Low-temperature structural transitions and T_c suppression in $La_{2-x}M_xCuO_4$ (M = Ba, Sr)

Y. Koyama
Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda, Shinjuku-ku, Tokyo 169, Japan
and Advanced Research Center for Science and Engineering, and Department of Materials Science and Engineering, Waseda University, Ohkubo, Shinjuku-ku, Tokyo 169, Japan

Y. Wakabayashi* and K. Ito
Department of Materials Science and Engineering, Waseda University, Ohkubo, Shinjuku-ku, Tokyo 169, Japan

Y. Inoue
Structural Analysis Section, Research Department, Nissan ARC Ltd., Yokosuka, Kanagawa 237, Japan
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Features of low-temperature structural transitions in $La_{2-x}M_xCuO_4$ (M=Ba, Sr) and $La_{1.880-y}Nd_ySr_{0.120}CuO_4$ have been investigated by means of electron diffraction in order to understand a physical origin of a T_c suppression observed in these oxides. A low-temperature orthorhombic (LTO)-to-*Pccn* structural transition was experimentally found in $La_{1.885}Sr_{0.115}CuO_4$, in addition to both an LTO-to-low-temperature tetragonal (LTT) one in $La_{1.875}Ba_{0.125}CuO_4$ and LTO-*Pccn*-LTT ones in $La_{1.880-y}Nd_ySr_{0.120}CuO_4$, which have already been reported. An important feature of these low-temperature transitions is that the transitions are characterized by the appearance of $\frac{1}{2}\frac{1}{2}0$-type superlattice spots in electron-diffraction patterns. On the basis of other experimental data such as the Seebeck coefficient as well as the present result, the superlattice spots are suggested to be due to the appearance of charge-density waves, which are regarded as an ordered polaron state. The T_c suppression in $La_{2-x}M_xCuO_4$ can therefore be explained in terms of a charge localization due to the charge-density waves.

I. INTRODUCTION

From recent experimental data it has been pointed out that there exists a strong coupling of the lattice and electronic systems in superconductivity of high-T_c superconductors such as $La_{2-x}M_xCuO_4$ (M=Ba, Sr) and $YBa_2Cu_3O_z$. In $La_{2-x}Ba_xCuO_4$, a strong suppression of T_c particularly occurs around $x=0.125$ where a low-temperature orthorhombic (LTO) phase transforms into a low-temperature tetragonal (LTT) one around 60 K on cooling.[1–3] Note that the LTO and LTT structures are, respectively, characterized by the tilt of a CuO_6 octahedron about one of the ⟨110⟩ directions and about two ⟨110⟩ ones with the same tilt angles. The tilt about two ⟨110⟩ directions is equivalent to that about one of the ⟨100⟩ directions. Very recently Kumagai *et al.* found an almost complete suppression of the superconductivity in $La_{2-x}Sr_xCuO_4$ with $x=0.115$ although no low-temperature transition has been reported so far.[4] It should be remarked that the oxygen isotope shift is much enhanced around $x=0.120$ in both systems.[5,6] In addition to $La_{2-x}M_xCuO_4$, a similar suppression has been observed in $La_{2-x-y}R_yM_xCuO_4$ with a replacement of La by R such as Nd.[7–12] A feature of the suppression in La-R-M-Cu-O is that the suppression occurs in a part of the *Pccn* and LTT regions in phase digrams, where the *Pccn* structure is produced from the tilt of the octahedron about two ⟨110⟩ directions with different tilt angles. From these experimental data, a correlation between the suppression of the superconductivity and low-temperature transitions is still an open question.

The transition to the LTT phase results in a buckling of the CuO_2 plane about one of the ⟨100⟩ directions, which produces two inequivalent sites for four oxygen atoms of the CuO_6 octahedron in the CuO_2 plane. In the LTT phase, two oxygen atoms are in the CuO_2 plane while other two atoms move out of it. Barisic and Zelenko suggested that the two inequivalent sites lead to an oxygen-oxygen charge transfer, which result in charge-density waves (CDW's) in the LTT phase.[13] In other words, the stabilization of the LTT phase is due to the appearance of the CDW in the CuO_2 plane. According to Bonesteel, Rice, and Zhang,[14] on the other hand, a spin-orbit coupling in doped La_2CuO_4 gives rise to a novel coupling between phonons related to the tilt of the octahedron and electrons and a large band splitting in the LTT phase is expected. Because of a large gap at (π00) in the LTT structure, the band splitting can help stabilizing the LTT phase.

In this situation, in order to clarify the correlation between the T_c suppression and the low-temperature structural transitions, we have investigated features of the low-temperature transitions in the La cuprates mainly by means of electron diffraction. In electron-diffraction patterns, as a result, we found both forbidden spots indicating a low-temperature transition in $La_{1.885}Sr_{0.115}CuO_4$ and superlattice spots suggesting the appearance of the CDW in particular concentrations of Ba and Sr in the La cuprates. Although preliminary data were already reported in our previous papers,[15] in this paper we describe the details of experimentally obtained features of the low-temperature transitions and discuss the origin of the T_c suppression in the La cuprates.

