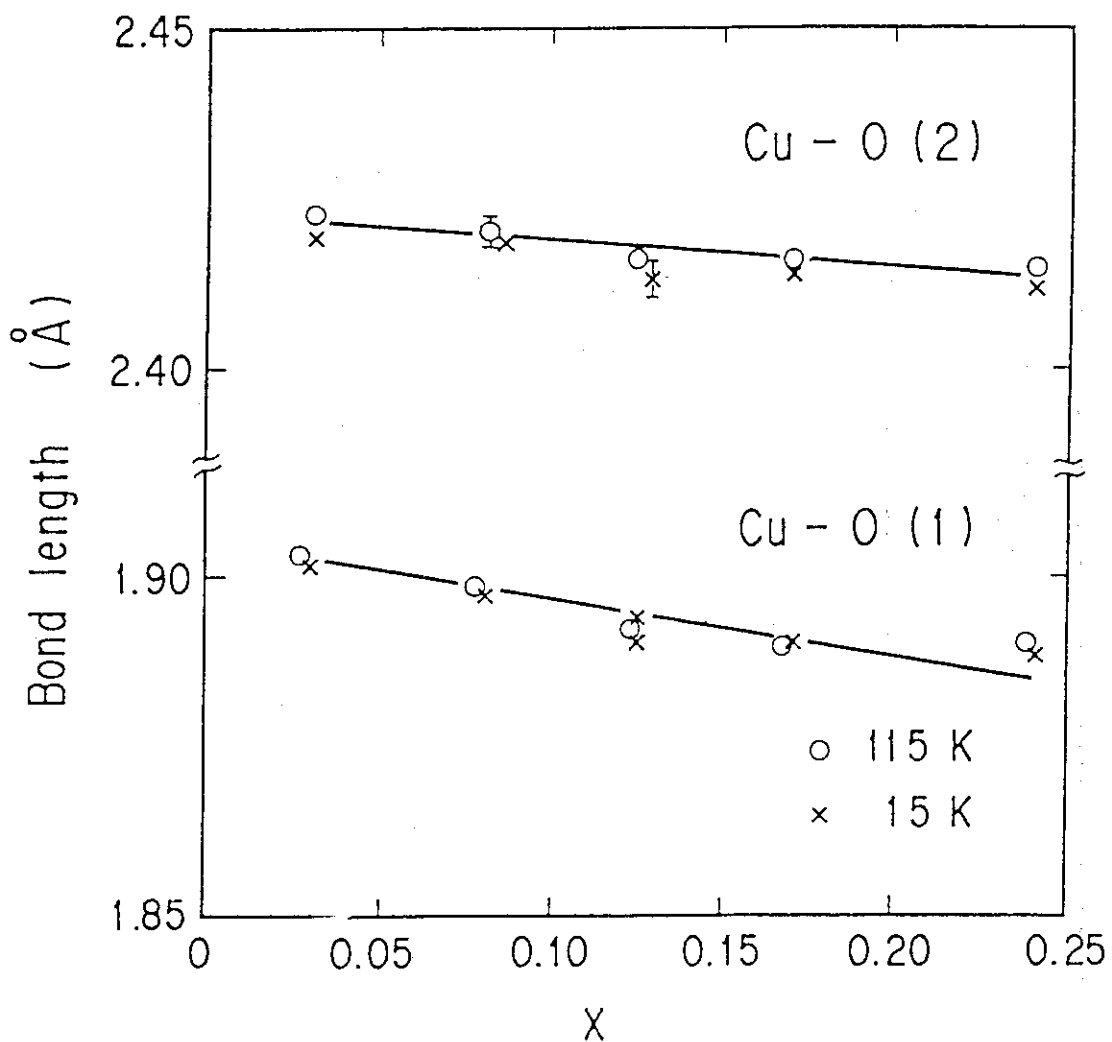


Fig. 8 Bond lengths Cu-planar O(1) and Cu-apical O(2) of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ at 115 K (o) and 15 K (x) as a function of x.

