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Diffraction evidence for oxygen-vacancy ordering in annealed $Ba_2YCu_3O_{7-\delta}$ ($0.3 \lesssim \delta \lesssim 0.4$) superconductors

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Diffuse streaks centered at $q=(\frac{2}{5},0,0)$ and $(\frac{1}{2},0,0)$ have been observed in annealed $Ba_2YCu_3O_{7-\delta}$ with $0.3 \lesssim \delta \lesssim 0.4$, which has a T_c of 60 K and a Meissner effect equivalent to the 90-K phase. We interpret the presence of the diffuse streaking as a result of short-range oxygen vacancy ordering. The vacancy ordering has a short correlation length in the *a*-axis direction and a long correlation length in the *b*-axis direction along the Cu-O chains. The ordered structure is completely uncorrelated parallel to the *c* axis.

The physical properties, resistivity, magnetic susceptibility, and the temperatures of the structural phase transition and of the superconducting transition of the high-T_c oxide superconductors are quite sensitive to oxygen stoichiometry, and specifically to the positions of the oxygen atoms. In particular, the perovskite-based $Ba_2YCu_3O_{7-\delta}$ compound exists over a range of oxygen concentration, $0 \le \delta \le 1$, having its electronic behavior changing from superconducting near $\delta=0$, to semiconducting for $\delta \simeq 1$.

The importance of stoichiometry and the spatial arrangement of oxygen on the physical properties of $Ba_2YCuO_{7-\delta}$ was recently shown by Cava *et al.*[1] Figure 1 shows the change of T_c and resistivity with oxygen composition. The plateau at $T_c=60$ K and the minimum in resistivity (along with a maximum in susceptibility[1]) suggest oxygen-vacancy ordering is present in the composition range $0.3 \lesssim \delta \lesssim 0.4$.

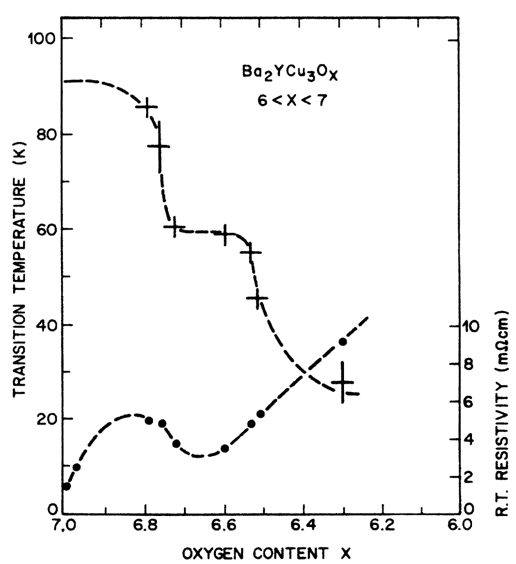

FIG. 1. Oxygen stoichiometry dependence of the resistive superconducting transition temperature in $Ba_2YCu_3O_x$ for $6.3 \le x \le 7$. Vertical bars indicate the (10–90)% resistive transition width, with the midpoint marked with a cross. Also shown are the room-temperature resistivities.

In this Rapid Communication we present the results of electron diffraction studies which confirm the presence of short-range oxygen-vacancy ordering. Bulk polycrystalline $Ba_2YCu_3O_{7-\delta}$ was prepared by a gettered annealing technique. The details of the preparation technique have been described elsewhere.[1] The $T_c=60$ K material exhibited a Meissner effect equivalent to that observed in the 90-K phase. Samples for transmission electron microscopy (TEM) studies were prepared either by crushing the bulk samples or by polishing and then ion milling. No differences were found in the samples prepared by these two methods, as far as diffraction studies were concerned. TEM studies were carried out in a JEOL 2000 FX electron microscope operating at 200 kV. Two samples with $\delta=0.2$ and $\delta=0.28$ were examined.