II. EXPERIMENTAL PROCEDURE

In the present work, we have examined features of low-temperature structural transitions for $La_{2-x}Ba_xCuO_4$ around $x=0.125$, $La_{2-x}Sr_xCuO_4$ around $x=0.120$, and $La_{1.880-y}Nd_ySr_{0.120}CuO_4$. Since a sample preparation for both La-Sr-Cu-O and La-Nd-Sr-Cu-O is basically the same as that for La-Sm-Sr-Cu-O, which was described in our previous paper,[8] only a procedure for La-Ba-Cu-O is mentioned here. Samples of La-Ba-Cu-O were made from initial powders of La_2O_3, $BaCO_3$, and CuO. Powder samples were obtained by a mechanical mixing and subsequent calculation at 1173 K for 24 h in air. Pellets made from these powders were sintered for 24 h in air in the following four temperatures; 1223, 1273, 1323, and 1373 K, and annealed at 673 K for 48 h in O_2. Flakes obtained by crushing the pellets were used as a specimen for the observation by transmission electron microscopy. The observation was made by means of an H-800-type transmission electron microscope equipped with a liquid-helium reservoir in a temperature range between 15 K and room temperature. Intensities of diffraction spots in electron-diffraction patterns were measured by photodensitometry.[8] It should be remarked that owing to both the stability of temperature in taking patterns and the effect of electron beam irradation intensities were mainly measured from patterns obtained during the heating process. In other words, we have seriously examined a change in the pattern, which is related to an annihilation of the diffraction spots characterizing the low-temperature phases. The reversibility of the intensities during the cooling and subsequent heating processes was, of course, checked in the present work.

La-Ba-Cu-O exhibits high-temperature tetragonal-(HTT) -LTO-LTT successive transitions while HTT-LTO-*Pccn*-LTT transitions occur in La-Nd-Sr-Cu-O. From neutron-diffraction data,[16,17] these transitions are well understood to be due to a condensation of phonon modes at the X point in the HTT structure, which are directly related to the tilt of the CuO_6 octahedron. When order parameters of the transitions are assumed to be (Q_1,Q_2) corresponding to the phonons with $\mathbf{q}=\frac{1}{2}[110]$ and $\frac{1}{2}[1\bar{1}0]$, the LTT structure is represented by $|Q_1|=|Q_2|\neq 0$ and the *Pccn* one by $|Q_1|\neq|Q_2|$ ($|Q_1|\neq 0$, $|Q_2|\neq 0$), while the LTO one is characterized as $|Q_1|\neq 0$ ($|Q_2|=0$) or $|Q_2|\neq 0$ ($|Q_1|=0$). In electron-diffraction patterns, then $(h/2)(k/2)l$ superlattice spots (h,k, odd integer: l, integer) appear for the LTO, *Pccn*, and LTT structures although an extinction rule of the superlattice spots for the LTO structure is different from that for the *Pccn* and LTT ones. Note that there exists no superlattice spot with $l=0,(h/2)(k/2)0$, in the patterns. Among these structures, a characteristic feature of diffraction patterns for the *Pccn* and LTT structures is the appearance of forbidden spots with $l=0$ in the HTT and LTO ones, the 100 and 010 spots, although it is unfortunately impossible to determine either the *Pccn* structure or the LTT one only from their extinction rules. Experimental data obtained by other techniques such as x-ray and neutron diffractions were needed for a final structural determination. On the basis of these features of the crystal structures in the low-temperature transitions, in this paper we represent electron-diffraction patterns with an electron incidence parallel to the [001] direction. In addition, diffraction spots in patterns are indexed in terms of the HTT structure.

III. EXPERIMENTAL RESULTS

A. Features of the LTO-to-LTT transition in $La_{2-x}Ba_xCuO_4$

Let us first describe features of electron-diffraction patterns in the low-temperature transition of La-Ba-Cu-O. Figure 1 represents an electron-diffraction pattern taken from $La_{1.875}Ba_{0.125}CuO_4$ at 19 K. In the pattern, there exist two types of diffraction spots, in addition to fundamental spots due to the K_2NiF_4-type structure with no distortion. One is the above-mentioned forbidden spots marked by A and clearly indicates that the specimen has the LTT structure, as was determined by x-ray and neutron diffractions.[1-3] The other is a superlattice spot B located at $(h/2)(k/2)0$, the X point, which is a characteristic feature of the pattern in $La_{1.875}Ba_{0.125}CuO_4$. As is well known in electron diffraction, it is possible that the superlattice spot originates from multiple scattering. Although it is hard to avoid the multiple scattering, we tried to check a possibility of the scattering by rotating the specimen about the [110] direction. Figure 2 shows a diffraction pattern at 19 K, in which only the spots along the [110] direction are basically excited. The superlattice spots are clearly seen at the $\frac{1}{2}\frac{1}{2}$ 0-type positions, so that the spots do not seem to be due to the multiple scattering. Because there is no superlattice spot resulting from the