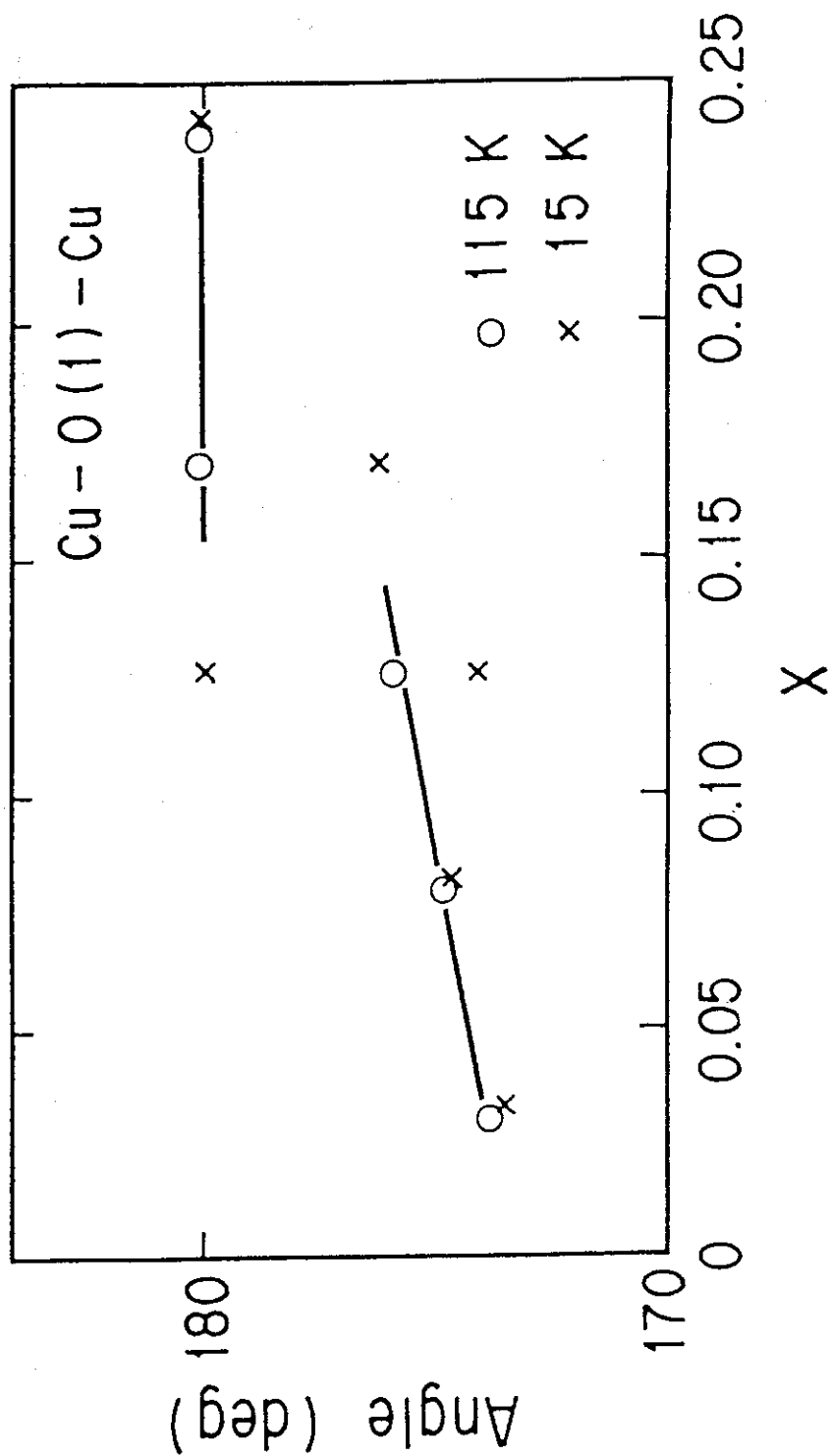


Fig. 9 Bond angle Cu-O(1)-Cu of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ at 115 K (o) and 15 K (x) as a function of x.

