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Modulation structure and phase transformation in a Cu-rich La-Cu-O oxide

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The modulation structure in the bc plane of a phase-separated Cu-rich $La_2CuO_{4.003}$ oxide was studied using transmission electron microscopy. Upon an electron beam irradiation at 93 K, a phase transformation from superconducting phase to antiferromagnetic phase was observed and identified based on the analysis of the different reflection conditions for the two space groups of the two phases, i.e., D_{2h}^{23} or $Fmmm$ for the superconducting phase and D_{2h}^{18} or $Bmab$ for the antiferromagnetic phase. For the superconducting phase it is found that the modulation vector changes from $0.041[06\bar{8}]^*$ toward $0.027[04\bar{8}]^*$ during the electron-beam irradiation. Electron energy-loss spectroscopy results are also presented showing that the Cu-rich $La_2CuO_{4.003}$ oxide has indeed phase-separated into hole-rich superconducting phase and hole-poor antiferromagnetic insulating phase. [S0163-1829(99)00505-6]

I. INTRODUCTION

As an ideal model material, La_2CuO_4 has attracted considerable attention due to the interest in studying the mechanism of high transition temperature (high-T_c) superconductivity. This is because the La_2CuO_4 system possesses a simple and typical structure among high-T_c superconductors and exhibits desirable properties upon doping. In this system one can effectively intercalate excess oxygen into interstitial sites and create holes in the Cu-O plane.[1] Due to the relatively high mobility of oxygen dopant, a $La_2CuO_{4+\delta}$ crystal with excess oxygen content in the range $0.01\leqslant\delta\leqslant0.06$ tends to phase separate into oxygen-rich and oxygen-poor regions, resulting in the coexistence of a superconducting phase and an antiferromagnetic phase, both with an orthorhombic structure in the same specimen.[2,3] According to the neutron scattering data,[4] the crystallographic symmetry of the superconducting phase corresponds to a space group of $D_{2h}^{23}-Fmmm$, while that of the antiferromagnetic phase corresponds to $D_{2h}^{18}-Bmab$. Although the stripe-phase[5] and incommensurate modulation structure[6,7] have been reported to occur in the phase-separated $La_2CuO_{4+\delta}$ system, no direct evidence for the corelationship between them has been reported. According to the phase diagram of the La-Cu-O system,[8] phase separation is expected to occur only for sufficiently high excess oxygen content, i.e., for $\delta>0.01$. The phenomenon of phase separation occurring in the range of $\delta\approx$ 0.01 to 0.055 in $La_2CuO_{4+\delta}$ has been extensively explored.[9,10] More recently, by doping the $La_2CuO_{4+\delta}$ ($\delta=0.003$) with a small amount of Cu, Zhao *et al.*[11] were able to detect phase separation in this system via magnetization measurement. In this communication we will be concerned with the Cu-doped $La_2CuO_{4+\delta}$ system. It is the aim of the present study to show that for this system phase separation may occur for a very small oxygen content, i.e., for $\delta<0.01$, and to provide direct experimental evidence for the phase transformation from a superconducting phase to an antiferromagnetic phase upon an electron-beam irradiation. The direct connection between the incommensurate modulation structure and phase separation is also confirmed.

II. EXPERIMENTAL PROCEDURE

The main idea behind the present study of the Cu-rich $La_2CuO_{4+\delta}$ system is that the presence of a small amount of excess Cu in $La_2CuO_{4+\delta}$ may enhance the antiferromagnetic exchange interaction and therefore prompt phase separation in the system.[7] To study the influence of Cu content on the phenomenon of phase separation, a La-Cu-O sample with composition of La:Cu = 2:1.06 (atomic ratio) was prepared using the conventional solid-state reaction method.[11] Step x-ray analysis[11] revealed that the as-prepared sample is single phased. The excess oxygen value was measured by the gas effusion spectra method,[12] giving $\delta=0.003$.[7] Magnetization measurement indicated that a superconducting phase with $T_c\sim35$ K coexists with an antiferromagnetic phase with a Néel temperature $T_N\sim$ 244 K. An incommensurate modulation structure was also revealed by the electron-diffraction technique at liquid-nitrogen temperature,[7] while for the