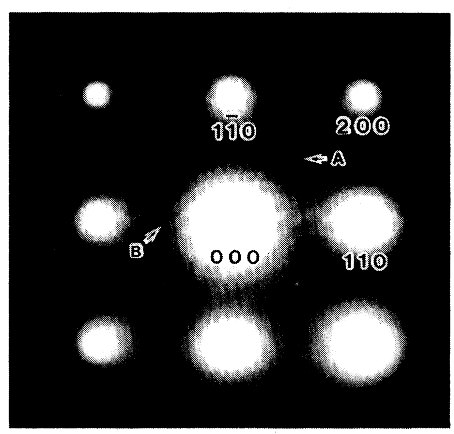

FIG. 1. Electron-diffraction pattern of $La_{1.875}Ba_{0.125}CuO_4$ at 19 K. An electron incidence is parallel to the [001] direction. Diffraction spots are indexed in terms of the HTT structure.

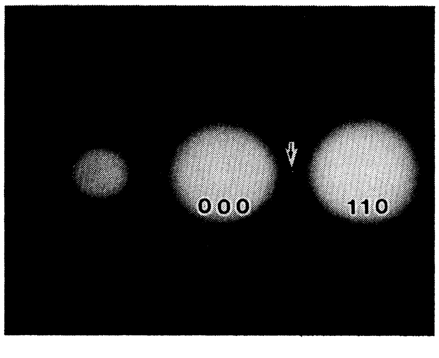

FIG. 2. Electron-diffraction pattern of $La_{1.875}Ba_{0.125}CuO_4$, taken at 19 K. Only the spots along the [110] direction are basically excited in order to check the multiple scattering. $\frac{1}{2}\frac{1}{2}0$-type superlattice spots are seen in the pattern, as indicated by an arrow.

tilt of the octahedron in the case of the electron incidence parallel to the [001] direction, another origin of the superlattice spot should be discussed on the basis of other experimental data as well as the present result. The details of the discussion on the origin will be described in Sec. V. In addition, a feature of the superlattice spot is that an intensity of the spot with $\mathbf{q}=\frac{1}{2}[1\bar{1}0]$ is much weaker than that with $\mathbf{q}=\frac{1}{2}$ [110].

Figure 3 shows intensities at the 100 and $\frac{1}{2}\frac{1}{2}0$ positions in diffraction patterns at various temperatures for $La_{1.875}Ba_{0.125}CuO_4$. In the figure, a thick solid line is a theoretical curve calculated on the basis of Landau theory for the LTO-to-LTT transition and a thin solid line for the $\frac{1}{2}\frac{1}{2}0$ position is just a visual guide. The details of the analysis using the Landau theory will be mentioned later. As was described earlier, we took diffraction patterns mainly during the heating process in the present work. Hence, we explain features of a change in both intensities on heating. When the specimen is heated up from 19 K, the intensity at the 100 position is lowered and exhibits a rapid decrease around 70 K, which should correspond to the LTT-to-LTO transition on heating. Actually, the theory predicts a transition temperature $T_{LTO-LTT}$ of 69 K. A characteristic feature is that on further heating the intensity decreases gradually until about 180 K. It should be remarked that the LTO-to-HTT transition was found to take place at 180 K from diffraction patterns with different incidences. In other words, a finite intensity is still observed at the 100 position in the LTO phase and may support a proposal made by Billinge, Kwei, and Takagi that a long-range structure of the LTO phase results from coherent superpositions of the local LTT variants.[18] As for the $\frac{1}{2}\frac{1}{2}0$ superlattice spot, when the temperature is raised, the intensity decreases and reaches zero at $T_{LTO-LTT}$ of 69 K. The superlattice spot is then detected only in the LTT phase. That is, the superlattice spot exhibits a different behavior from the 100-type forbidden spot. This also suggest that the multiple scattering is not an origin of the superlattice spot.

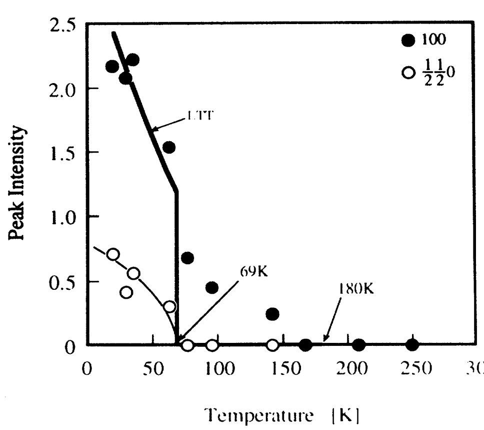

FIG. 3. Change in intensities at the 100 and $\frac{1}{2}\frac{1}{2}0$ positions in reciprocal space as a function of temperature. Measured intensities of the spots are normalized with respect to a background intensity and are plotted by solid circles for the 100 position and open circles for the $\frac{1}{2}\frac{1}{2}0$ one.