Examination of the $\delta=0.28$ sample by TEM revealed the presence of twin boundaries commonly observed in the orthorhombic phase of the oxide superconductors.[2] Selected area electron diffraction patterns obtained from a single twin domain with (001) orientation exhibited narrow diffuse streaking, elongated along the a^* direction, with intensity maxima at $Q=(h,k,l)+q$, where $q=(\frac{2}{5},0,0)$. This is shown in Fig. 2(a). Figure 2(b) shows a similar diffraction pattern obtained from an adjacent domain. As expected from the crystal symmetry across a twin boundary,[2] the diffuse streaking has now rotated 90° to that of Fig. 2(a), with peaks again at $q=(\frac{2}{5},0,0)$. A microdensitometer trace of the diffuse streaking along the a^* direction [Fig. 2(c)] clearly shows that the intensity of the diffuse streaking has peaks around $(\frac{2}{5}\,0,0)$ and $(\frac{3}{5},0,0)$. The diffuse streaking is visible at room temperature. Its visibility is enhanced significantly at lower temperatures due to a reduction in thermal diffuse scattering. All electron diffraction patterns shown in this work were obtained at a temperature ~100 K. In addition to the diffuse streaking centered at $q=(\frac{2}{5},0,0)$, we have also observed from other grains narrow diffuse streaking with $q=(\frac{1}{2},0,0)$, extending roughly from $q=(\frac{1}{3},0,0)$ to $(\frac{2}{3},0,0)$ as shown in Fig. 3(a). A microdensitometer trace shows that the diffuse intensity peaks around $q=(\frac{1}{2},0,0)$ [Fig. 3(b)]. Both types of diffuse

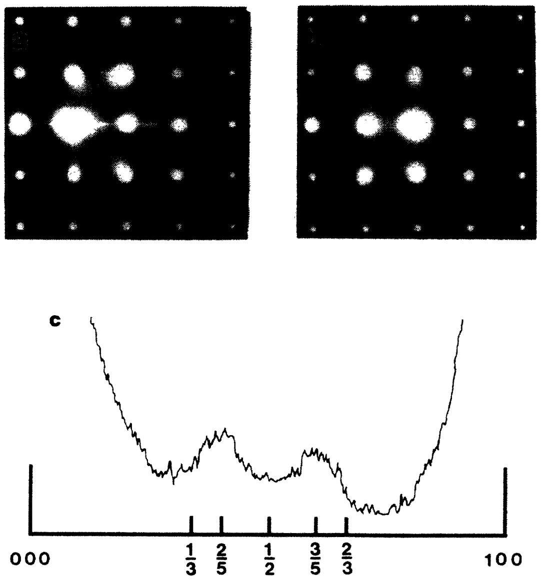

FIG. 2.(a) Electron diffraction pattern of the (001) zone axis from a single twin domain. Note narrow diffuse streaking along a^* direction with intensity maxima at $(\frac{2}{5},0,0)$ positions; (b) diffraction pattern of the (001) zone axis from a twin domain adjacent to that of 2(c) Microdensitometer trace along a^* direction showing peaks in the diffuse streaking at $(\frac{2}{5},0,0)$ and $(\frac{3}{5},0,0)$.

