Ordering phenomena in the tetragonal superconductor $CaBaLaCu_3O_{7-\delta}$

A. H. Carim,* A. F. de Jong, and D. M. de Leeuw
Philips Research Laboratories, Postbox 80 000, NL-5600 JA Eindhoven, The Netherlands
(Received 22 June 1988)

We have found ordering phenomena in the new, tetragonal superconducting material $CaBaLaCu_3O_{7-\delta}$ using transmission electron microscopy. High-resolution electron microscopy combined with image simulation was used to estimate the occupancy of the cation sites. Using the symmetry and extinctions observed in the electron-diffraction patterns, we derive a model explaining the observed phenomena. The model combines oxygen ordering in the CuO planes with lanthanum and barium ordering.

The recent synthesis of the compound $CaBaLaCu_3O_{7-\delta}$ has provided a new high-temperature superconducting system with unusual properties.[1] The material is a tetragonal bulk superconductor with a T_c of 80 K, and contains no twins. Other tetragonal, superconducting $YBa_2Cu_3O_{7-\delta}$ analogs have been reported,[2,3] but it is still not clear how the tetragonality (caused by oxygen disorder in the CuO planes) affects superconductive properties. We have found that the oxidation behavior of $CaBaLaCu_3O_{7-\delta}$ is quite different from that exhibited by $YBa_2Cu_3O_{7-\delta}$. Upon heating samples in an oxygen ambient the equilibrium oxygen content will not decrease below 6.5 (at 900 °C), which is significantly above the oxygen content of $YBa_2Cu_3O_{7-\delta}$. This has important consequences for the interpretation of the defect chemistry. We have discovered evidence for ordering phenomena in this new tetragonal superconducting system. Transmission electron diffraction patterns indicate an ordering which can be described by a supercell having axes twice as large as the basic unit cell (which is, in turn, isomorphous to tetragonal $YBa_2Cu_3O_{7-\delta}$). High-resolution electron microscopy (HREM) shows the unit-cell structure but does not identify the source of the unit-cell doubling. We discuss several ordering models in the framework of the symmetry imposed by the electron diffraction patterns, and propose a model for the structure of $CaBaLaCu_3O_{7-\delta}$ based on oxygen ordering in the CuO planes combined with lanthanum and barium ordering.

Pressed pellets of $CaBaLaCu_3O_{7-\delta}$ were produced by methods described elsewhere.[1] Samples for transmission electron microscopy were prepared by crushing the pellets and dispersion of the resulting particles on a holey carbon film. Philips 400T and 430ST instruments were utilized, operated at 120 and 300 kV, respectively. The latter was used for HREM and has a demonstrated point-to-point resolution of better than 0.20 nm.

The material examined in the present study was largely single phase, and consisted of nearly defect-free untwinned grains. The electron diffraction patterns obtained along [001] and [100] zone axes contain all of the reflections expected from the tetragonal unit cell (having $a = 0.38655$ nm and $c = 1.16354$ nm at room temperature). Long exposures revealed additional weak reflections as shown in Fig. 1. The [001] zone axis pattern