In addition to $x=0.125$, we have checked the appearance of the forbidden and superlattice spots in $La_{2-x}Ba_xCuO_4$, where no transition has been reported so far. As a result, the present work confirmed the previous result experimentally. In other words, the low-temperature transition in $La_{2-x}Ba_xCuO_4$ is restricted only around $x=0.125$.

B. Features of a low-temperature transition in $La_{2-x}Sr_xCuO_4$

Because the strong T_c suppression was recently found in $La_{2-x}Sr_xCuO_4$ with $x=0.115$,[4] a low-temperature structural transition seems to be expected, just as in the case of $La_{1.875}Ba_{0.125}CuO_4$ around $x=0.125$. From this motivation, we have examined the details of crystal structures of $La_{2-x}Sr_xCuO_4$ around $x=0.120$ in lower temperatures. Figure 4 is an electron-diffraction pattern of $La_{1.885}Sr_{0.115}CuO_4$ at 17 K. As is seen in Fig. 4, features of the pattern in $La_{1.885}Sr_{0.115}CuO_4$ are quite the same as those in $La_{1.875}Ba_{0.125}CuO_4$. That is, both the 100-type forbidden and $\frac{1}{2}\frac{1}{2}0$-type superlattice spots are clearly observed in the pattern. This obviously indicates that $La_{2-x}Sr_xCuO_4$ with $x=0.115$ exhibits a low-temperature transition accompanying the appearance of the superlattice spots at the $\frac{1}{2}\frac{1}{2}0$-type positions of diffraction patterns. Because the low-temperature transition has not been found by x-ray and neutron diffractions, the transition should not accompany a change in a crystal system. A crystal structure of the low-temperature phase is then understood to be the *Pccn* structure with the orthorhombic system, not the LTT structure with the tetragonal system. Therefore, there exists the LTO-to-*Pccn* transition in $La_{1.885}Sr_{0.115}CuO_4$.

Intensities at the 100 and $\frac{1}{2}\frac{1}{2}0$ positions in reciprocal space of $La_{1.885}Sr_{0.115}CuO_4$, measured by photodensi-

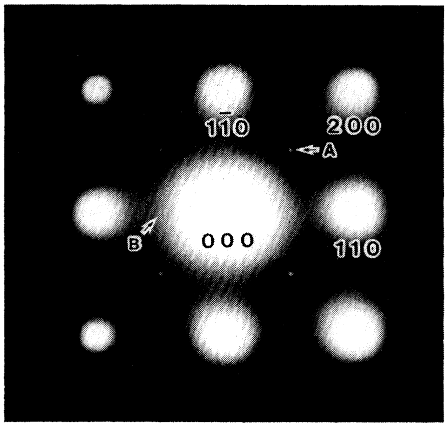

FIG. 4. Electron-diffraction pattern of $La_{1.885}Sr_{0.115}CuO_4$ at 17 K. In the pattern, 100-type forbidden spots A and $\frac{1}{2}\frac{1}{2}0$-type superlattice spots B are clearly observed.

tometry, are plotted in Fig. 5. Note that solid lines in the figure are depicted as a visual guide . When the specimen is heated from 17 K, both intensities decrease together and become zero at 104 K. This means that the *Pccn*-to-LTO transition takes place at 104 K in $La_{1.885}Sr_{0.115}CuO_4$ on heating and the $\frac{1}{2}\frac{1}{2}0$-type superlattices pots appear in the *Pccn* phase, as in the case of the LTT phase of $La_{1.875}Ba_{0.125}CuO_4$. That is, the same thing happens in $La_{2-x}M_xCuO_4$ (M =Ba,Sr) although the concentration of x =0.115 for M =Sr is different from that of x =0.125 for M =Ba. In addition to the LTO-to-*Pccn* transition, an analysis of diffraction patterns with other incidences showed that the LTO-to-HTT transition occurs at 250 K. As is seen in Fig. 5, no finite intensity at the 100 position can be detected in the LTO phase, unlike $La_{1.875}Ba_{0.125}CuO_4$.

We have also examined detailed features of crystal structures in $La_{2-x}Sr_xCuO_4$ with x different from x =0.115. In the vicinity of x =0.115, only a structural fluctuation related to the low-temperature transition was found in lower temperatures. The LTO-to-*Pccn* transition is then concluded to occur only in $La_{2-x}Sr_xCuO_4$ with x =0.115.

