Microstructure of $Pb_2Sr_2ACu_3O_8$ superconductors: New structures and superstructures

R. Hull, J. M. Bonar, L. F. Schneemeyer, R. J. Cava, J. J. Krajewski, and J. V. Waszczak

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

(Received 5 December 1988)

We report a detailed study of the microstructure of the new class of high-T_c superconductors, $Pb_2Sr_2ACu_3O_8$, by transmission electron microscopy and diffraction. Several new structural and superstructural variants are observed for $A =$ Eu+Sr, Dy+Ca/Sr, or Dy+Sr. Approximately 50% of the individual crystals analyzed displayed weak violation of the c centering present in x-ray macroscopic structure determination, and superstructure variants with modulation vectors parallel to **a** and/or **b** were observed in ~25% of the Eu+Sr crystals analyzed. In the $A =$ Dy+Sr structures only, structure modulations were observed along [110] and [1$\bar{1}$0] directions.

The discovery of a new class of high-T_c superconductors based upon the composition $Pb_2Sr_2ACu_3O_8$ (Ref. 1) has established a new range of structures displaying this phenomenon. The structure of these materials, as determined from x-ray diffraction[1] and shown in Fig. 1, differs from that of $YBa_2Cu_3O_{7-x}$ (Refs. 2 and 3), Bi-Sr-Ca-Cu-O (Refs. 4–8), and Tl-Ba-Ca-Cu-O (Refs. 9–11) based systems primarily in the structure between the Cu-O planes, with Sr-O/Pb-O/Cu/Pb-O/Sr-O planes separating the copper-oxygen double layers. The simplest cell consistent with the observed x-ray intensities is c centered with $a = 5.40$ Å, $b = 5.43$ Å, and $c = 15.74$ Å. In this work, we report a detailed and systematic study of the microstructure of these new compounds, with $A =$ Eu+Sr, Dy+Sr, or Dy+Ca/Sr. The existence of a range of structural and superstructural variants in the host structure is demonstrated.

Single crystals of the superconducting compounds were grown from PbO-rich melts, using precursor techniques

described elsewhere.[1] Samples were prepared for electron microscopy by crushing under methanol single-crystal fragments extracted from the melt, and transferring the resultant suspension onto holey carbon films ~50 Å thick. The microstructure of individual crystal fragments was then analyzed by transmission electron diffraction and imaging using JEOL 2000FX and JEOL 4000EX electron microscopes operated at 200 kV. By systematic analysis of crystal symmetry via electron diffraction and structural uniformity via electron imaging, we have been able to both identify new structural variants in this system, and to statistically determine the preponderance of these various phases.

The fracture habits of the samples studied produced comparable proportions of fragments fractured parallel and perpendicular to the **c** axis. The magnitude of the unit-cell lattice parameters was consistent with the x-ray structure determination[1] within the accuracy afforded by our measurements.

Shown in Fig. 2(a) is a typical electron diffraction pattern in the **a***-**b*** reciprocal lattice plane from a sample with $A =$ Eu+Sr and exhibiting the symmetry predicted by x-ray diffraction. In Fig. 2(b), we show another **a***-**b*** diffraction pattern of a fragment from the same preparation, but in this case exhibiting extra 5.4-Å [010] and [100] reflections which violate the c centering of the structure. In Fig. 2(c), we show an **a***-**b*** pattern which exhibits superstructure reflections parallel to **a*** or **b*** (in conventional transmission electron diffraction, magnetic lens distortions prevent us from being able to determine the sense of the orthorhombicity between **a** and **b**) and with a modulation vector amplitude of 4.6 ± 0.2 a or b in this direction. In other superconducting ceramics, superstructure modulations have been observed as a function of oxygen stoichiometry (attributed to ordering of oxygen vacancies) in $YBa_2Cu_3O_{7-x}$ (Refs. 12 and 13), an incommensurate superlattice with a period ~4.8 b is typically observed in Bi-Sr-Ca-Cu-O (see, e.g., Refs. 6 and 7), and a similar incommensurate superstructure, albeit generally less well defined and of varying wavelength, has been observed in Tl-Ba-Ca-Cu-O materials (see, e.g., Ref. 14). The origin of the superstructure in the Bi and Tl materials has not yet been unambiguously identified: possible models include substitution of Ca^{2+} (Ref. 15) or vacancies
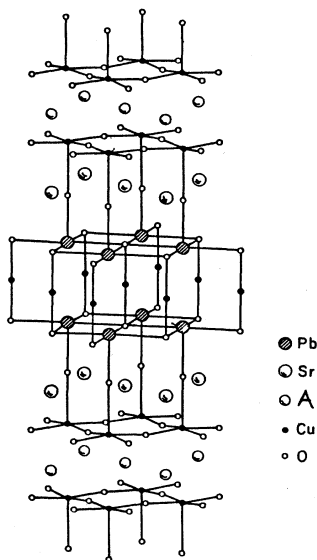