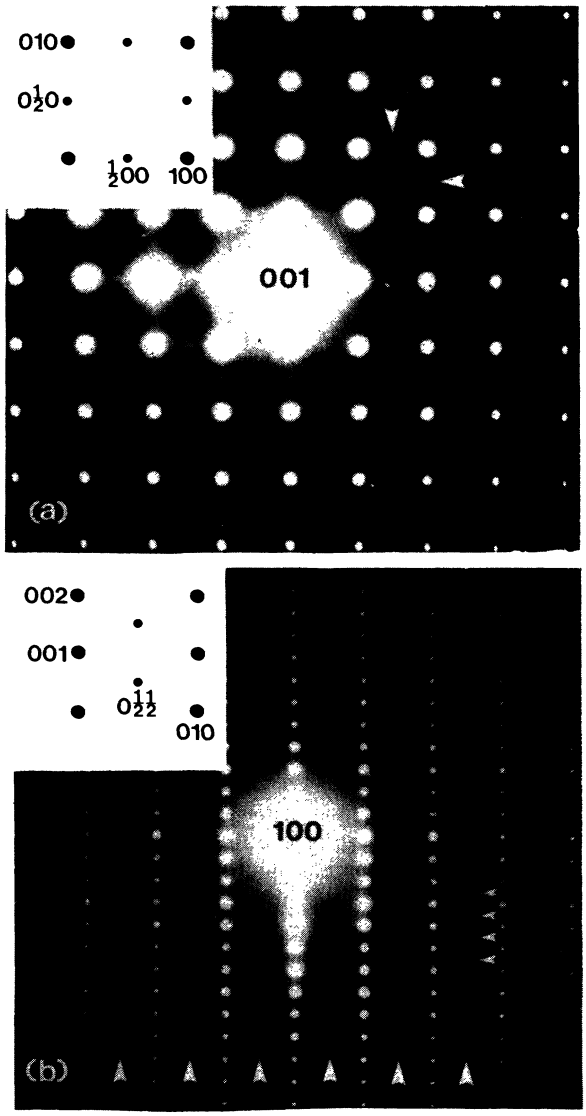

FIG. 1. Transmission electron-diffraction patterns from $CaBaLaCu_3O_{7-\delta}$ taken along (a) the [001], and (b) the [100] zone axes. Long exposures were necessary to reveal the weak additional reflections (arrows). The extra spots are schematically indicated (insets), and indexed on the basis of a tetragonal unit cell with $a = 0.38655$ nm and $c = 1.16354$ nm.

in Fig. 1(a) contains distinct but diffuse spots at positions $(\frac{1}{2}\,0\,0)$ and $(0\,\frac{1}{2}\,0)$ with respect to the basic unit cell. However, the $(\frac{1}{2}\,\frac{1}{2}\,0)$ reflections are not observed. In Fig. 1(b) the [100] diffraction pattern from this material is shown. Spots at $(0\,\frac{1}{2}\,\frac{1}{2})$-type positions can be distinguished, embedded within broad streaks of intensity extending along the c^* axis. A supercell with $a_s = 2a$ and $c_s = 2c$ is in principle necessary in order to describe these patterns. Streaking in the [100] diffraction pattern along the c^* axis and the diffusiveness of the extra spots in the [001] pattern indicate that the ordering is not perfect over long distances. We will, therefore, continue to index planes and diffraction spots with respect to the basic unit cell.

HREM micrographs taken with the electron beam aligned along the [001] and [100] axes exhibit large defect-free areas. As is shown in the HREM images of Fig. 2, no evidence of doubling of the a and/or c axes can be observed. In order to clarify the positions of the cations in the basic unit cell, HREM image simulations were performed for the [100] imaging orientation. The model used for the calculations assumed the $YBa_2Cu_3O_{7-\delta}$ structure[4–6] with Ca and La substituted into the Y positions and Ba and La occupying the Ba positions randomly, since earlier studies indicated that very little Ca could be substituted onto the Ba sites in $YBa_2Cu_3O_{7-\delta}$. Because the amount of Ca on the Y sites is at the moment not accurately known, we calculated several images for models with varying [Ca]/[La] ratios on the Y site. Lowering the Ca content to 50% did not change the image of very thin (5 nm) specimens very much, but HREM images did not match when compared with simulations in which only La was assumed on the Y site. A simulated image for 100% Ca (at a defocus of -40 nm and sample thickness of 4.5 nm) is shown in Fig. 2(c) (inset) and matches the experimental features quite well. The defocus of the experimental image was checked independently via the diffractogram. A more thorough account of experimental and simulated HREM imaging of $CaBaLaCu_3O_{7-\delta}$ will appear separately.[7]