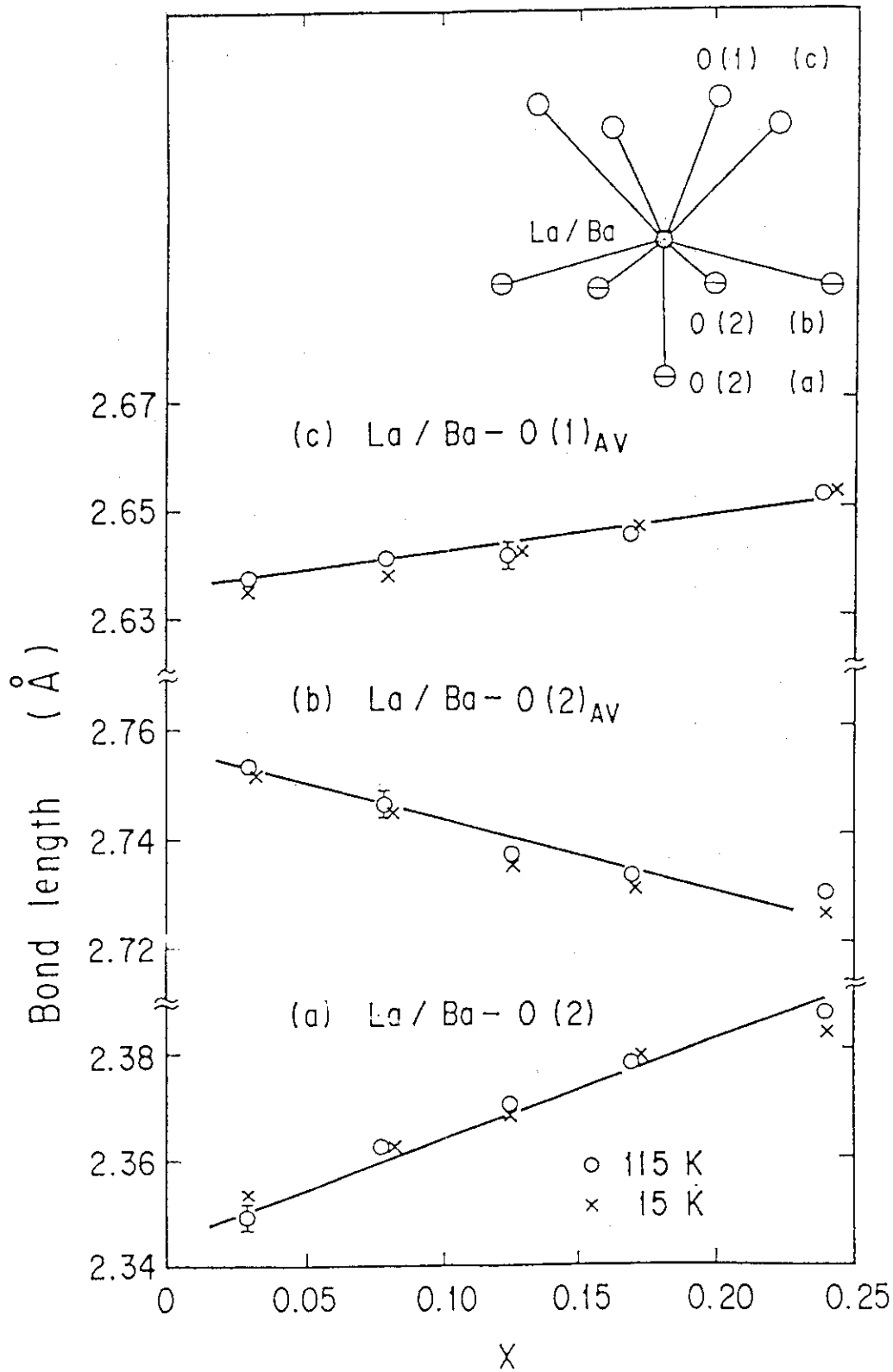


Fig. 10 Bond lengths La/Ba-O(1) and O(2) of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ at 115 K (o) and 15 K (x) as a function of x. (a) the length between La/Ba and the apical O(2) in the plane of the other La/Ba atom, (b) the average length between La/Ba and apical O(2) in its own La/Ba plane and (c) the average length between La/Ba and O(1) in the Cu plane.