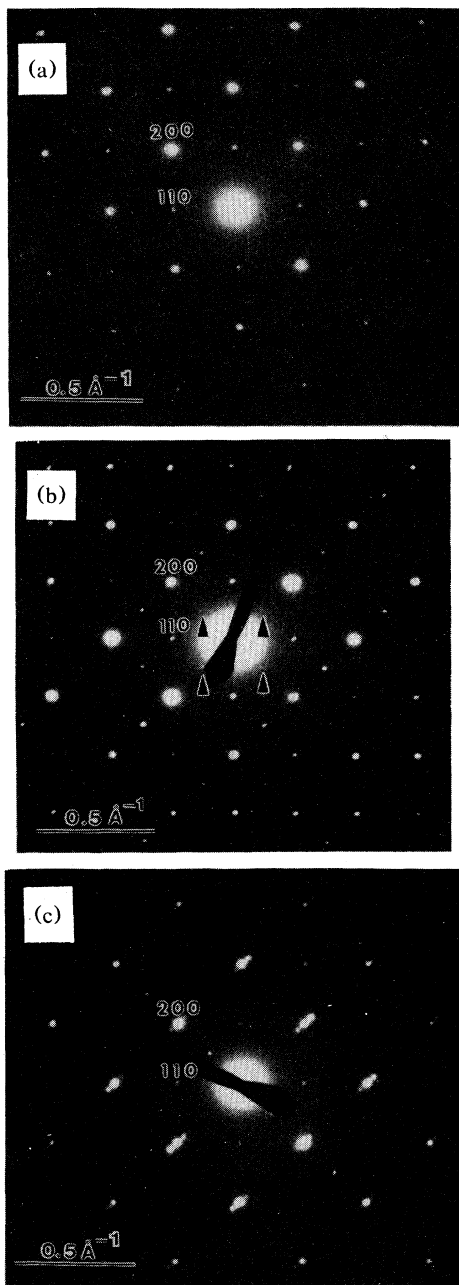FIG. 1. Structure of $Pb_2Sr_2ACu_3O_8$ high-T_c superconductors (from Ref. 1).

⊘ Pb
◯ Sr
○ A
• Cu
○ O

FIG. 2. Electron diffraction patterns from the a^*-b^* plane of A =Eu+Sr crystals: (a) Fundamental c centered 5.4-Å unit cell, consistent with the x-ray structure determination of Fig. 1; (b) with extra [010] or [100] reflections (indicated by arrows) implying a primitive 5.4-Å unit cell; and (c) with superstructure modulation along a^* or b^*. Reflections are indexed on the basis of a 5.4-Å c centered unit cell as in Ref. (1). Note that the assignation of [h00] vs [0k0] directions is arbitrary.
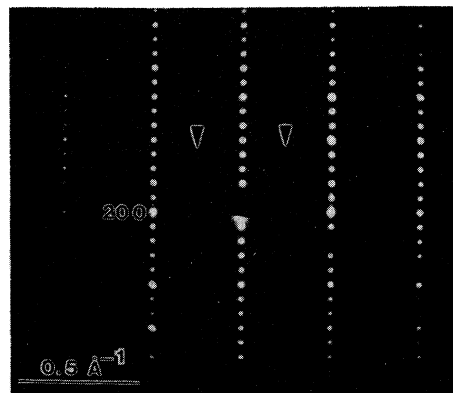