Explanation of the observed phenomena requires the consideration of ordering of the cations Ca, La, and Ba as well as oxygen ordering. Oxygen-vacancy ordering is well known in $YBa_2Cu_3O_{7-\delta}$, with different ordering models for different oxygen content and temperature.[8] In the $CaBaLaCu_3O_{7-\delta}$ compound no order-disorder transition has been observed and the compound remains tetragonal.[1] Therefore, we suggest that if oxygen ordering is involved, it must be combined with the cation ordering that may take place at higher temperatures. On the other hand, we have found no evidence for doubling of the unit-cell axes in either x-ray-diffraction diagrams or in HREM images of thin specimens as shown above. This means that the effect must be very weak in terms of (a difference in) the scattering power of the involved atoms, which points to oxygen ordering and/or La and Ba ordering. Keeping these restrictions in mind, there are few models which fulfill the symmetry requirements imposed by the electron-diffraction patterns. Most of the models one might propose at first sight will give rise to pronounced $(\frac{1}{2}\,\frac{1}{2}\,0)$-type spots. Furthermore, the supercell (of size

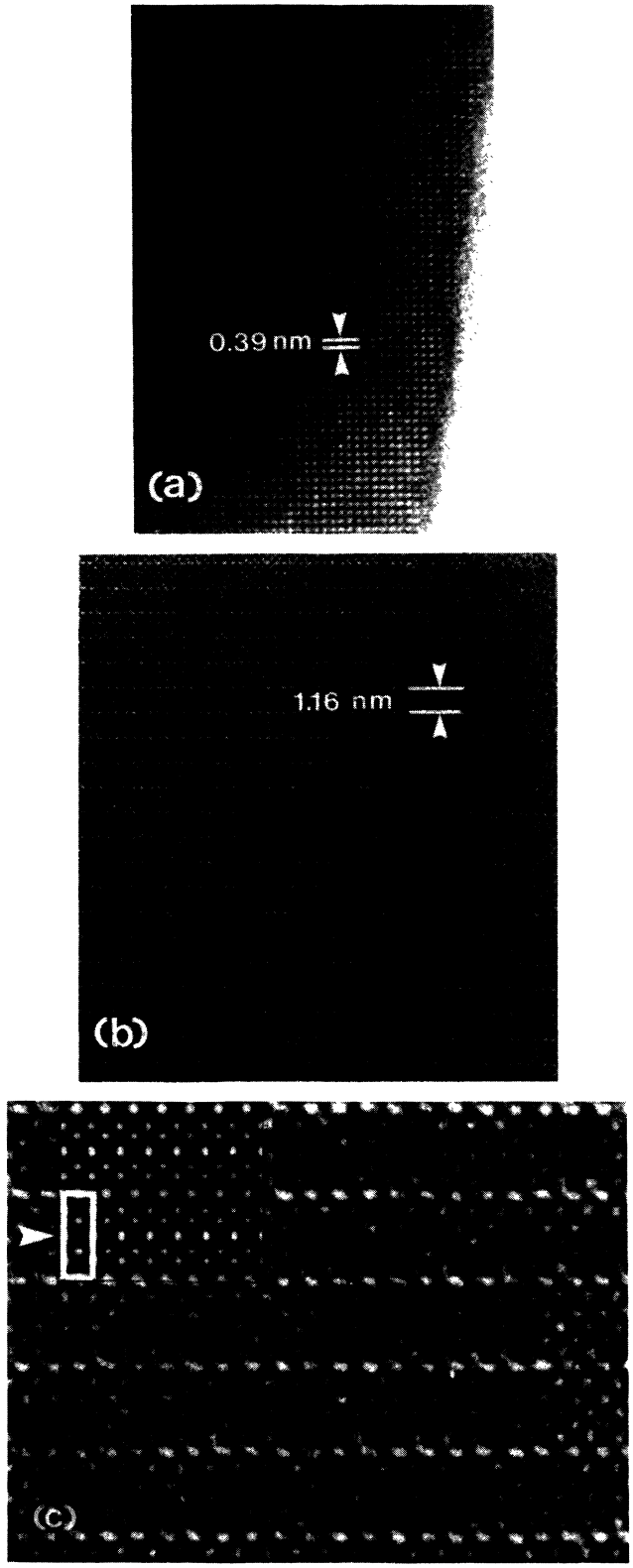

FIG. 2. HREM images obtained along the [001] and the [100] directions. (a) [001] image, with the length of the a axis (or, equivalently, the b axis) indicated. (b) [100] image with the length of the c axis indicated. (c) High-magnification lattice image obtained along the [100] axis, with a simulated image inserted. The unit cell is outlined, with the arrow pointing at the Ca-containing site in the middle of the unit cell.

$2a \times 2b \times 2c$) must retain a fourfold symmetry around the c axis.

One viable model which accounts for the observed phenomena is presented in Fig. 3. The basic structure is taken as that of $YBa_2Cu_3O_{7-\delta}$ with Ca occupying the Y sites and Ba and La sharing the Ba positions. Figure 3(a) depicts the CuO plane and the Ba and La atoms directly above and below this plane. Half of the available oxygen sites in this CuO layer must be empty for the stoichiometry to be correct. We propose that the oxygen atoms are "clustered" in units of four atoms around pairs of lanthanum atoms. This arrangement permits ($\frac{1}{2}$ 00)- and (0 $\frac{1}{2}$ 0)-type reflections, while ($\frac{1}{2}$ $\frac{1}{2}$ 0) reflections will be very weak or extinct.