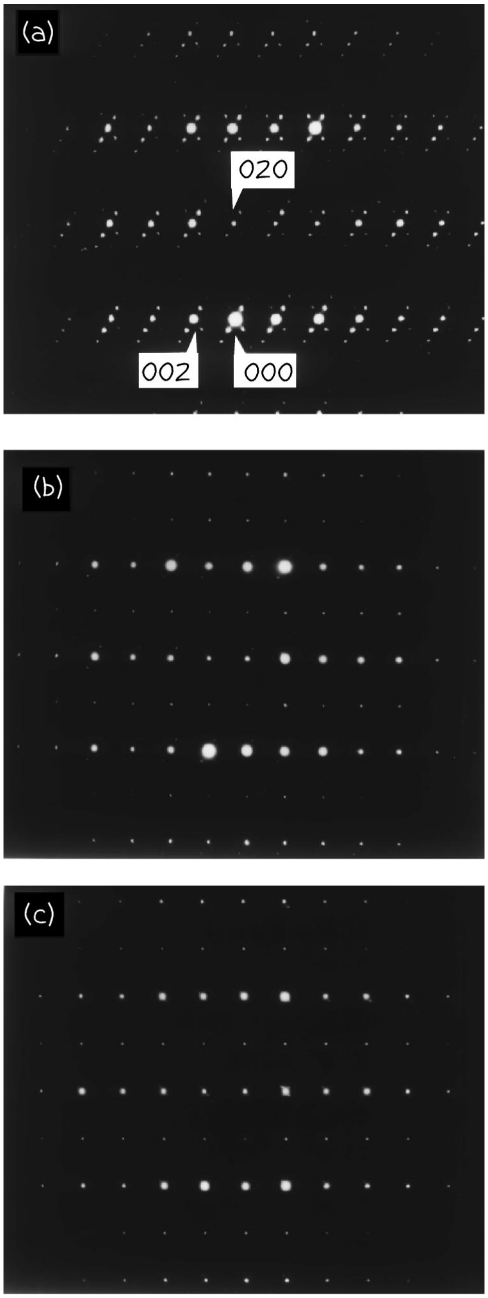

FIG. 1. [100] zone electron-diffraction patterns taken at 93 K after different times of electron-beam irradiation (a) before irradiation; (b) after 2 min (c) after 5 min electron-beam irradiation. The primary beam energy is 200 keV.

sample with La:Cu = 2:1 prepared by the same procedure, no phase separation was detected.[11] To distinguish the doping effect of oxygen from that of copper, a sample prepared with an atomic ratio of La:Cu=2:1.06 was Ar annealed at 800 °C for 8 h and was examined. Neither phase separation nor incommensurate modulation structure was observed. This observation may be ascribed to the fact that almost all the excess oxygen atoms in the sample were extracted during the process of Ar annealing, indicating that the existence of excess oxygen was responsible for the occurrence of the observed modulation and phase separation. Nevertheless, in all previous studies no direct real space evidence was given which confirms the spatial separation of the superconducting and antiferromagnetic phases, as well as their relation to the charge-density wave. In what follows we will be concerned with the original mechanism from which the incommensurate modulation and phase separation were resulted and show a phase transformation from the superconducting phase to the antiferromagnetic phase based on the analysis of the different reflection conditions for the two space groups.[13] In this work, the transmission electron microscopy (TEM) experiments were carried out using a Philips field-emission gun transmission electron microscope CM200/FEG which is equipped with a liquid-nitrogen Gatan cooling double-tilt stage and a Gatan energy filtering system.

III. RESULTS

Using an Ising model Emery and his collaborators[14] predicted that charge stripes together with antiphase spin domains would occur in the CuO_2 planes as a competition between the long-range part of the Coulomb interaction and the tendency toward phase separation. Extensive experimental and theoretical studies suggested that, in the $La_2CuO_{4+\delta}$ system, mobile holes tend to form an ordered state (charge ordering) when their concentration reaches a certain value,[2,3,15] resulting in a modulation structure. Figure 1(a) is a [100] zone axis electron-diffraction pattern taken at 93 K from the Cu-riched $La_2CuO_{4+\delta}$ specimen with $\delta = 0.003$. Incommensurate modulation superlattice spots are clearly shown in the figure. To estimate the incommensurate modulation vector, one may connect the [000] spot and the array of sattelite spots associated with the main spot by a straight line and extrapolate the line until it intersects with one of the main diffraction spots from the matrix. In Fig. 1(a) the straight line intersects with the $[06\bar{8}]^*$ diffraction spot. Having divided the modulation vector length by the length of the vector $[06\bar{8}]^*$, we obtained an expression for the incommensurate

TABLE I. Reflection conditions corresponding to space groups *Bmab* and *Fmmm*, respectively.