FIG. 3. Electron diffraction pattern along either the [100] or [010] axis of an A =Dy+Ca/Sr crystal. Note the systematic rows of reflections from the 5.4-Å periodicity along a or b in the structure (indicated by arrows).

(Ref. 16) onto Sr^{2+} sites, oxygen vacancy ordering (Ref. 17) or displacements of Bi or Si atoms (see, e.g., Refs. 6 and 18). We note also that the period of this superstructure can vary with Pb substitution for Bi.[19,20]

All three of the above structures have been observed on several occasions. For the A =Eu+Sr material which we have studied in most detail, of fifteen patterns recorded from distinct fragments in the a^*-b^* plane, seven were identical to Fig. 2(a), i.e., they exhibited neither detectable 5.4-Å reflections nor superstructure reflections. Of the remaining crystals, seven exhibited 5.4-Å spacing which violates the c centering. Of these seven crystals, three exhibited a monodirectional superstructure modulation, as shown in Fig. 2(c). These three crystals showing the superstructure all exhibit a 5.4-Å reflection perpendicular to the modulation direction, but not parallel to it. In structures such as in Fig. 2(b) which do not contain the superstructure, the 5.4-Å spacing, if present, occurs in both orthogonal [100] and [010] directions. Thus we have determined that approximately 50% of the individual crystal fragments in the A =Eu+Sr structure exhibit a violation of c centering which is strong enough to produce a 5.4-Å reflection of sufficient intensity to be detectable on the photographic negative. These statistics are approximately comparable for the A =Dy+Sr and A =Dy +Ca/Sr structures. In total, for all three structures, out of 49 individual fragments analyzed in the a^*-b^* plane, 29 (i.e., ~60%) exhibited the 5.4-Å reflections. We note also that in a preliminary study of ceramic material which has been synthesized in this present system, we have also detected this c-centering violation for A =Y+Sr (Ref. 1).

The 5.4-Å periodicity is also frequently evident in electron diffraction patterns recorded from a^*-c^* or b^*-c^* reciprocal lattice planes, as indicated in a pattern recorded from an A =Dy+Ca/Sr fragment in Fig. 3. The strength of the systematic c-centering violating reflections in this pattern indicates that their presence is not likely to be due to penetration of intensity from higher-order Laue zones, as could conceivably be the case in the a^*-b^* patterns where the reciprocal lattice spacing parallel to the electron beam (c^* =0.0248 Å^{-1}) is relatively small.