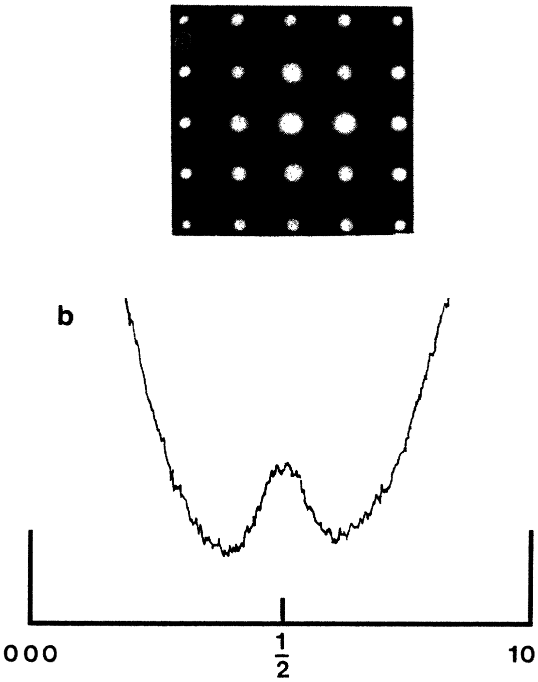

FIG. 3.(a) Electron diffraction pattern of the (001) zone axis from a grain with $(\frac{1}{2},0,0)$ intensity maxima. Here the selected area aperture covers two twin domains. (b) Microdensitometer trace from (a) along a^* direction.

streaking are common.

By tilting the sample with respect to various symmetry axes, it appears that the diffuse streaking has the shape of a ribbon running parallel to the c^* direction; thus, implying no ordering among chains along the c direction. We believe that some buckling of the O-Cu-O chain may exist due to the presence of the vacancies. It appears that disorder of the O-Cu-O linear chains is confined only to the b-c plane since the diffuse streaking is quite narrow along a^* suggesting very good ordering in that direction. Grains with $q=(\frac{1}{2},0,0)$ correspond to every other row along the a direction being totally vacant of oxygen along the b axis. Those grains with $q=(\frac{2}{5},0,0)$ have a more complex ordering.

Various types of diffuse streaks have been reported[3-5] previously in $Ba_2YCu_3O_{7-\delta}$ superconductors. In these cases, diffuse streakings along a^*, b^*, c^*, or other directions are found to change from area to area in a sample and, furthermore, a change of oxygen stoichiometry seems to have very little effect on the presence of various types of diffuse streaks. In our case, only diffuse streaks along the b^* direction are found and they are centered either at $q=(\frac{2}{5},0,0)$ or $(\frac{1}{2},0,0)$. Moreover, in our low-temperature annealed samples, diffuse streaking is only observed for samples with $0.3 \lesssim \delta \lesssim 0.4$ at the 60-K plateau. A sample with $\delta=0.2$ where T_c starts to fall sharply from 90 K did not reveal any diffuse streaking. This is the first time one can correlate the absence (or appearance) of diffuse streaks to the oxygen stoichiometry. Recently Tanaka, Terauchi, Tsuda, and Ono[5] reported the observation of diffuse streaking centered at $q=(0,\frac{1}{2},0)$ in $Ba_2YCu_3O_{7-\delta}$ with $\delta=0.1-0.2$. They attributed the $q=(0,\frac{1}{2},0)$ streaking to a charge-density wave instability of the one-dimensional O−Cu−O linear chains along the b^* direction. Resistivity versus temperature curves[1] for various values of oxygen stoichiometry show a metallic behavior for δ near $\frac{1}{3}$. These data, along with that of Fig. 1, rule out the existence of a charge-density wave as the cause of the diffuse streaking in our samples. Also, the diffuse streaking remains diffuse down to a temperature of ~20 K.

Within the range of oxygen composition in Fig. 1, vacancy ordering can exist for various ratios, such as $\frac{1}{3}$, $\frac{1}{4}$, $\frac{2}{5}$, $\frac{3}{8}$, and $\frac{1}{2}$. The sample studied in this work had $0.3 \lesssim \delta \lesssim 0.4$, as measured by oxygen weight loss. Our observations of grains with either $q=(\frac{2}{5},0,0)$ or $(\frac{1}{2},0,0)$ diffuse streaking strongly support oxygen-vacancy ordering in this material, but may indicate microscopically nonuniform oxygen loss. The orthorhombic superconducting grains have a high twin density (on the order of 10^5 boundaries cm^{-2}), whereas, the nonsuperconducting phase has no twin boundaries. Since our samples are polycrystalline, and with ~10% of the material not twinned, one would expect a complex oxygen diffusion behavior. Oxygen diffusion will be fastest along high-diffusivity paths such as grain and twin boundaries. These surface diffusion pathways could affect not only the oxygen-vacancy ordering uniformity, but also the weight loss measurement assumption that δ is microscopically uniform throughout the sample.