C. Features of low-temperature transitions in $La_{1.880-y}Nd_ySr_{0.120}CuO_4$

Crawford *et al.* reported that $La_{1.880-y}Nd_ySr_{0.120}CuO_4$ exhibit the LTO-to-*Pccn* transition in $0<y\leq 0.200$ and the LTO-*Pccn*-LTT successive transitions in $0.200<y\leq 0.600$.[7] Note that T_c is strongly suppressed in the latter range. Our investigation on the low-temperature transitions confirmed the existence of these transitions. Among oxides examined in the present work, we describe experimental data on $La_{1.480}Nd_{0.400}Sr_{0.120}CuO_4$ here. An electron-diffraction pattern of this oxide, taken at 16 K, is shown in Fig. 6. The pattern exhibits the exactly same features as Figs. 1 and 4; that is, the existence of the 100-type forbidden and $\frac{1}{2}\frac{1}{2}0$-type superlattice spots. A feature of the pattern in La-Nd-Sr-Cu-O is that intensities of both spots are much stronger than those for La-Ba-Cu-O and La-Sr-Cu-O. From a change in the intensities measured from diffraction patterns taken at various temperatures, it was also understood that there exist the LTT-to-*Pccn* transition around 100 K and the *Pccn*-to-LTO one around 150 K. Since features of the change are essentially the same as those shown in Figs. 3 and 5, a temperature dependence of both intensities in $La_{1.480}Nd_{0.400}Sr_{0.120}CuO_4$ is not shown here. It should be remarked that the determined transition temperatures are consistent with the stronger intensities of the forbidden and superlattice spots at 16 K, but much higher than

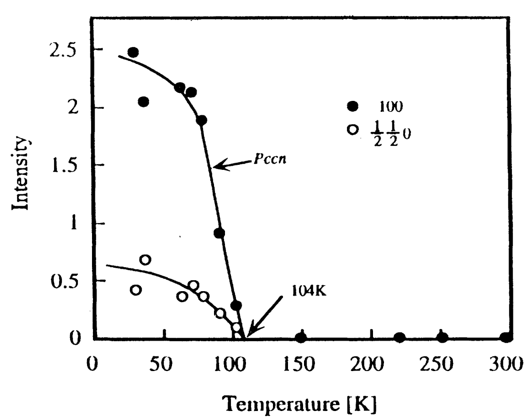

FIG. 5. Change in intensities of the 100 forbidden and $\frac{1}{2}\frac{1}{2}0$ superlattice spots as a function of temperature for $La_{1.885}Sr_{0.115}CuO_4$. Measured intensities of the forbidden and superlattice spots are, respectively, plotted by solid and open circles.

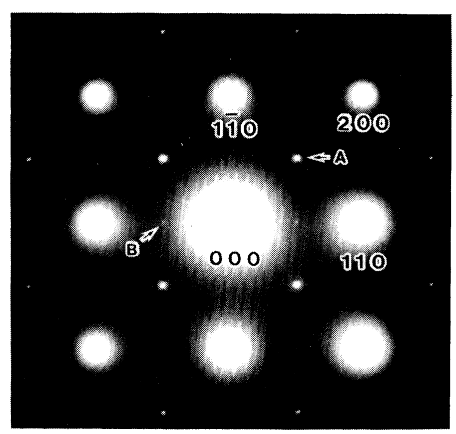

FIG. 6. Electron diffraction pattern of $La_{1.480}Nd_{0.400}Sr_{0.120}CuO_4$ at 16 K. There exist both the 100-type forbidden spots A and the $\frac{1}{2}\frac{1}{2}0$-type superlattice spot B in the (001) diffraction pattern.

those reported by Crawford *et al.*[7] The reason for this discrepancy is not understood yet. In addition to these features, the $\frac{1}{2}\frac{1}{2}0$-type superlattice spots were found to appear in the *Pccn* and LTT phases below the LTO-to-*Pccn* transition. This is obviously compatible with the result obtained in $La_{2-x}M_xCuO_4$ (M=Ba, Sr).

IV. ANALYSIS OF THE LTO-TO-LTT TRANSITION ON THE BASIS OF LANDAU THEORY

As is understood from Fig. 3, it is difficult to determine the transition temperature of the LTO-to-LTT transition in $La_{1.875}Ba_{0.125}CuO_4$ because of the finite intensity in the LTO phase. Then we apply the Landau theory to the LTO-to-LTT transition in $La_{1.875}Ba_{0.125}CuO_4$ in order to do it. According to Axe *et al.*,[2] a free energy for the LTO-to-LTT transition can be expanding using a set of the order parameters (Q_1, Q_2), as

$$F=F_0+a_0(T-T_0)(Q_1^2+Q_2^2)+b(Q_1^2+Q_2^2)^2 +c(Q_1^4+Q_2^4) +d(Q_1^8+Q_2^8)+e(Q_1^{12}+Q_2^{12}) , \quad (1)$$

where F_0 is the free energy of the HTT phase, and T and T_0 are the temperature and transition temperature of the HTT-to-LTO transition, respectively. Note that the above free energy can explain the LTO-to-LTT transition by assuming $c=c_0T^2+c'$, just as in the case of the LTO-*Pccn*-LTT transition.[8] After the order parameters were obtained by minimizing the above free energy, a theoretical intensity of the forbidden spot at each temperature was calculated by substituting atomic coordinates obtained from the parameters into a structure factor in the kinematical theory of diffraction. As for the temperature, the calculation was made using T normalized with respect to T_0 and the normalized temperature is converted into an actual temperature. When it is assumed that $a_0=1.00$, $T_0=1.00$, $b=4.23\times10^3$, $c_0=-2.52\times10^{-1}$, $c'=4.00\times10^{-2}$, $d=-3.23\times10^5$, and $e=1.99\times10^{12}$ for $La_{1.875}Ba_{0.125}CuO_4$, the theoretical curve drawn by the thick solid line in Fig. 3 is in good agreement with the experimental intensities. The transition temperature $T_{LTO-LTT}$ is then determined to be 69 K, which is compatible with the transition temperatures obtained by other experimental techniques such as x-ray diffraction.[1-3]