Lattice structure images reveal the basic features of the structure as revealed in Fig. 4(a) which represents a [110] or [1$\bar{1}$0] phase-contrast image of the thin edge of a fragment of the A =Dy+Ca/Sr sample. The corresponding electron diffraction pattern is shown in Fig. 4(b). In the limit of an extremely thin crystal (where interactions of
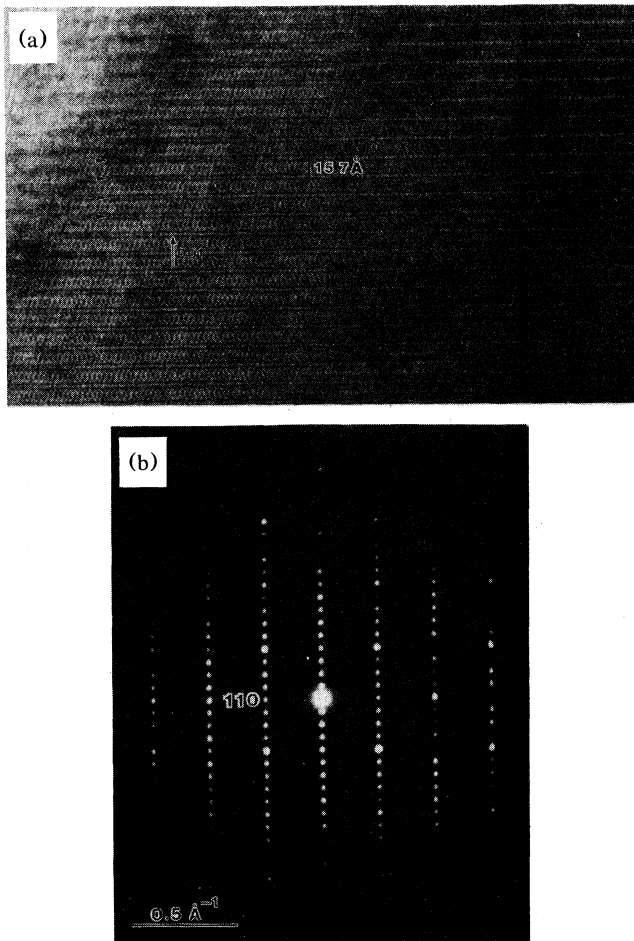
FIG. 4. (a) Lattice structure image and (b) electron diffraction pattern along a [110] or [1$\bar{1}$0] axis of an A=Dy+Sr crystal. The midpoints (at z=0.5 c) between Pb planes are indicated by arrows in (a).

The greater uniformity of the new $Pb_2Sr_2ACu_3O_8$ materials is also evidenced by the absence of streaking of diffraction maxima along the c^* axis in electron diffraction patterns. In addition, no evidence for intergrowth of a $YBa_2Cu_3O_7$-type structure has yet been detected by us.

Finally, we note that we have detected other structural variants in this system and have frequently observed strong evidence for twinning or other planar disorder (appearing as side lobes or discrete minima to main Bragg reflections in the electron diffraction patterns) in these structures. In Fig. 5(a), recorded from the a^*-b^* plane of an A=Sr+Eu fragment, a two-dimensional array of subsidiary diffraction maxima is observed along both a^* and b^*. The distance between adjacent maxima along a or b is equivalent to 5.2 ± 0.2 a or b in real space. In principle this diffraction pattern is consistent with the electron beam being parallel to a twist axis in the material;[25] such faults are known to be common in the Bi-Sr-Ca-Cu-O materials,[26] for example. However, note that in this structure, the 3.7-Å fundamental [110]-type reflection is absent, as well as the [010]-type 5.4-Å reflection, suggesting a structural variant in addition to the presence of the twist axis. This is the only structure in which we have observed the absence of the [011]-type reflections. A similar
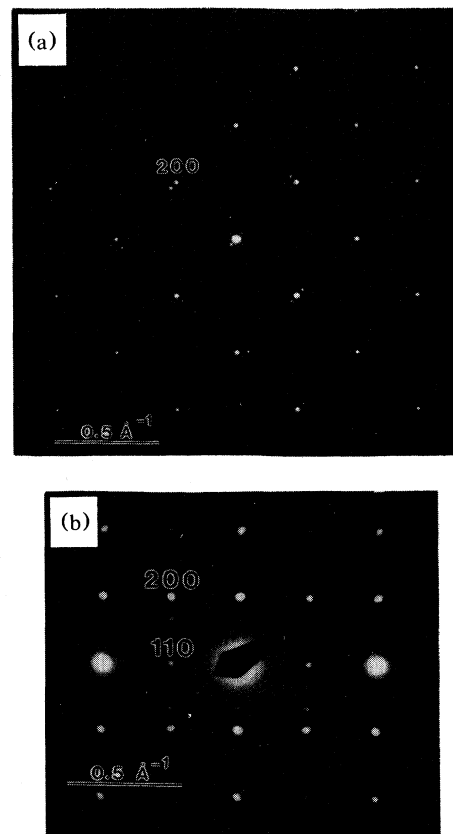
the specimen with the incident electrons modifies their phases only weakly) imaged under specific electron microscope operating conditions (objective lens set at Scherzer defocus with an objective aperture excluding all electrons scattered from real-space periodicities less than microscope point-to-point resolution), lattice structure images of a periodic object approximate to the projected crystal potential.[21] It is found that the image at the thinnest edge of the crystal in Fig. 4(a) broadly corresponds to the projected potential and images from thicker regions of the crystal also show gross features predicted by dynamical electron scattering theory, as has been confirmed by comparison of experimental images with simulated images calculated using the multislice algorithm.[22] Unit-cell midpoints (i.e., at z=0.5c) between the most heavily scattering lead planes are indicated by arrows in the figure. We note that in lower magnification images recorded perpendicular to the c axis, we see very little evidence for intergrowths of material with a different lattice parameter along c, in marked contrast to Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O materials which exhibit polymorphic series with varying c axis (see, e.g., Refs. 14, 23, and 24).