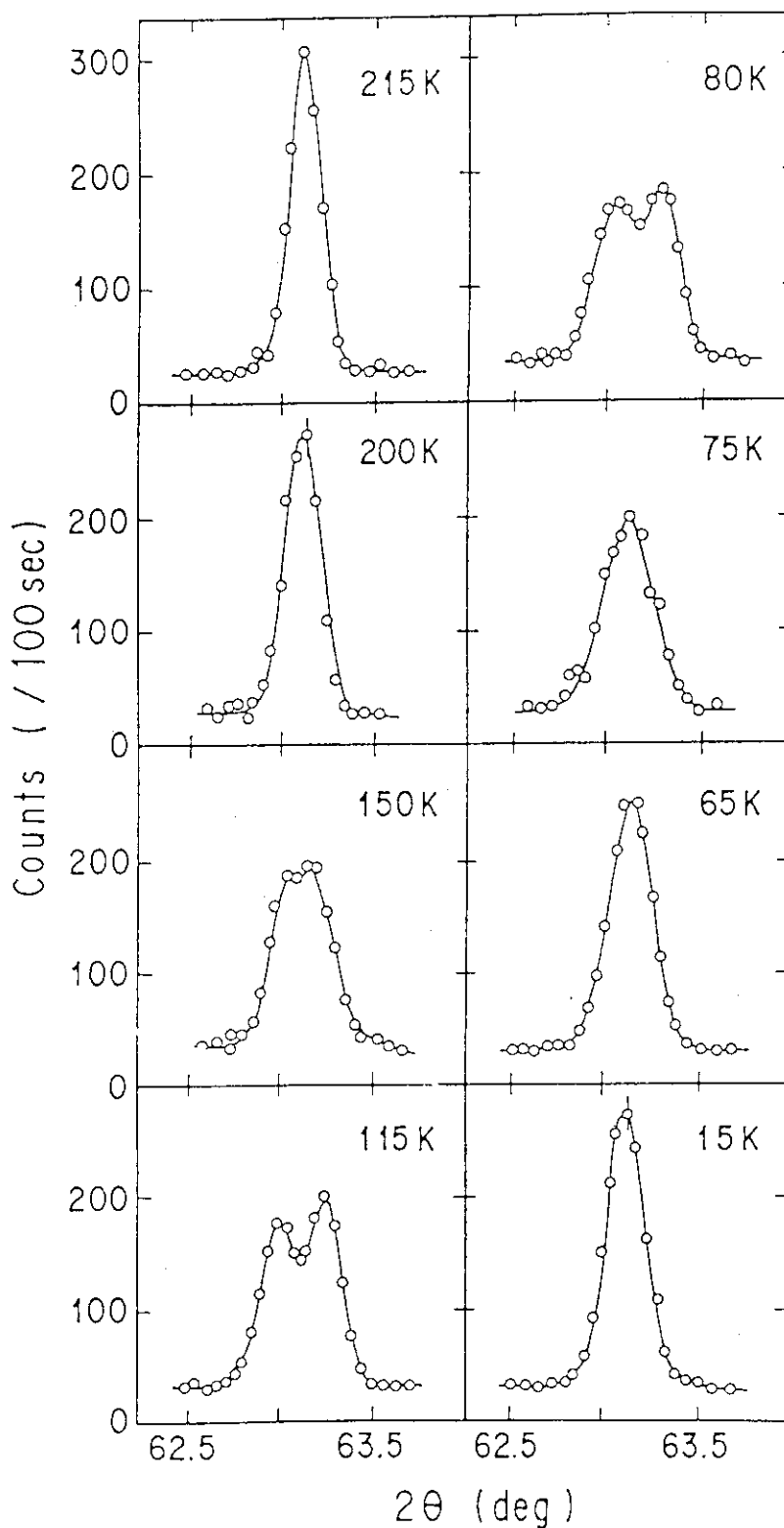


Fig. 11 Temperature dependence of the $(2\ 2\ 0)_{\text{HTT}}$ reflection of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.125$) at ambient pressure. The system undergoes a HTT-LTO phase transition at about 202 K, and then a LTO-LTT phase transition at around 78 K. The data are fitted with one or two Gaussians. The bars show typical errors in the measurements. The instrumental resolution is 0.2 deg.