In addition to ordering in the a-b plane, there is a tendency for the clusters to be displaced in successive CuO layers by a displacement vector of $a\langle 110\rangle$. In Fig. 3(b) the supercell with $a_s = 2a$ and $c_s = 2c$ is schematically shown. It is a primitive cell but projecting the structure in the b-c plane renders a centered plane cell where (0 $\frac{1}{2}$ 0)- and (00 $\frac{1}{2}$)-type reflections are forbidden, and (0 $\frac{1}{2}$ $\frac{1}{2}$) reflections allowed. This is in agreement with the [100] diffraction pattern shown in Fig. 1(b). Projecting the structure in the a-b plane removes the doubling of the a and b axes, thus weakening the ($\frac{1}{2}$ 00)- and (0 $\frac{1}{2}$ 0)-type spots considerably [see Fig. 1(a)]. Still ($\frac{1}{2}$ $\frac{1}{2}$ 0) spots remain forbidden in this model.

Figure 4 is a simulated dynamical diffraction pattern along [001] for $CaBaLaCu_3O_{7-\delta}$ in which the effects of ordering as sketched in Fig. 3(a) are included. Upper-layer Laue zone effects were included in this calculation by dividing the model structure along the c axis in four different slices. The simulated pattern is in excellent agreement with the one that was experimentally obtained [Fig. 1(a)]. Periodic displacement of the clusters along the c axis is not included; increasing order of this sort diminishes the intensities of the ($\frac{1}{2}$ 00) and (0 $\frac{1}{2}$ 0) reflections. On the other hand, diffraction patterns taken along the [101] axis exhibited strongly enhanced half-order spots, which can be understood because the clusters are then partly aligned with the electron beam.

In principle, one of the ordering effects (oxygen or La/Ba) will suffice to explain the observed phenomena. However, a combined ordering is quite reasonable if we look at the valencies and ionic radii of the cations: $r(Ba^{2+}) = 0.134$ nm, $r(La^{3+}) = 0.106$ nm, and $r(Ca^{2+}) = 0.099$ nm.[9] It seems plausible that indeed oxygen atoms will cluster around lanthanum atoms. Moreover, an oxygen ordering which depends in turn on La/Ba ordering at high temperatures would fit in well with the apparent lack of an order-disorder transition at moderate tempertures and the discontinuities in the thermogravimetric analysis of $CaBaLaCu_3O_{7-\delta}$ in the 900–1000 °C temperature range.[1] Although it has been suggested[3] that oxygen ordering in the CuO plane [Cu(1) site] is not an important parameter for the T_c in (tetragonal) $YBa_2Cu_3O_{7-\delta}$-like compounds, it may be that the combined oxygen and La/Ba ordering influences the electronic