FIG. 5. a^*-b^* electron diffraction patterns: (a) A two-dimensional array of subsidiary Bragg maxima along a and b in an A=Sr+Eu crystal (note the absence of [110]-type reflections); and (b) a threefold periodicity along [110] and [1$\bar{1}$0] in an A=Dy+Sr crystal.

diffraction pattern has also been observed in $A = $Dy/Sr crystals.

In Fig. 5(b), we show a structure which we have frequently observed in a^*-b^* reciprocal lattice planes of $A = Dy+$Sr crystals, which exhibits a three times periodicity along the [110] and/or [1$\bar{1}$0] directions. These structures have not been observed in the $A = Eu+$Sr or $A = Dy+$Ca/Sr structures. We also note that we have observed two subvariants of this structure: It may either be one-dimensional along either [110] or [1$\bar{1}$0] in which case the 5.4-Å reflections are not present, or it may be two-dimensional along both [110] and [1$\bar{1}$0], in which case the 5.4-Å reflections are present. It does not appear that this structure is consistent with either twinning or twist boundaries in the basal plane. Careful measurements of the exact positions of the subsidiary diffraction maxima, however, reveal that they are not exactly equally spaced, with a few percent variation between adjacent maxima. This may be consistent with planar faults on planes other than the basal plane. The systematic absence or presence of [100] and [010] reflections, however, again suggest additional interesting structural variations.

In summary, the microstructure of three of the new $Pb_2Sr_2ACu_3O_8$ class of high-T_c superconductors has been studied using TEM. The compositions studied were $A = Eu+$Sr ($T_c \sim 60$ K), Dy$+$Ca/Sr ($T_c \sim 60$ K), and Dy$+$Sr ($T_c \sim 15$ K). All structures frequently exhibited [100] and [010] reflections in the a^*-b^* reciprocal lattice which violate the c centering of the structure determined by x-ray diffraction. In the $A = Sr+$Eu crystals, approximately 50% of diffraction patterns recorded in this plane showed the 5.4-Å spacing. If the host structure determined by x-ray diffraction is assumed to be c centered with $a = 5.4$ Å, or (actually equivalently from the single-crystal data of Ref. 1) primitive with $a = 3.8$ Å, we tentatively assign these relatively weak 5.4-Å reflections to be indicative of a 5.4-Å primitive unit cell. The origin of this weak c-centering violation remains unclear.

We have also observed in approximately 25% of the $A = Eu+$Sr crystals in the a^*-b^* plane, a superstructure modulation along either a^* or b^* of magnitude 4.6 ± 0.2 a or b. The only structural difference detected between the $A = Dy+$Sr material with a relatively low T_c of 15 K and the $A = Dy+$Ca/Sr and $A = Eu+$Sr materials with $T_c \sim 60$ K is the presence of extra reflections along [110] and/or [1$\bar{1}$0] in many fragments of the former structure. Further work is underway to determine the exact nature of this structure.