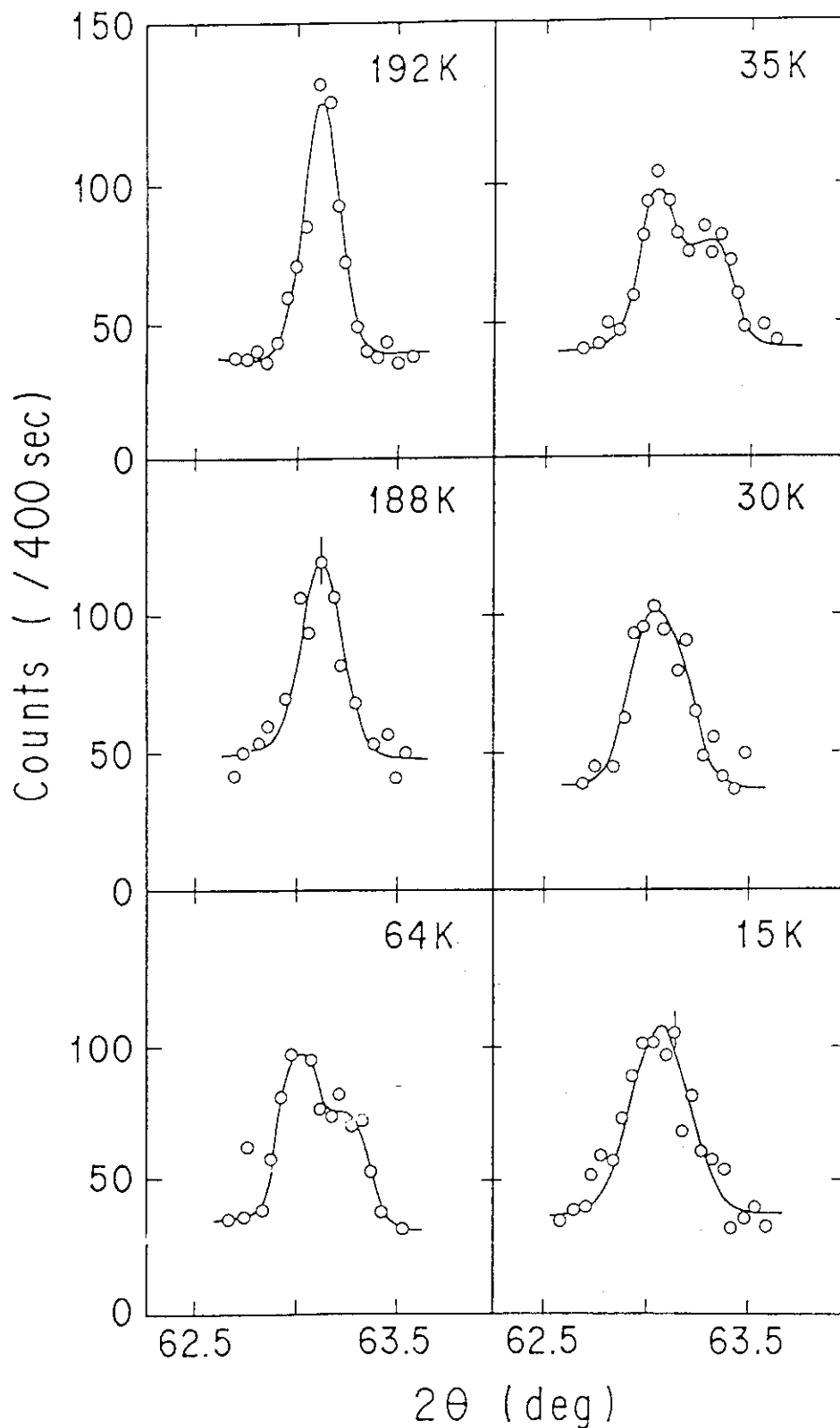


Fig. 12 Temperature dependence of the $(2\ 2\ 0)_{\text{HTT}}$ reflection of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.125$) under 0.35 GPa. The system undergoes a HTT-LTO phase transition at about 190 K, and then a LTO-LTT phase transition at around 30 K. The data are fitted with one or two Gaussians. The bars show typical errors in the measurements. The instrumental resolution is 0.2 deg.