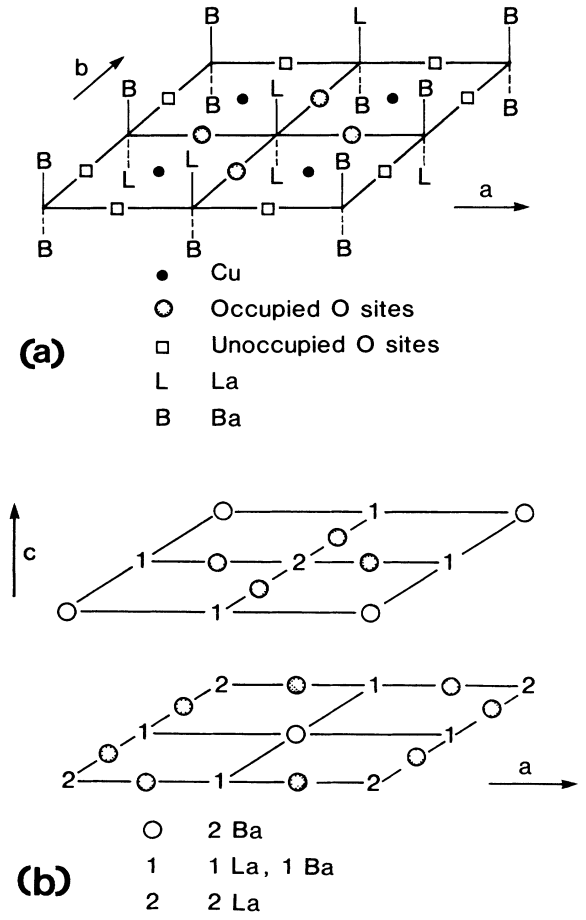

FIG. 3. Ordering model for $CaBaLaCu_3O_{7-\delta}$. (a) Arrangement of atoms in the CuO and (Ba,La)O planes. For clarity, the Cu atoms are drawn in the middle of the basic units. The indicated Ba and La atoms occupy sites directly above or below the CuO plane. (b) Displacement of oxygen and lanthanum "clusters" around alternate CuO planes. Cu and vacancy sites (not indicated) as in (a).

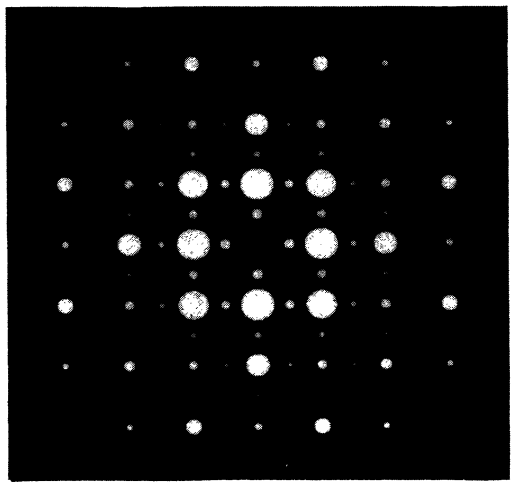

FIG. 4. Simulated dynamical diffraction pattern along [001], based on the model as shown in Fig. 3(a) but without the staggering of oxygen and lanthanum clusters in alternate CuO planes.

structure in the CuO_2 planes [Cu(2) site]. Preliminary results indicate that there may be a correlation between ordering and T_c in $CaBaLaCu_3O_{7-\delta}$ compounds with varying [La]/[Ba] ratio.