In conclusion, it is clear that the new $Pb_2Sr_2ACu_3O_8$ class of high-T_c superconductors offers the same rich variety of structures as previous superconducting ceramics. The existence of these new high-T_c ceramics provides further insight into the superconducting phenomenon.

[1] R. J. Cava, B. Batlogg, J. J. Krajewski, L. W. Rupp, L. F. Schneemeyer, T. Siegrist, R. B. van Dover, P. Marsh, W. F. Peck, Jr., P. K. Gallagher, S. H. Glarum, J. H. Marshall, R. C. Farrow, J. V. Waszczak, R. Hull, and P. Trevor, Nature (London) **336**, 211 (1988).

[2] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Reitman, S. Zahurak, and G. P. Espinoza, Phys. Rev. Lett. **58**, 1676 (1987).

[4] C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

[5] C. W. Chu, J. Bechtold, L. Gao, P. H. Hor, Z. J. Huang, R. L. Meng, Y. Y. Sun, Y. Q. Wang, and Y. Y. Hue, Phys. Rev. Lett. **60**, 941 (1988).

[6] J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Bogel, Phys. Rev. B **36**, 226 (1987).

[7] S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. van Dover, R. M. Fleming, S. H. Glarum, S. Nakahara, R. Farrow, J. J. Krajewski, S. M. Zahurak, J. W. Wasczak, J. H. Marshall, P. Marsh, L. W. Rupp, Jr., and W. F. Peck, Phys. Rev. B **38**, 893 (1988).

[8] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. Pt. 2 **27**, L209 (1988).

[9] Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 55 (1988); **332**, 138 (1988).

[10] L. Gao, Z. J. Huang, R. L. Meng, P. H. Hor, J. Bechtold, Y. Y. Sun, C. W. Chu, Z. Z. Sheng, and A. M. Hermann, Nature (London) **332**, 623 (1988).

[11] A. W. Hewat, E. A. Hewat, J. Brynestad, H. Mook, and E. D. Specht, Physica C **152**, 438 (1988).

[12] C. Chaillot, M. A. Alario-Franco, J. J. Capponi, J. Chevanas, J. L. Hodeau, and M. Marezio, Phys. Rev. B **36**, 7118 (1987).

[13] D. J. Werder, C. H. Chen, R. J. Cava, and B. Batlogg, Phys. Rev. B **38**, 5130 (1988).

[14] H. W. Zandbergen, G. van Tendeloo, J. van Landuyt, and S. Amelinckx, Appl. Phys. A **46**, 233 (1988).

[15] S. Horiuchi, H. Maeda, Y. Tanaka, and Y. Matsui, Jpn. J. Appl. Phys. Pt. 2 **27**, L1172 (1988).

[16] P. L. Gai and P. Day, Physica C **152**, 335 (1988).

[17] K. Hiraga, M. Hirabayshi, M. Kikuchi, and Y. Syono, Jpn. J. Appl. Phys. Pt. 2 **27**, L573 (1988).

[18] Y. Gao, P. Lee, P. Coppens, M. A. Subramanian, and A. W. Sleight, Science **241**, 954 (1988).

[19] R. Hull and R. J. Cava (unpublished).

[20] C. H. Chen, D. J. Werder, G. P. Espinosa, and A. S. Cooper, Phys. Rev. B **39**, 4686 (1989).

[21] See, for example, J. C. H. Spence, *Experimental High Resolution Electron Microscopy* (Clarendon, Oxford, 1981).

[22] P. Goodman and A. Moodie, Acta Crystallogr. Sect. A **30**, 280 (1974).

[23] H. W. Zandbergen and P. Groen, Solid State Commun. **66**, 397 (1988).

[24] M. Hervieu, C. Michel, B. Domenges, Y. Laligant, A. Lebail, G. Ferey, and B. Raveau, Mod. Phys. Lett. B **2**, 491 (1988).

[25] E. A. Hewat, J. J. Caponi, R. J. Cava, C. Chaillot, M. Marezio, and J. L. Tholence (to be published).

