LA-UR -88-569

CONF-880481--1

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TITLE ORDERED STRUCTURES IN $YBa_2Cu_3O_{7-y}$, $La_{2-x}Sr_xCuO_{4-\partial}$ AND RELATED PEROVSKITES

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DE88 006461

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SUBMITTED TO MRS Extended Abstract Book on High Temperature Superconductors
Reno, NV
April 4, 1988

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FORM NO. 836 R4
ST. NO. 2629 5/81

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ORDERED STRUCTURES IN $YBa_2Cu_3O_{7-y}$, $La_{2-x}Sr_xCuO_{4-\partial}$ AND RELATED PEROVSKITES

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ABSTRACT

Electron microscopy and electron diffraction studies have been performed on the superconducting oxides $YBa_2Cu_3O_{7-y}$, $GdBa_2Cu_3O_{7-y}$ and $La_{2-x}Sr_xCuO_{4-\partial}$ as well as the related perovskites La_2CuO_4, Eu_2CuO_4 and Gd_2CuO_4. Extra reflections are commonly observed in all the cases. For example, in the 123 compounds, in situ heating leads to transformations from orthorhombic to tetragonal with a loss of twin structure; on cooling the oxygen vacancies re-order in the basal plane to give 1/3(100)* or 1/4(110)* diffraction spots. In tetragonal Eu_2CuO_4 and Gd_2CuO_4, the [001] diffraction patterns often have extra spots at 1/2(110)* or at 1/4(110)* positions. Extra spots are also observed in La_2CuO_4 (orthorhombic) but this is probably due to the space group being primitive rather than centered. These observations are discussed in terms of the ordering of oxygen vacancies in the Cu-O planes of the various perovskite structures.

EXPERIMENTAL TECHNIQUES

The $YBa_2Cu_3O_{7-y}$ specimens were prepared as described previously[1]. The La_2CuO_4, Eu_2CuO_4 and Gd_2CuO_4 material were grown as single crystal flakes from a PbO or CuO flux. Specimens for transmission electron microscopy (TEM) were prepared either by grinding in a mortar and pestle or by ion milling using a liquid nitrogen specimen cooler. TEM was performed on a Philips EM400T operating at 120kV.

RESULTS

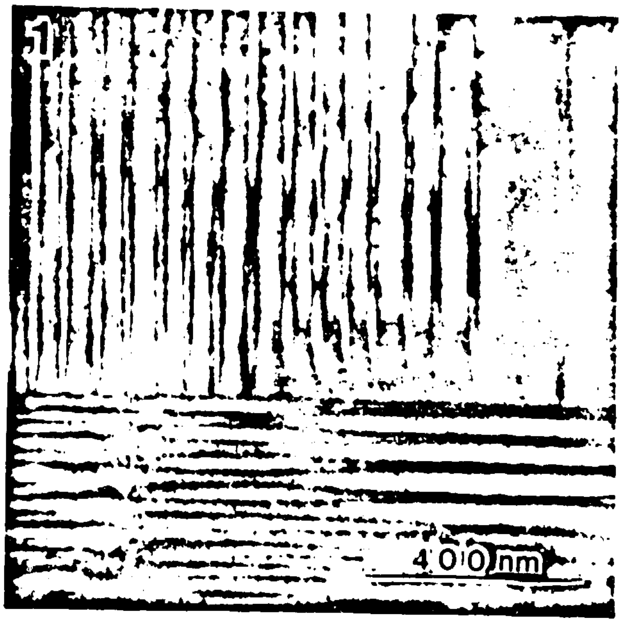
Superconducting 123 material always contains twins on {110} planes (Fig. 1) which are formed to accomodate the shape change during the transformation from tetragonal to orthorhombic at ~700^{o}C. The twins can be removed by heating, by irradiation or by reduction in the vacuum of the microscope. For the case of pulse heating with the electron beam, if the specimens are cooled immediately, then the twin structure is restored. If significant oxygen loss occurs, other ordered structures are observed (Fig. 2). Fig. 2(b) shows extra reflections at 1/3(100)* and 2/3(100)* positions indicating a probable unit cell $a_T \times 3a_T \times c_T$ (T refers to the tetragonal unit cell) while Fig. 2(c) shows extra reflections at 1/4(110)* and 1/2(110)* indicating a probable unit cell $a_T\sqrt{2} \times 2a_T\sqrt{2} \times c_T$. Possible schemes of oxygen vacancy ordering are given in the discussion.

La_2CuO_4 also undergoes a transformation from tetragonal to orthorhombic, in this case at ~200^{o}C, while $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ transforms at ~200K. Again twins are the most prominent feature of the microstructure at ambient temperature in La_2CuO_4 (Fig. 3) and they can be induced in the Sr-containing material by in situ cooling. However, the twins in the 123 and 214 materials have a quite different origin. In 123 material, the oxygen vacancies order (diffusively) so as to form Cu-O chains along the two possible axes in the basal plane. In 214 material, the distortion to the orthorhombic structure occurs non-diffusively and there is detectable vacancy ordering. However, we have detected extra reflections consistent with Pccn symmetry [2], moreover, on cooling La_2CuO_4 reflections are observed at (110)* positions in the [001] zone which are streaked along <110>*, indicating a possible new phase.