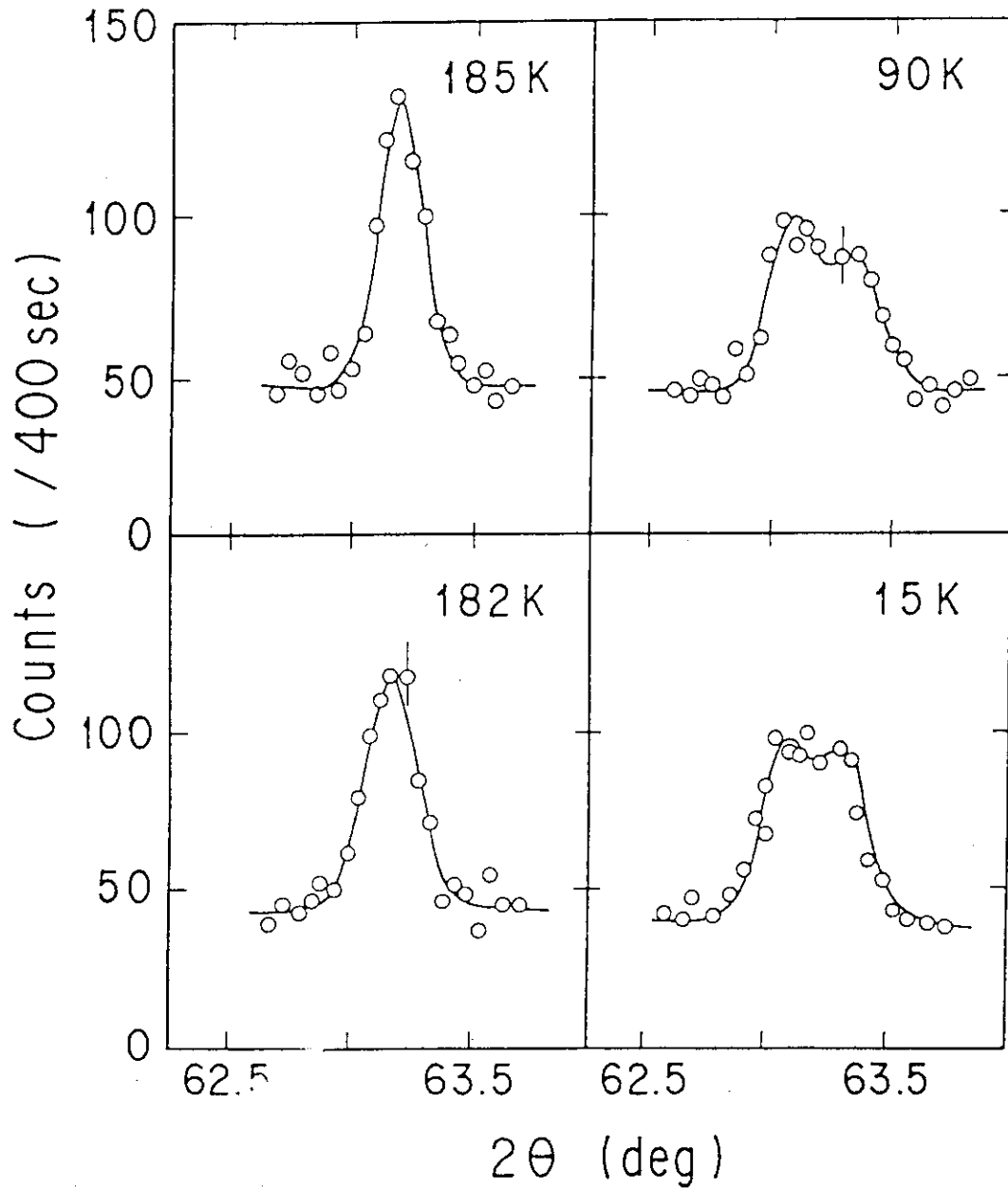


Fig. 13 Temperature dependence of the $(2\ 2\ 0)_{\text{HTT}}$ reflection of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.125$) under 0.7 GPa. The system undergoes a HTT-LTO phase transition at about 183 K. The data are fitted with one or two Gaussians. The bars show typical errors in the measurements. The instrumental resolution is 0.2 deg.