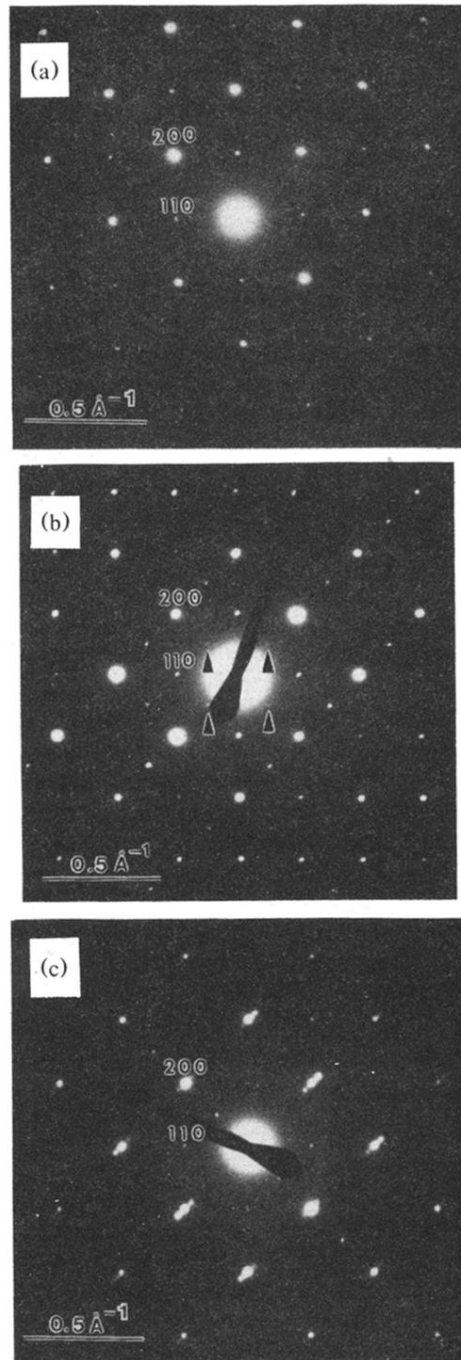[26] C. H. Chen, D. J. Werder, S. H. Liou, H. S. Chen, and M. Hong, Phys. Rev. B **37**, 9834 (1988).