Space group	$D_{2h}^{18}-Bmab$	$D_{2h}^{23}-Fmmm$
Reflection conditions (Ref. 13)	$hkl{:}h+l=2n$	$hkl{:}h+k,h+l,k+l=2n$
	$hk0{:}h,k=2n$	$hk0{:}h,k=2n$
	$h0l{:}h,l=2n$	$h0l{:}h,l=2n$
	$0kl{:}l=2n$	$0kl{:}k,l=2n$
	$h00{:}h=2n$	$h00{:}h=2n$
	$0k0{:}k=2n$	$0k0{:}k=2n$
	$00l{:}l=2n$	$00l{:}l=2n$

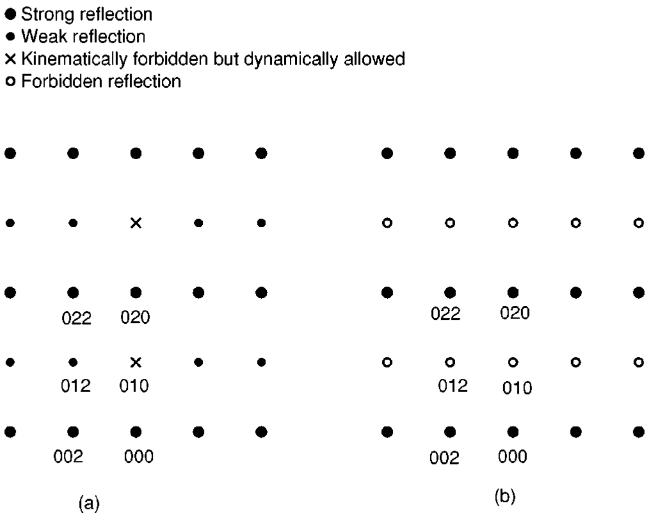

FIG. 2. Schematic illustration of the [100] zone electron-diffraction patterns corresponding to *Bmab* symmetry and *Fmmm* symmetry.

modulation vector $q \approx 0.041[06\bar{8}]^*$, or alternatively $0.246b^* - (1/3)c^*$. The other set of incommensurate modulation with the vector of $q \approx 0.041[068]^*$ might be resulted from a different domain. Similar diffraction patterns with a vector of $q \approx 0.21b^* + (1/3)c^*$ were even reported by Lanzara *et al.*[6] for a $La_2CuO_{4+\delta}$ single crystal with δ as large as 0.1 below 150 K. It should be noted that the modulation detected in the present sample differs from that observed in the usual $La_2CuO_{4+\delta}$ system[8,15] in that the modulation structure was induced with an excess oxygen content ($\delta = 0.003$) which is much smaller than that used in the previous studies,[8] indeed more than three times smaller than the minimum oxygen content ($\delta = 0.01$) observed previously. In the present Cu-doped La-Cu-O system, a possible mechanism is for the Cu dopants to substitute La sites and therefore enhance the antiferromagnetic exchange interaction.[5,7] As a result the holes are forced to segregate. In some regions, a high concentration of holes may be achieved giving superconductivity below the transition temperature even though the average content of the excess oxygen of the whole sample is very small.