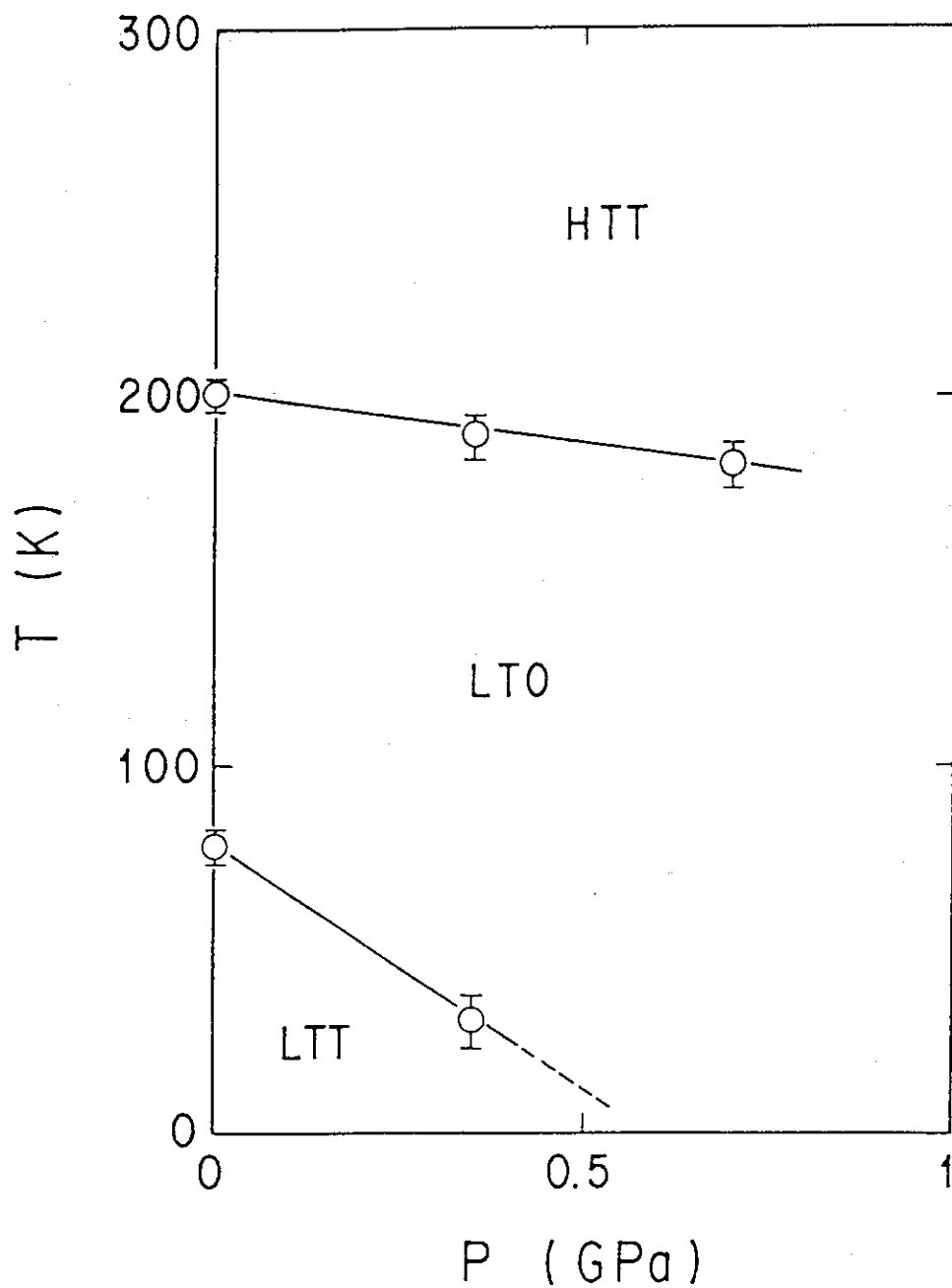


Fig. 14 Temperature-pressure phase diagram on the crystal structure for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.125$). HTT, LTO and LTT denote high-temperature tetragonal, low-temperature orthorhombic and low-temperature tetragonal, respectively.

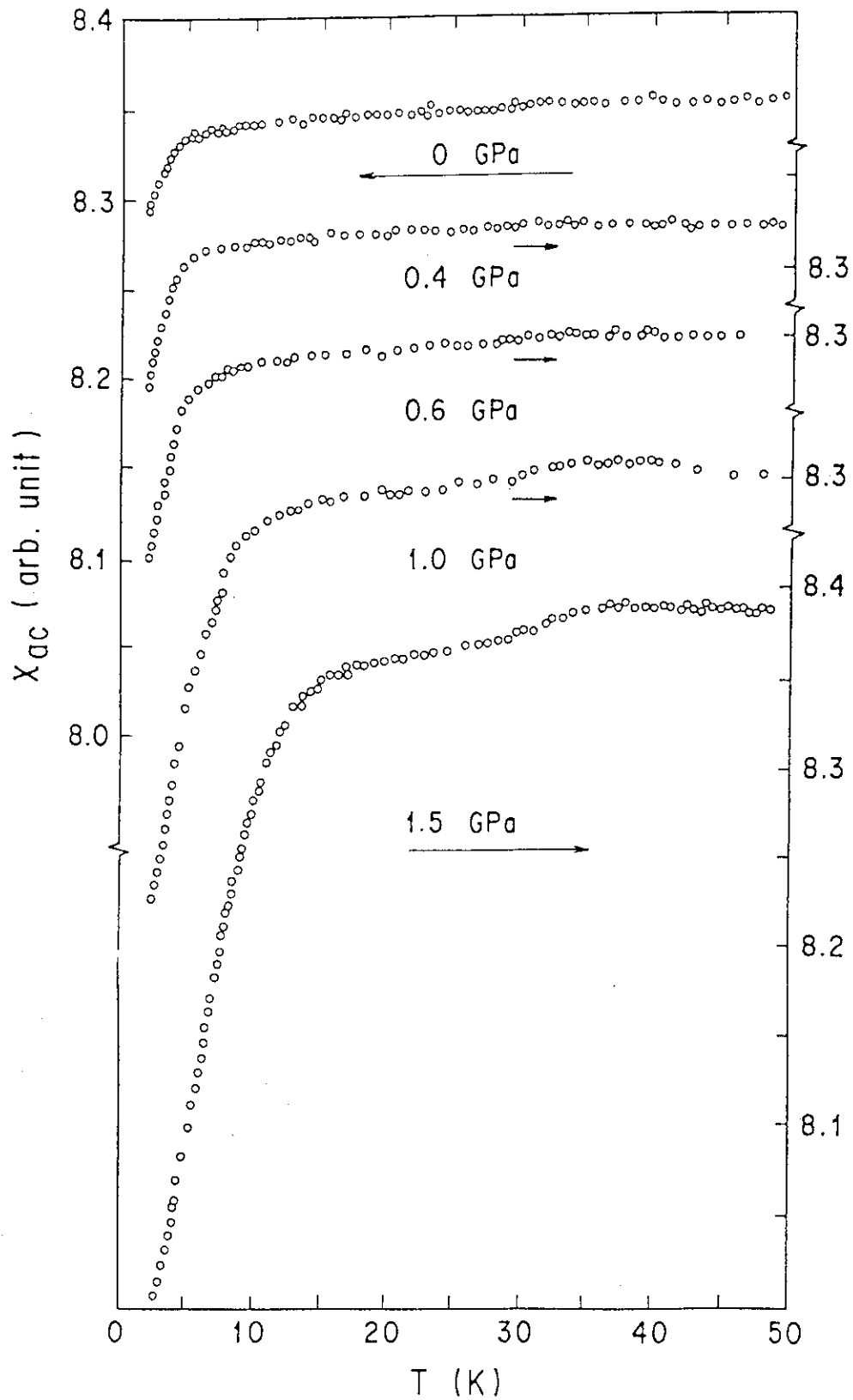


Fig. 15 Temperature dependence of the magnetic susceptibility of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.125$) under high pressures.