V. DISCUSSION

From the present experimental data, the La cuprates exhibiting the strong T_c suppression were found to undergo the following low-temperature structural transitions accompanying the $\frac{1}{2}\frac{1}{2}0$-type superlattice spots in electron-diffraction patterns; the LTO-to-LTT transition in $La_{1.875}Ba_{0.125}CuO_4$, the LTO-to-*Pccn* one in $La_{1.885}Sr_{0.115}CuO_4$, and the LTO-*Pccn*-LTT successive ones in $La_{1.880-y}Nd_ySr_{0.120}CuO_4$ around $y=0.400$. A remarkable feature for $La_{2-x}M_xCuO_4$ (M=Ba, Sr) is that the appearance of the transitions is restricted only in the particular concentrations of $x=0.125$ for $La_{2-x}Ba_xCuO_4$ and $x=0.115$ for $La_{2-x}Sr_xCuO_4$. In La-*R*-*M*-Cu-O, on the other hand, it has been reported that the low-temperature transitions take place in a wide range of the Ba and Sr concentrations and the T_c suppression occurs in a part of the *Pccn* and LTT phases. That is, the concentration range, in which T_c is strongly suppressed, does not coincide with that in which the transitions occur. In addition, we have very recently examined features of low-temperature transitions in La-*R*-*M*-Cu-O with R=Nd and Sm and found that the superlattice spots basically appear only around $x=0.125$ for La-*R*-Ba-Cu-O and around $x=0.115$ for La-*R*-Sr-Cu-O although the spots are observed even at $x=0.120$ in La-Nd-Sr-Cu-O. This means that the low-temperature transition does not always accompany the $\frac{1}{2}\frac{1}{2}0$-type superlattice spot. This also suggests that the superlattice spot is not due to the multiple scattering. The details of the obtained result will be published elsewhere. Only the T_c suppression around $x=0.125$ for La-*R*-Ba-Cu-O and around $x=0.115$ for La-*R*-Sr-Cu-O is therefore concluded to be directly related to the appearance of the $\frac{1}{2}\frac{1}{2}0$-type superlattice spots. In other words, another origin of the T_c suppression should be needed in order to explain a whole range of the Ba and Sr concentrations. In this discussion, however, we focus on the suppression related to the appearance of the superlattice spot in $La_{2-x}M_xCuO_4$ with no replacement of La by R because there exists a direct correspondence among the low-temperature transitions, the appearance of the superlattice spot, and the T_c suppression.

There are both the 100-type forbidden spots exhibiting the low-temperature transitions and the $\frac{1}{2}\frac{1}{2}$ 0-type superlattice spots in the electron-diffraction patterns taken from the *Pccn* and LTT phases. In reciprocal space, the 100-type and $\frac{1}{2}\frac{1}{2}0$-type spots are related to band splittings at $(\pi00)$ and $[(\pi/2)(\pi/2)0]$, respectively. It is obvious that the magnitude of the splitting at $(\pi00)$ is affected by the coupling between the tilt distortion and an electronic state via the spin-orbit coupling, as pointed out by Bonesteel, Rice, and Zhang.[14] On the other hand, the location of the superlattice spot is the same X point, at which the tilt phonons are condensed in the low-temperature transitions. The transitions then seem to be stabilized by the appearance of the superlattice spot only in the particular concentrations of Ba and Sr. Because the two inequivalent sites for the oxygen atoms result in the oxygen-oxygen charge transfer,[13] the CDW is presumably the most appropriate origin of the superlattice spot. It is worth noticing that the CDW can be regarded as an ordered polaron state, a polaron solid. Therefore, it seems that the T_c suppression in $La_{2-x}M_xCuO_4$ is not due to the transition itself; that is, the tilt of the octahedron, but originates from a charge localization due to the formation of the CDW. We also stress that the oxygen isotope effect enhanced around $x=0.120$ is undoubtedly related to the low-temperature transitions with the appearance of the superlattice spot.