To test whether the modulation structure results from the mobile holes, we have exposed the sample in the electron microscope to an irradiation of a bright electron beam and the electron-diffraction patterns were recorded for different irradiating time. When being irradiated by the incident electron beam, both the direction and the magnitude of the incommensurate modulation vector change with the irradiating time. Shown in Fig. 1(b) is a [100] zone axis diffraction pattern taken from the same area as Fig. 1(a) after an irradiation for 2 min. The vector q corresponding to Fig. 1(b) was measured by the same procedure as described above, being $\sim 0.054[04\bar{6}]^*$, i.e., the magnitude becomes smaller and the direction rotates toward the c axis. Shown in Fig. 1(c) is another diffraction pattern from the same area as Fig. 1(a), but for an irradiation time of 5 min. The vector q changes further to become $\sim 0.027[04\bar{8}]^*$. It is seen that after an irradiation of 5 min, the direction of the vector changes from $[06\bar{8}]^*$ to $[04\bar{8}]^*$ and the magnitude of the vector was evidently decreased, meaning that the modulation distance in real space was evidently increased. Among other effects, the electron-beam irradiation may result in an increase in temperature of the sample. The vector of the modulation structure depends on the competition between the antiferromagnetic exchange interaction and the thermal fluctuation. The former forces holes to segregate and form an ordering state in the hole-rich region, while the latter prefers a random hole distribution in the whole sample. Therefore, the temperature increase due to the irradiation may change the local distribution of holes and result in a different modulation period and direction. These is also evidence that the observed incommensurate modulation results from the mobile holes, for this kind of electron beam irradiation, is not strong enough to cause the other atoms in this sample to redistribute so quickly.

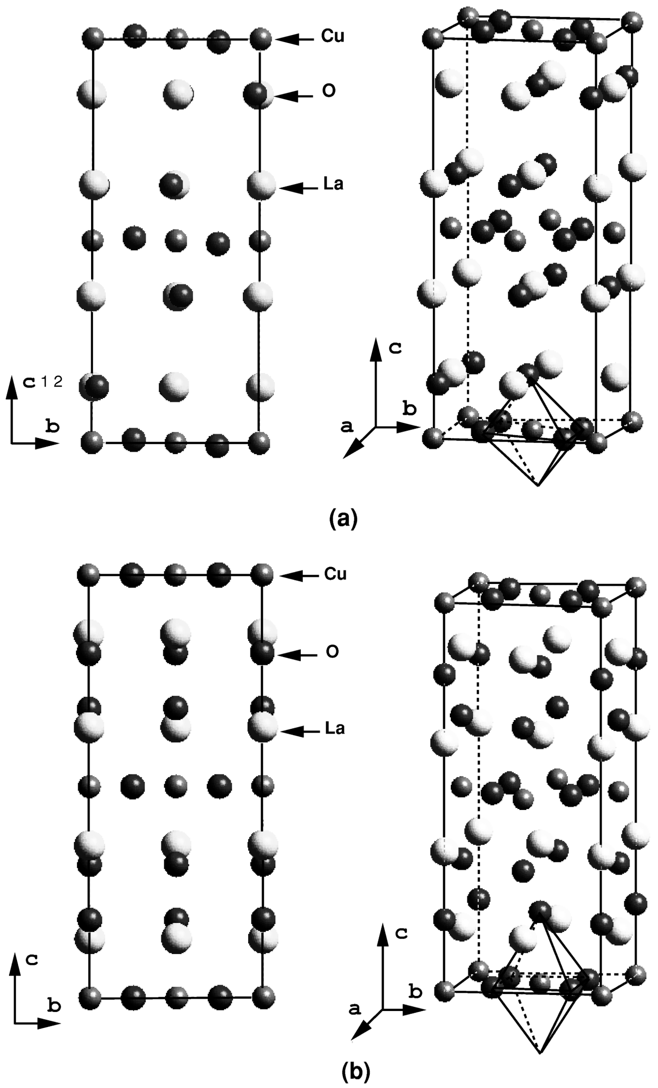

FIG. 3. [100] projection and three-dimensional atomic model corresponding to the (a) *Bmab* and (b) *Fmmm* structure.