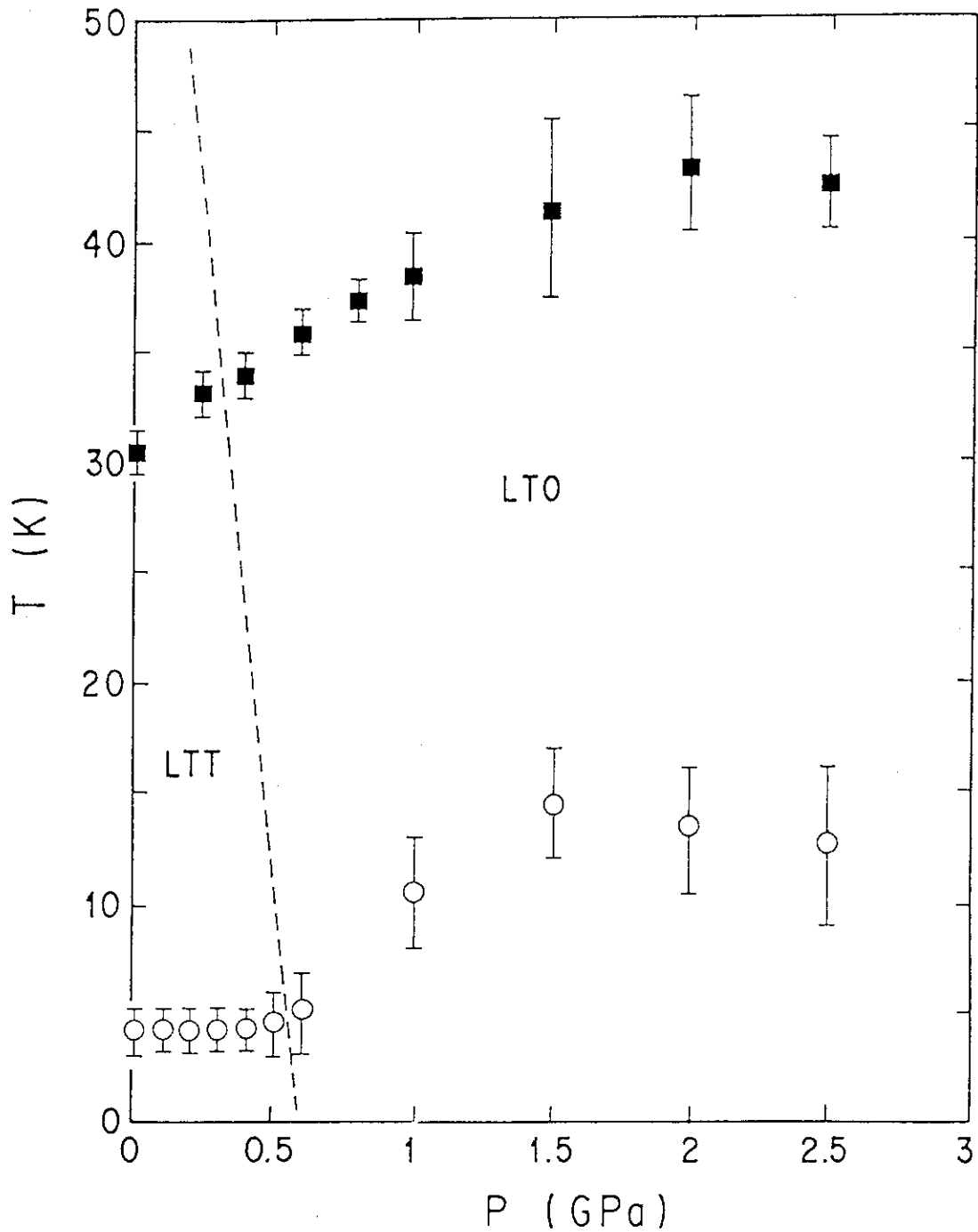


Fig. 16 Pressure dependence of the superconducting transitions for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.125$). The solid squares show the transition temperature of the trace of superconductivity at higher temperatures. The open circles show the transition temperature of the bulk superconductivity at lower temperatures.