Both Eu_2CuO_4 and Gd_2CuO_4 have a space group I4/mmm with a triple perovskite unit cell (different from the other two structures). In both cases extra reflections are frequently observed in the diffraction patterns. Fig. 4(a) shows an example with extra reflections at 1/4(110)*, 1/2(110)* and 3/4(110)* while Fig. 4(b) shows extra reflections at 1/2(110)* only. Domains or precipitates are associated with this ordering (Fig. 5). No difference in cation chemistry could be detected by x-ray spectrometry and so we assume that the effect is caused by oxygen non-stoichiometry and consequent oxygen vacancy ordering. Fig. 4(a) could be associated with a $a_T\sqrt{2} \times 2a_T\sqrt{2} \times c_T$ unit cell and Fig. 4(b) with a $a_T\sqrt{2} \times a_T\sqrt{2} \times c_T$ unit cell.

DISCUSSION

We shall confine ourselves to discussing the oxygen ordering. In all cases there is a Cu-O square basal net which is most susceptible to loss of oxygen and the introduction of oxygen vacancies. Examples of such nets and their corresponding diffraction patterns are shown in Fig. 6. Fig. 6(a) is a net with a 50% occupancy of oxygen sites giving rise to the Cu-O chains in $YBa_2Cu_3O_7$. If one third of the chains are vacant (corresponding to $YBa_2Cu_3O_{6.67}$), then the diffraction pattern in Fig. 6(b) arises. This is similar to Fig. 2(b) and could correspond to the 55K superconductor which is reported at about this stoichiometry [3]. The La_2CuO_4 and Eu_2CuO_4 structures ideally have fully occupied square nets. However, possible schemes for 25% vacancy occupation are shown in Figs. 6(c) and 6(d) which can explain the diffraction pattern in Figs. 4(a) and (b). A similar scheme to Fig. 6(c) in 123 material with 75% vacancy occupation (i.e. vacant and occupied sites reversed) can explain the diffraction pattern in Fig. 2(c) and would correspond to $YBa_2Cu_3O_{6.5}$.



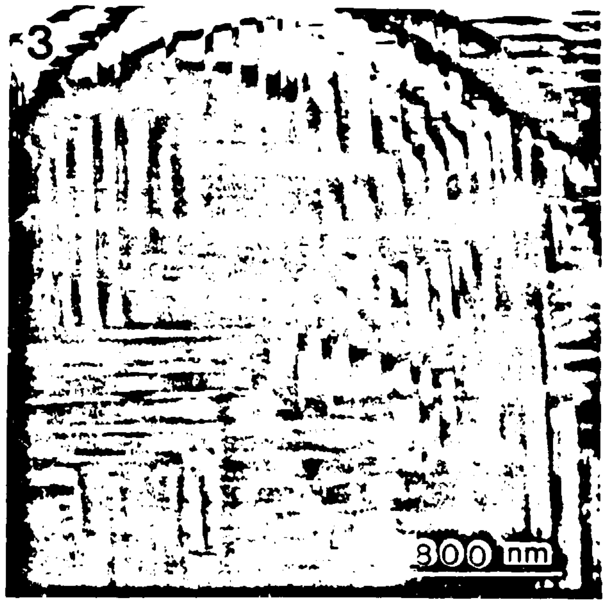
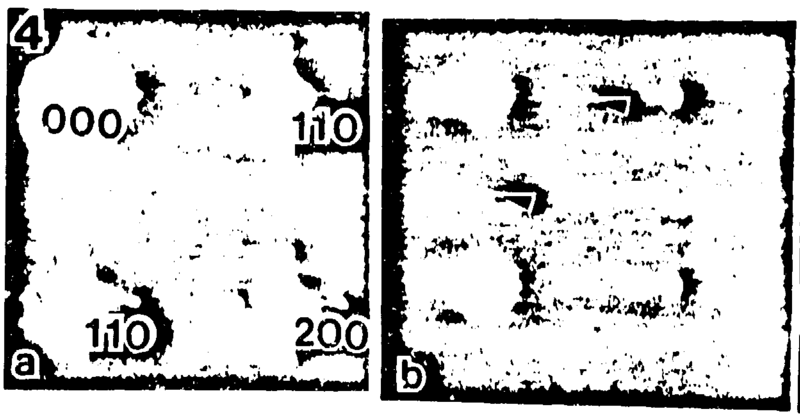


Fig. 1: {110} Twins in $YBa_2Cu_3O_{7-y}$ observed along [001].

Fig. 3: {110} Twins in $La_2Cu\,O_4$ observed along [001].

Fig. 2: [001] SAD patterns in $YBa_2Cu_3O_{7-y}$: (a) showing spot doubling due to twins, (b) after pulse heating, (c) after aging for 1 day.