Kumagai *et al.* reported that in addition to the strong T_c suppression in $La_{1.885}Sr_{0.115}CuO_4$ an antiferromagnetic order of Cu moments appears around $x=0.120$ in $La_{2-x}M_xCuO_4$ (M=Ba,Sr).[4] An important feature of the antiferromagnetic order is that the transition temperatures T_N in both system have maxima; $T_N^{max}=35$ K in $La_{1.875}Ba_{0.125}CuO_4$ and 15 K in $La_{1.885}Sr_{0.115}CuO_4$, respectively. On the basis of the above discussion, it seems that the antiferromagnetic order results from the charge localization due to the CDW. On the other hand, Bonesteel *et al.* pointed out that the spin-orbit coupling leads to a stabilization of a commensurate antiferromagnetic state in the presence of a sufficiently large tilt distortion.[14] This means that the spin-orbit coupling is one of possible origins for the appearance of the antiferromagnetic order. The following experiment result should be remarked. In both $La_{1.875}Ba_{0.125}CuO_4$ and $La_{1.885}Sr_{0.115}CuO_4$, the Seebeck coefficient exhibits a strong temperature dependence and has a negative value.[19,20] Because the Seebeck coefficient is basically related to a derivative of a density of states with respect to energy at E_F, the band splitting due to the CDW never results in the negative coefficient. Therefore, the negative coefficient results from the structural transition itself, the tilt of the octahedron. In other words, origins of physical properties observed around $x=0.120$ can be divided into two groups. One is due to the tilt of the octahedron and the other is caused by the CDW. The most important thing to be noted is that, because the Seebeck coefficient belonging to the former group exhibits the negative value in lower temperatures, a conspicuous effect of the tilt to the electronic state is expected in a different concentration from $x=0.120$. This means that the tilt is not a direct origin of both the T_c suppression and the antiferromagnetic order observed around $x=0.120$. Therefore, both phenomena should be concluded to be caused by the charge localization due to the CDW.

The *Pccn* and LTT phases exist in a wide range of the Ba and Sr concentrations in $La_{2-x-y}R_yM_xCuO_4$ with $R=$Nd and Sm. This fact suggests that the low-temperature transitions in La-*R*-*M*-Cu-O do not mainly come from the electronic origin, but seem to be due to an atomic misfit, which is evaluated as the tolerance factor. Although the atomic misfit leads to the transitions, however, the large tilt distortion produces a large band splitting at $(\pi 00)$, which can result in both the stabilization of the LTT phase and the T_c suppression. The T_c suppression due to the spin-orbit coupling is then possible in $La_{2-x-y}R_yM_xCuO_4$ with $R=$Nd and Sm, as suggested by Büchner *et al.*[21]

It is time to discuss a response of the lattice system to the CDW. Because the superlattice spots appear at the $\frac{1}{2}\frac{1}{2}0$-type positions, the response should be a planar breathing displacement consisting of the oxygen atoms surrounding the Cu atom, as pointed out by Mattheiss.[22] In the present work, we concretely calculated intensities of the $\frac{1}{2}\frac{1}{2}$ 0-type superlattice spots for the breathing displacement on the basis of the kinematical theory of diffraction. A feature of the K_2NiF_4-type structure is that there are two CuO_2 layers, $z=0$ and $\frac{1}{2}$, in a unit cell. When a phase of the breathing displacement in the $z=0$ layer is fixed, two types of displacements are possible in the $z=\frac{1}{2}$ layer and one displacement has a phase shift of π against the other. That is, there are two variants for the breathing displacement. From the calculation, the breathing displacement for each variant is understood to result in the appearance of the superlattice spots only along one of two $\langle 110\rangle$ directions. This is obviously compatible with the experimental result that the intensity of the spot with $\mathbf{q}=\frac{1}{2}[1\bar{1}0]$ is weaker than that with $\mathbf{q}=\frac{1}{2}[110]$.

The details of microstructures of the LTT phase in $La_{1.875}Ba_{0.125}CuO_4$ were investigated by means of transmission electron microscopy by Chen *et al.*[23,24] According to their data, the LTT phase is characterized as a fine mixture of the LTT and *Pccn* phases. That is, there is remarkable structural disorder in the LTT phase. From this fact, the CDW is understood to have a relatively short coherent length and must be localized. Because of the very weak intensity of the superlattice spot, unfortunately it is difficult to take dark field images using it. Microstructures related to the CDW could not be then examined in the present work.

Very recently Zhu *et al.* have examined the details of the microstructure of the LTT phase in $La_{2-x}Ba_xCuO_4$ with $x=0.120$ by means of a transmission electron microscope with a specially designed objective aperture.[25] They showed that the LTT phase appears along the boundary between two LTO domains. In addition, both the 100-type forbidden and $\frac{1}{2}\frac{1}{2}0$-type superlattice spots were also found in diffraction patterns of the LTT phase for $x=0.120$. On the basis of the fact that the intensity of the superlattice spot increases with decreasing temperature, they attribute the superlattice spot to the double diffraction via large **g** vectors. That is, the continuous increase in the intensity of the superlattice spot on cooling is interpreted to be due to the increased coupling resulting from the reduction of the Debye-Waller factor. It should be noticed however that the double diffraction is very sensitive to a deviation from the Bragg condition. Therefore, it is very hard to obtain a systematic change in the intensity with respect to temperature. Because of this fact, the continuous increase in the intensity on cooling never rules out a possibility that the superlattice spot is real. The existence of the superlattice spot should be discussed on the basis of both physical properties such as the Seebeck coefficient and features of diffraction patterns taken from the LTT phases in other La cuprates. From the result described in the present paper, we believe that the superlattice spot actually exists in $La_{2-x-y}R_yM_xCuO_4$ with x of about 0.120.