In conclusion, we have investigated the new tetragonal superconductor $CaBaLaCu_3O_{7-\delta}$ with transmission electron microscopy. From HREM images it could be concluded that the basic unit cell of this structure must be very similar to that of $YBa_2Cu_3O_{7-\delta}$, with Ca on the Y sites and La on the Ba and (probably) Y sites. From electron diffraction patterns it must be concluded that there is an ordering which doubles all unit-cell axes. We propose a model of combined oxygen and La and Ba ordering that can explain the observed phenomena. Calculated electron-diffraction patterns match the experimental ones very well. This finding may have important consequences for the understanding of the correlation between oxygen ordering and T_c.

Note added. After submission of the original manuscript, we received an unpublished report which agrees with our observation of ordering phenomena in this compound by electron diffraction.[10] The oxygen content of 7.5 reported in that work leads to a different structural model. The measured oxygen content in our samples has never exceeded 7.0 (see Ref. 1).

We gratefully acknowledge the provision of samples by C. A. H. A. Mutsaers, x-ray-diffraction diagrams by H. C. A. Smoorenburg, and support from C. W. T. Bulle-Lieuwma on high-resolution electron microscopy.

---

*Present address: Department of Chemical and Nuclear Engineering and Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131.

[1]D. M. de Leeuw, C. A. H. A. Mutsaers, H. A. M. van Hal, H. Verweij, A. H. Carim, and H. C. A. Smoorenburg, Physica C (to be published).

[2]C. U. Segre *et al.*, Nature (London) **329**, 227 (1987).

[3]Gang Xiao *et al.*, Nature (London) **332**, 238 (1988).

[4]R. M. Hazen *et al.*, Phys. Rev. B **35**, 7238 (1987).

[5]J. J. Capponi *et al.*, Europhys. Lett. **3**, 1301 (1987).

[6]R. Beyers *et al.*, Appl. Phys. Lett. **50**, 1918 (1987).

[7]A. F. de Jong and A. H. Carim (unpublished).

[8]G. van Tendeloo and S. Amelinckx, J. Electron Microsc. Tech. **8**, 285 (1988).

[9]*CRC Handbook of Chemistry and Physics,* 68th ed., edited by R. C. Weast (CRC, Boca Raton, 1987), p. F-159.

[10]W. T. Fu, H. W. Zandbergen, C. J. van der Beek, and L. J. de Jongh, Physica C (to be published).