In principle, electron irradiation damage should also be taken into consideration when exposing the sample to a bright electron beam. However, the irradiation damage effect may be excluded by examining the diffraction patterns at elevated temperatures compared to the liquid-nitrogen temperature, without the intended electron-beam irradiation.[7] An

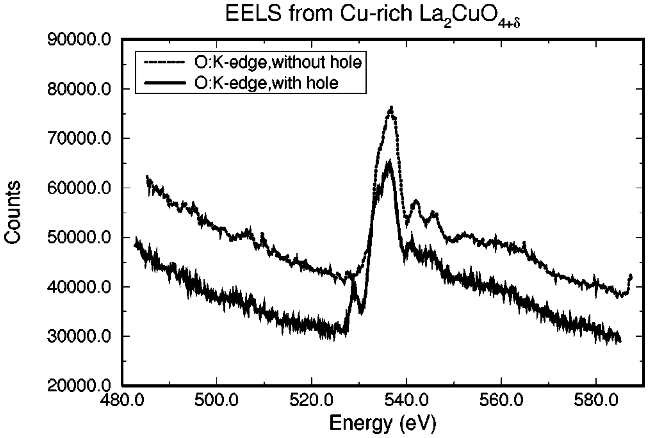

FIG. 4. EELS spectrums from two neighboring regions.

incommensurate modulation vector of $q \sim 0.048\langle 04\overline{10}\rangle^*$ was observed for the same Cu-rich sample from a $[100]$ zone diffraction pattern taken at room temperature, showing the same tendency with the series of the diffraction patterns as shown in Fig. 1. The areas showing this kind of incommensurate modulation feature are much less at room temperature than at liquid-nitrogen temperature, because the liquid-nitrogen temperature modulation structure will not necessarily be kept to room temperature.

Another striking feature for Figs. 1(b) and 1(c) is the appearance of an array of weak spots between two arrays of the bright diffraction spots from the matrix, meaning that the crystallographic symmetry changes upon the electron-beam irradiation. The lately appeared spots are due to the planes of $(0\ k\ l)$ with $k=2n+1$ and $l=2n$. The reflection conditions corresponding to a space group of $D_{2h}^{18}-Bmab$ and $D_{2h}^{23}-Fmmm$ are collected in Table I, and the corresponding [100] zone-diffraction patterns are schematically illustrated in Fig. 2. The small open circle in diffraction pattern indicates the forbidden diffraction spot, while × indicates that the diffraction is forbidden but will appear through the multidiffraction process. Comparing the diffraction patterns and reflection conditions, we know that the diffraction pattern in Fig. 1(a) is consistent with the crystallographic symmetry of $Fmmm$, while those in Figs. 1(b) and 1(c) are consistent with $Bmab$. In the current sample, phase separation has been confirmed by magnetization measurement,[7] i.e., a superconducting phase with a space group of $Fmmm$ (Ref. 4) (not necessarily in superconducting state) and a nonsuperconducting phase with space group of $Bmab$ (Ref. 4) coexist in the same sample. Since the above three diffraction patterns in Fig. 1 are taken from exactly the same area, we may conclude that a phase transformation occurred from a superconducting phase with symmetry of $Fmmm$ to an antiferromagnetic phase with $Bmab$ symmetry upon electron-beam irradiation. As discussed above, the irradiation effect will result in a redistribution and diminution of mobile holes in the local area, while the diminution of mobile holes will promote the antiferromagnetic ordering (i.e., the $\frac{1}{2}$ spin at the Cu site will align better), therefore the nonsuperconducting antiferromagnetic phase forms. This is consistent with the crystallographic consideration that the diminution of holes returns the local area to the state with ordered distortion and rotation of CuO_6 octahedra and the $Bmab$ symmetry is consequently formed.