VI. CONCLUSION

In addition to both $La_{1.875}Ba_{0.125}CuO_4$ and $La_{1.880-y}Nd_ySr_{0.120}CuO_4$, the low-temperature transition in $La_{1.88}Sr_{0.115}CuO_4$ was experimentally detected as the appearance of the 100-type forbidden spots in electron-diffraction patterns. The low-temperature transitions only in $La_{1.875-y}R_yBa_{0.125}CuO_4$ and $La_{1.885-y}R_ySr_{0.115}CuO_4$ accompany the $\frac{1}{2}\frac{1}{2}$ 0-type superlattice spots, which suggest the appearance of the CDW. Because the CDW can be identified as the polaron solid, the polaron lattice should be formed in the particular concentrations of Ba and Sr in the La cuprates. The charge localization caused by the CDW must be a physical origin of the T_c suppression in $La_{2-x}M_xCuO_4$ (M = Ba, Sr) around $x = 0.120$.

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*Present address: Fujitsu Ltd., 1405 Ohmaru, Inagi, Tokyo, 206, Japan.

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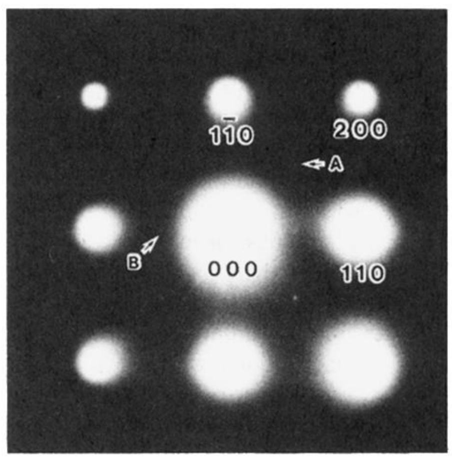

FIG. 1. Electron-diffraction pattern of $La_{1.875}Ba_{0.125}CuO_4$ at 19 K. An electron incidence is parallel to the [001] direction. Diffraction spots are indexed in terms of the HTT structure.

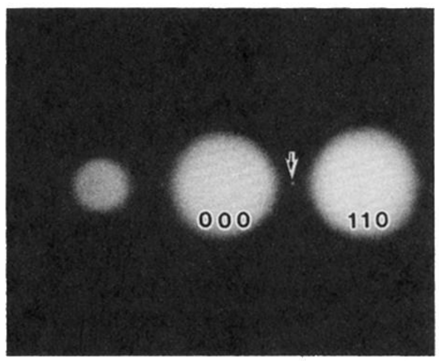

FIG. 2. Electron-diffraction pattern of $La_{1.875}Ba_{0.125}CuO_4$, taken at 19 K. Only the spots along the [110] direction are basically excited in order to check the multiple scattering. $\frac{1}{2}\frac{1}{2}0$-type superlattice spots are seen in the pattern, as indicated by an arrow.

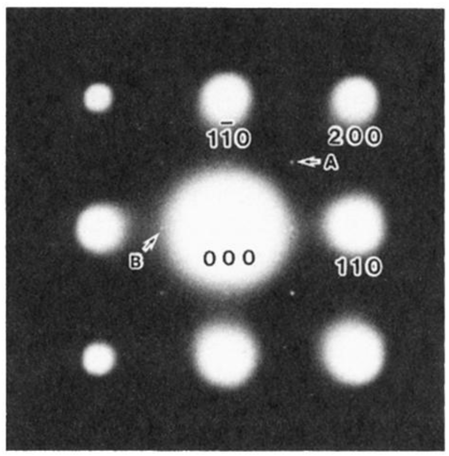

FIG. 4. Electron-diffraction pattern of $La_{1.885}Sr_{0.115}CuO_4$ at 17 K. In the pattern, 100-type forbidden spots *A* and $\frac{1}{2}\frac{1}{2}0$-type superlattice spots *B* are clearly observed.

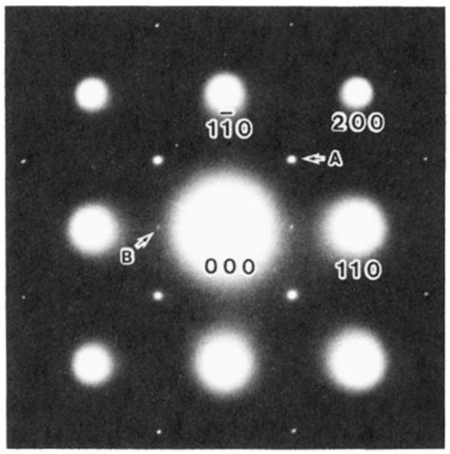

FIG. 6. Electron diffraction pattern of $La_{1.480}Nd_{0.400}Sr_{0.120}CuO_4$ at 16 K. There exist both the 100-type forbidden spots A and the $\frac{1}{2}\frac{1}{2}0$-type superlattice spot B in the (001) diffraction pattern.