FIG. 2. Electron diffraction patterns from the $\mathbf{a}^*$-$\mathbf{b}^*$ plane of $A =$ Eu + Sr crystals: (a) Fundamental c centered 5.4-Å unit cell, consistent with the x-ray structure determination of Fig. 1; (b) with extra [010] or [100] reflections (indicated by arrows) implying a primitive 5.4-Å unit cell; and (c) with superstructure modulation along $\mathbf{a}^*$ or $\mathbf{b}^*$. Reflections are indexed on the basis of a 5.4-Å c centered unit cell as in Ref. (1). Note that the assignation of [h00] vs [0k0] directions is arbitrary.
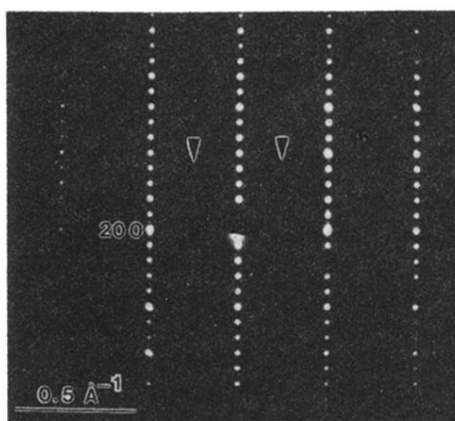
FIG. 3. Electron diffraction pattern along either the [100] or [010] axis of an $A = Dy + Ca/Sr$ crystal. Note the systematic rows of reflections from the 5.4-Å periodicity along **a** or **b** in the structure (indicated by arrows).
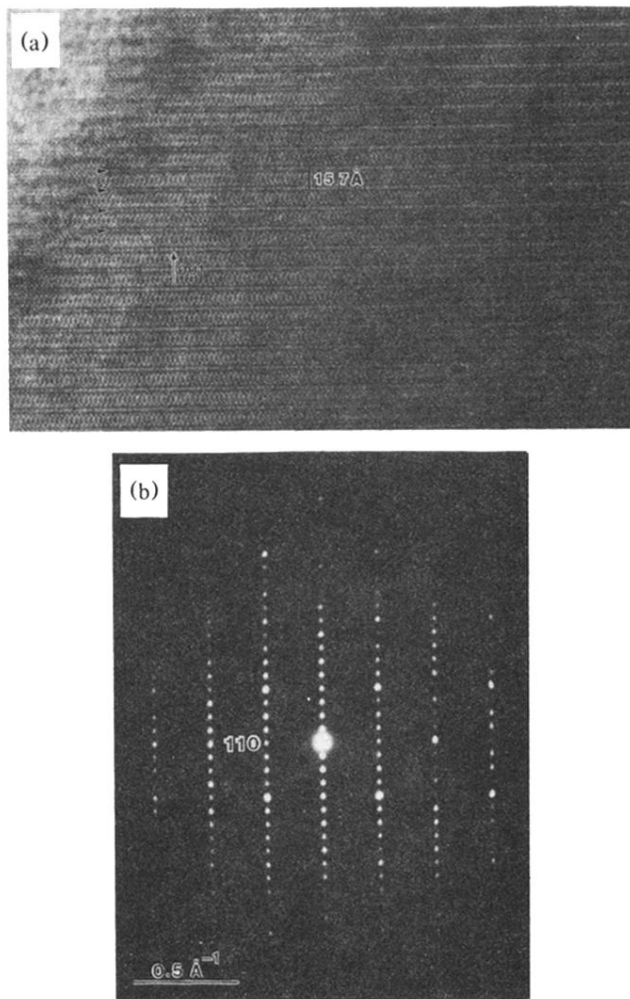
FIG. 4. (a) Lattice structure image and (b) electron diffraction pattern along a [110] or [1$\bar{1}$0] axis of an $A = $ Dy + Sr crystal. The midpoints (at $z = 0.5$ c) between Pb planes are indicated by arrows in (a).

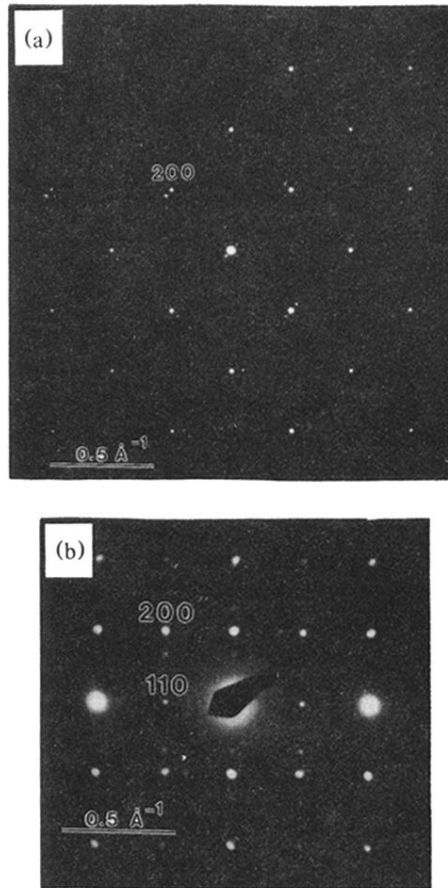FIG. 5. a^*-b^* electron diffraction patterns: (a) A two-dimensional array of subsidiary Bragg maxima along **a** and **b** in an $A = Sr + Eu$ crystal (note the absence of [110]-type reflections); and (b) a threefold periodicity along [110] and [1$\bar{1}$0] in an $A = Dy + Sr$ crystal.