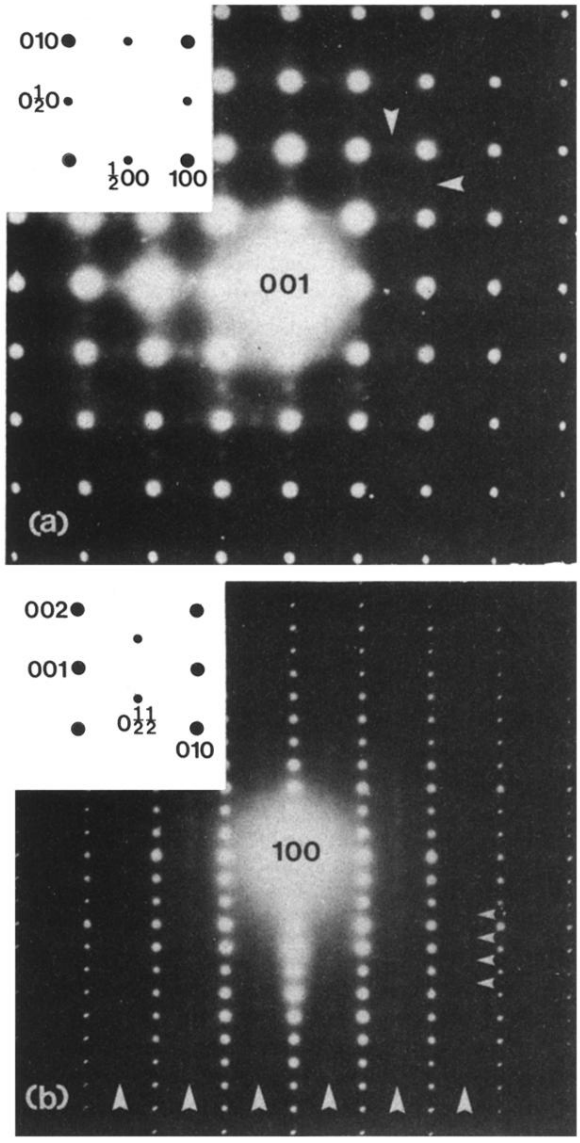

FIG. 1. Transmission electron-diffraction patterns from $CaBaLaCu_3O_{7-\delta}$ taken along (a) the [001], and (b) the [100] zone axes. Long exposures were necessary to reveal the weak additional reflections (arrows). The extra spots are schematically indicated (insets), and indexed on the basis of a tetragonal unit cell with $a = 0.38655$ nm and $c = 1.16354$ nm.