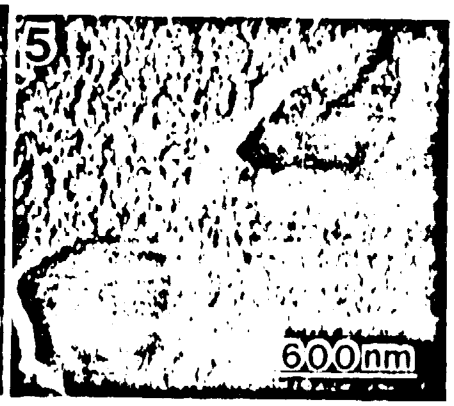


Fig. 4: [001] SAD patterns from two different regions of Eu_2CuO_4.

Fig. 5: Ordered regions corresponding to Fig. 4(a).

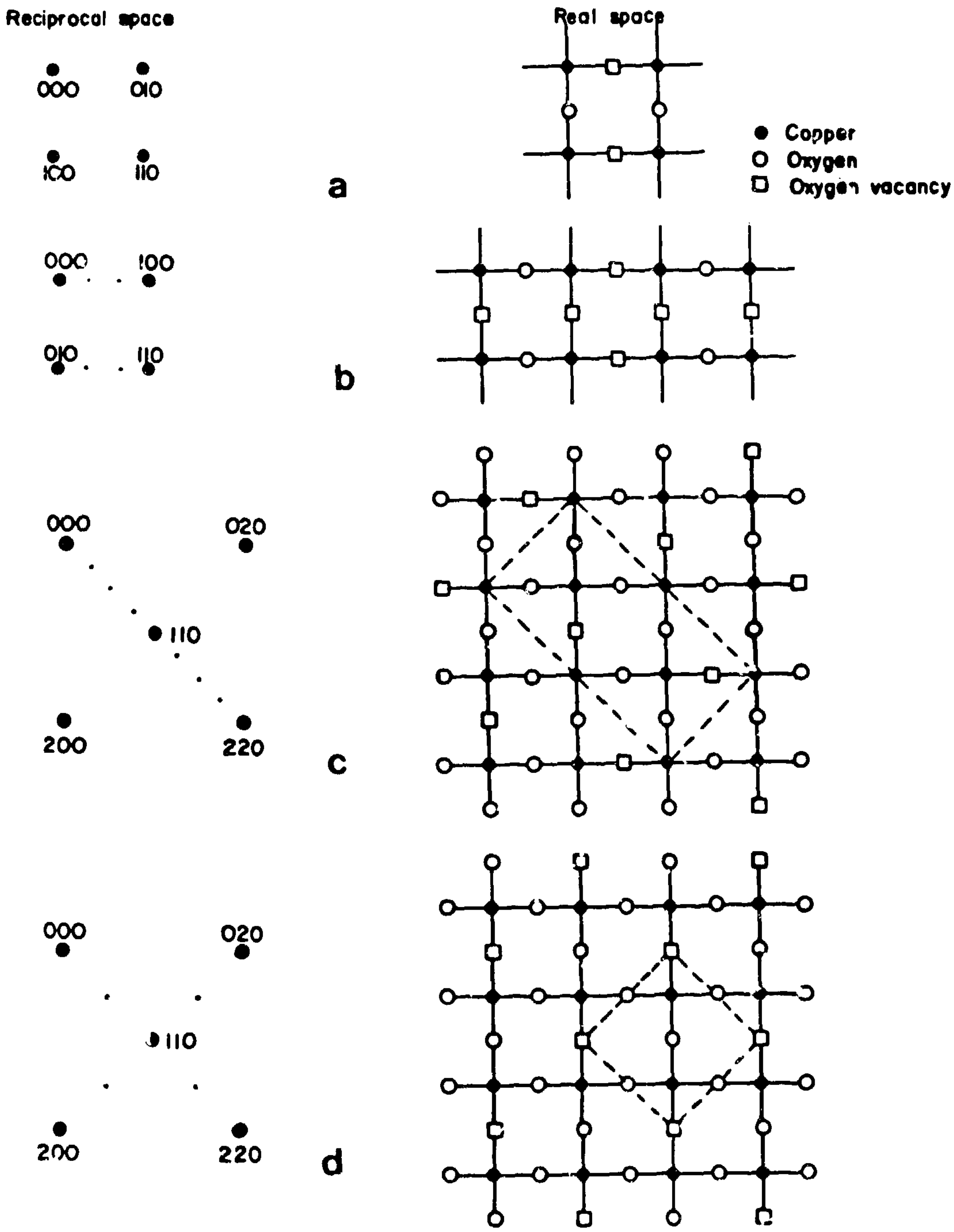


Fig. 6: Diffraction patterns and corresponding square Cu-O nets with various configurations of vacancies in the basal plane of (a) $YBa_2Cu_3O_7$, (b) $YBa_2Cu_3O_{6.67}$, (c) and (d) $Eu_2CuO_{3.5}$.