In summary, we have presented results of electron diffraction studies in support of the idea of oxygen-vacancy ordering in oxygen-deficient $Ba_2YCu_3O_{7-\delta}$ $(0.3 \lesssim \delta \lesssim 0.4)$ superconductors. We have observed diffuse streaking at $q = (\frac{2}{5},0,0)$ and $(\frac{1}{2},0,0)$. At this time, microscopic models for the two types of diffuse streaks have not been found. It is possible that other types of mechanisms (e.g., a displacive distortion) are also involved. Work to determine this is in progress. Electron diffraction results, together with resistivity and susceptibility measurements, make it quite certain that the origin of the diffuse streaking is due to oxygen-vacancy ordering and not to a charge density-wave distortion.

[1]R. J. Cava, B. Batlogg, C. H. Chen, E. A. Reitman, S. M. Zahurak, and D. J. Werder, Nature **329**, 423 (1987); R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. J. Werder, Phys. Rev. B **36**, 5719 (1987). Due to post specimen lens distortion, the diffuse streaks in these two references were assigned to the *b* axis where they should be along the *a* axis.

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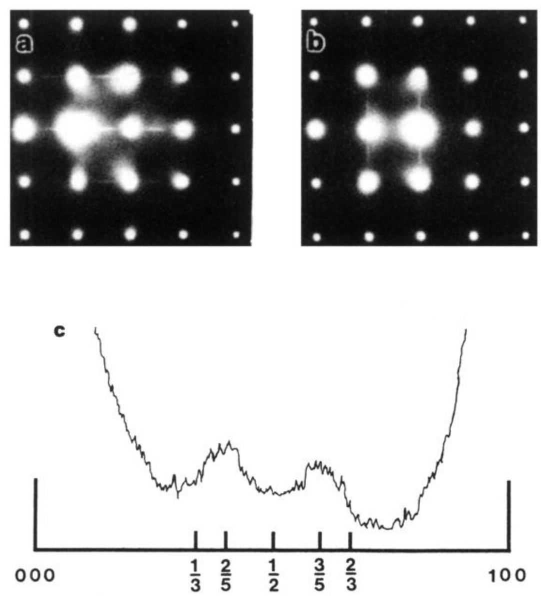

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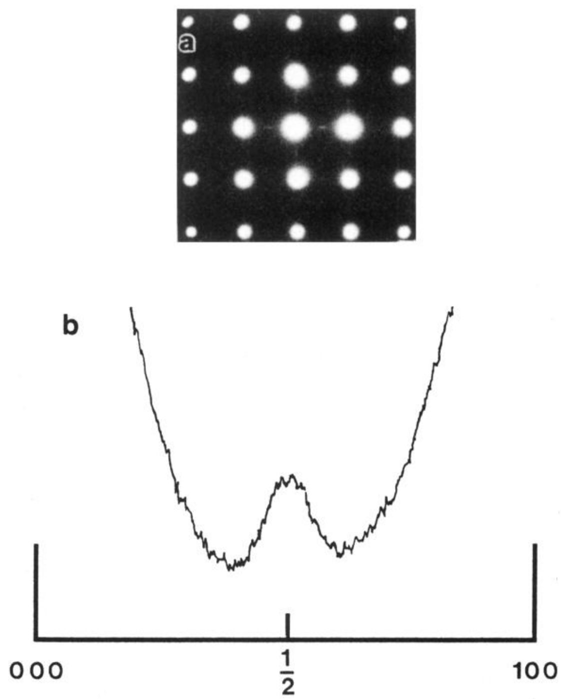

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