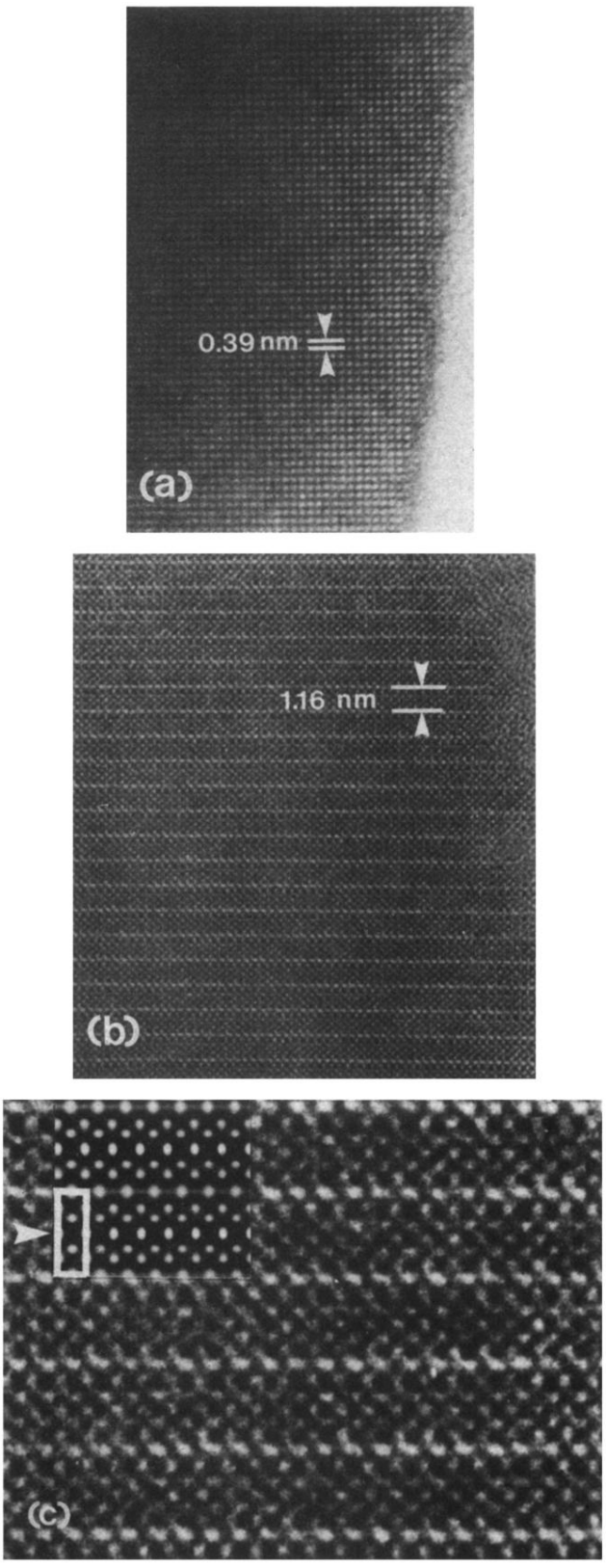

FIG. 2. HREM images obtained along the [001] and the [100] directions. (a) [001] image, with the length of the *a* axis (or, equivalently, the *b* axis) indicated. (b) [100] image with the length of the *c* axis indicated. (c) High-magnification lattice image obtained along the [100] axis, with a simulated image inserted. The unit cell is outlined, with the arrow pointing at the Ca-containing site in the middle of the unit cell.

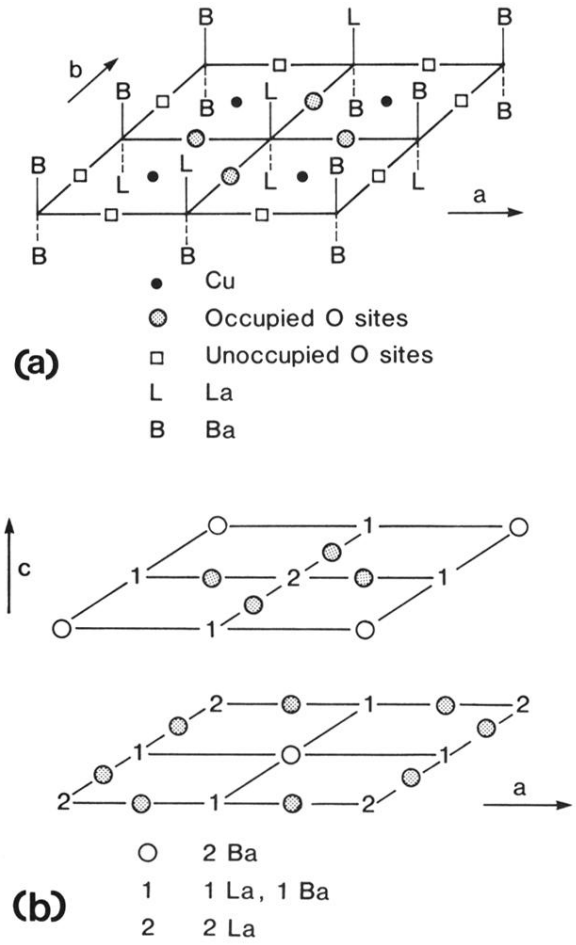

FIG. 3. Ordering model for $CaBaLaCu_3O_{7-\delta}$. (a) Arrangement of atoms in the CuO and (Ba,La)O planes. For clarity, the Cu atoms are drawn in the middle of the basic units. The indicated Ba and La atoms occupy sites directly above or below the CuO plane. (b) Displacement of oxygen and lanthanum "clusters" around alternate CuO planes. Cu and vacancy sites (not indicated) as in (a).

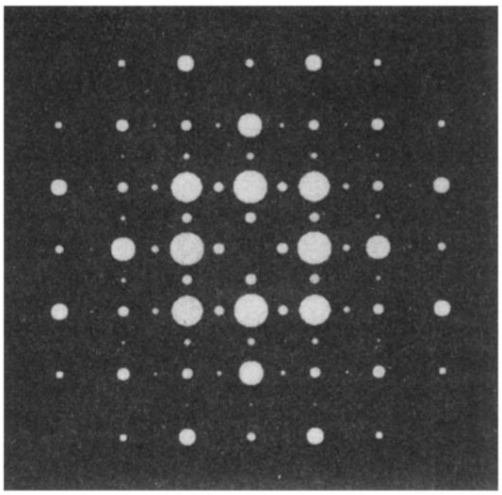

FIG. 4. Simulated dynamical diffraction pattern along [001], based on the model as shown in Fig. 3(a) but without the staggering of oxygen and lanthanum clusters in alternate CuO planes.