Diffraction pattern with the incommensurate modulation structure taken at room temperature[5] indicates also the appearance of diffraction spots corresponding to $(0kl)$ with $k=2n+1$ and $l=2n$, i.e., at room temperature we got a phase with the space group of $Bmab$. The Landau theory of phase transformation[16] states that the symmetry of the product phase is a subgroup of the parent phase and the atomic positions of the two structures are closely related by a set of order parameters. Considering the transformation between the superconducting and nonsuperconducting phases in the current case, there is a close relationship between the two corresponding structure symmetries: $Bmab$ is one of the maximal subgroups of $Fmmm$ with an index of 2.[13] The symmetry of $Bmab$ is an inherent structure of the La_2CuO_4 phase at low temperature and it is originated from the distortion and rotation of the CuO_6 octahedra in this system.[17] Corresponding to the unit cell of $Bmab$, Fig. 3(a) shows the $[100]$ projection and a three-dimensional atomic model, by using the data given in Ref. 4. One distorted and rotated CuO_6 octahedra is illustrated. From the symmetry of the $[100]$ projection, we may understand the appearance of the diffraction spots corresponding to the planes $(0\ k\ l)$ with $k=2n+1$ and $l=2n$. It seems that the concentration of holes can result in the $Fmmm$ symmetry, in which no ordered distortion and rotation of the CuO_6 octahedra are presented. This is because on the one hand, a phase cannot be superconducting unless the hole concentration reaches a certain value, on the other hand, a superconducting phase in this system has the $Fmmm$ symmetry.[4] In Fig. 3(b) is shown the $[100]$ projection and a three-dimensional atomic model corresponding to the $Fmmm$ symmetry. The absence of $(0\ k\ l)$ diffraction spots with $k=2n+1$ and $l=2n$ in the $[100]$ zone diffraction pattern [refer to Fig. 1(a)] can be understood upon the symmetry of the $[100]$ projection. The transformation between the $Bmab$ and the $Fmmm$ symmetries can be achieved based on the redistribution of holes which will be affected by the competition between the antiferromagnetic exchange interaction and temperature. With decreased temperature and therefore enhanced antiferromagnetic exchange interaction, the mobile holes will be forced to concentrate in some local areas, where the regular distortion and rotation of the octahedra are destroyed, and a symmetry of $Fmmm$, i.e., a superconducting phase is formed. This is what we have observed at liquid-nitrogen temperature [Fig. 1(a)]. Removal of holes from the $Fmmm$ phase will return the crystal back to its normal $Bmab$ phase composed of regularly tilted octahedras, i.e., phase transformation takes place from a superconducting phase with a symmetry of $Fmmm$ to a nonsuperconducting phase with a symmetry of $Bmab$.

To confirm that the incommensurate modulation (at 93 K before irradiation) does result from phase separation of hole-rich and hole-poor regions, we have collected electron energy loss spectroscopy (EELS) spectra from both the superconducting (solid curve) and antiferromagnetic (dotted curve) phases as shown in Fig. 4. The EELS spectrum taken from the superconducting phase (solid curve) shows that near the oxygen K absorption edge there exists a small pre-edge peak at about 529 eV, while in the EELS spectrum taken from the insulating antiferromagnetic phase (dotted curve) such a prepeak is absent. Qualitatively the results may be understood based on a three-band Hubbard model[18,19] of the electronic structure of CuO_2 planes involving one Cu $d_{x^2-y^2}$ orbital and two oxygen $p_{\sigma(x,y)}$ orbitals.

Above the Fermi level the bands are mainly the so-called *upper Hubbard band* (largely Cu d character) which is well separated from the lower *charge-transfer band* (largely O p character). The observed features of the EELS spectrum near the oxygen K edge involves transitions of electrons from the occupied O $1s$ core level into available empty states above the Fermi level. For the antiferromagnetic insulating phase the O $2p$ dominating charge-transfer band is completely filled and the EELS spectrum shows only those features (beyond 530 eV) involving transitions to the upper Hubbard and higher energy bands. The pre-edge peak involving the charge-transfer band at 529 eV is therefore absent. On the other hand, in the hole-rich superconducting phase the effect of the excess holes is to pull the Fermi level into the charge-transfer band (dominated by the O p orbitals) resulting in new empty (or hole) states mostly of the O p character above the Fermi level. The pre-edge peak of the EELS spectrum obtained from the superconducting phase (solid line) is then identified with transitions into the hole states in the charge-transfer band. We conclude therefore that the Cu-rich $La_2CuO_{4.003}$ crystal indeed phase separated into hole-rich (superconducting) and hole-poor (antiferromagnetic) phases.

IV. SUMMARY

In conclusion, we have directly observed incommensurate modulation and phase transformation in a Cu-rich $La_2CuO_{4+\delta}$ crystal with δ as small as 0.003. The vector of the modulation structure changes during electron-beam irradiation, suggesting that the modulation is related to the mobile holes within the crystal. EELS spectra obtained from different regions of the specimen confirm that the specimen has phase separated into hole-rich superconducting and hole-poor nonsuperconducting phases.

ACKNOWLEDGMENTS

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