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Twinning Effects in the Orthorhombic Form of a $Ba_2YCu_3O_{7-x}$ Superconductor

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Twinning effects in a $Ba_2YCu_3O_{7-x}$ superconductor (orthorhombic form) have been analyzed by X-ray diffraction techniques. Regions of reciprocal space surrounding the (220), the (2$\bar{2}$0), the (400), and the (040) reflections for each of three twinned crystals were mapped on a single crystal diffractometer. Various modes of twinning were modeled by computer and the results were compared to the observed intensity distribution in the proximity of these reflections. A twinning mode based on a main and a smaller satellite crystal, each contining a mirror along $h\bar{h}0$, with the satellite crystal rotated 90° relative to the main crystal gave the best agreement to the observed data.

Introduction

The Ames Laboratory of the Department of Energy has had an active program in superconductor research for a number of years. Hence, after the discovery of superconductivity above 90 K in the Ba–Y–Cu–O system (*1*), a number of groups in the laboratory began to investigate further the synthesis, properties, and bulk preparation techniques of the 1–2–3 type superconductors. As part of these studies, "single" crystals of $Ba_2YCu_3O_{7-x}$ were grown by K. Gschneidner and his group from CuO melts (*2*). We report herein X-ray structural studies of this material and, in particular, the mode of twinning it exhibits.

Crystallographic Studies

An apparently single-orientation crystal of the superconducting material of approximate dimensions 0.2 × 0.2 × 0.05 mm was mounted on a glass fiber using Duco cement and attached to a standard goniometer head. The crystal was centered on a four-circle DATEX X-ray diffractometer. Four preliminary ω-oscillation photographs were taken at various ϕ settings. The approximate positions of 10 reflections were selected from the photographs and used as input to an automatic indexing program (*3*). The resulting reduced cell and reduced cell scalars indicated a primitive orthorhombic lattice. Additional reflections having $2\theta > 25°$ were used to determine a more accurate orientation matrix. The unit cell parameters were determined to be a = 3.8187(14), b = 3.8692(14), c = 11.620(21) Å.

Intensity data were collected at room temperature (20°C) using Mo$K\alpha$ (λ = 0.70169 Å) radiation on the above diffractometer equipped with a graphite monochromating crystal and interfaced to a VAX station II/

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RC computer in a real-time mode. A total of 1043 intensities were measured, corresponding to reflections in the hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$ octants, using an ω-step scan technique with a scan half width of 0.5°. Many of the peak profiles obtained during data collection appeared abnormal. Data were collected to a maximum of sin θ/λ of 0.7 (60°—2Θ). No decay of the crystal during data collection was observed.

Intensity data were corrected for absorption (T_{min}/T_{max} = 0.020/0.084) as well as for Lorentz polarization effects. Because of the lack of a suitable reflection near $\chi = 90°$ to use for a Ψ-scan, a self-consistent empirical absorption correction (*4*) was used. Because of the large absorption coefficient (μ = 288.74 cm^{-1}), a θ-dependent correction was also applied. Of the 1043 reflections measured, the 829 that had $I > 3\sigma(I)$ were considered to be observed. Symmetry-equivalent reflections were averaged, yielding 305 reflections which were used for refinement (R_{av} = 0.040).

Refinement of the positional and thermal parameters was carried out in the space group *Pmmm*. A perovskite-like structure was used as the basis for the structural model. The positional and isotropic thermal parameters were refined using a full-matrix least-squares procedure (*5*). The positional parameters gave good agreement with those previously found using neutron data (*6–10*). However, when the anisotropic thermal parameters were refined, several of the atoms exhibited nonphysical behavior. This, along with the abnormal peak profiles obtained during data collection, led us to postulate that a twinning process was occurring.

Two additional crystals of the sample were mounted as described above and centered on the aforementioned diffractometer. Indexing of these crystals was performed in the same manner as described above. A computer program was written to scan a region of reciprocal space using a "step and count" technique. In this technique, the detector is moved through reciprocal space using a small stepsize, and the intensity of the diffracted beam is measured for several seconds after each step. For each of the three crystals, the regions of reciprocal space around the (220), the (2$\bar{2}$0), the (400), and the (040) reflections were scanned using a stepsize of 0.01 reciprocal lattice units in both h and k, and a counting time of 2 sec per point. These regions were each scanned a minimum of four times and the results of the scans were averaged for each crystal. The data were collected at room temperature (20°C). Plots of the averaged scans indicated that the shape of a given reflection was similar in each crystal. Representative plots of the observed intensity distribution for the (400), the (220), the (2$\bar{2}$0), and the (040) reflections are given in Fig. 1. Examination of the plots for each crystal clearly indicated that the samples used were not true single crystals and that a twinning process was occurring. The exact nature of the twinning is discussed below.

Twin Modeling

A computer program was written to generate the expected shape of a reflection for a given mode of twinning. The effect of instrument broadening was approximated by assuming a Gaussian reflection shape of the form

$$I_h = I_{h_0} \exp(-\alpha(h - h_0)^2),$$

where h_0 is a reciprocal lattice vector having integer indices, h is a reciprocal lattice vector, in the vicinity of h_0, having noninteger indices, in general, and α is an adjustable parameter which determines the width of the peak.

Three modes of twinning were modeled: (1) mirror planes along $hh0$ and $h\bar{h}0$, (2) a mirror plane along $h\bar{h}0$, and (3) a primary crystal containing a mirror along $h\bar{h}0$, with a smaller satellite, also containing a mirror along $h\bar{h}0$, rotated 90° relative to the orienta-

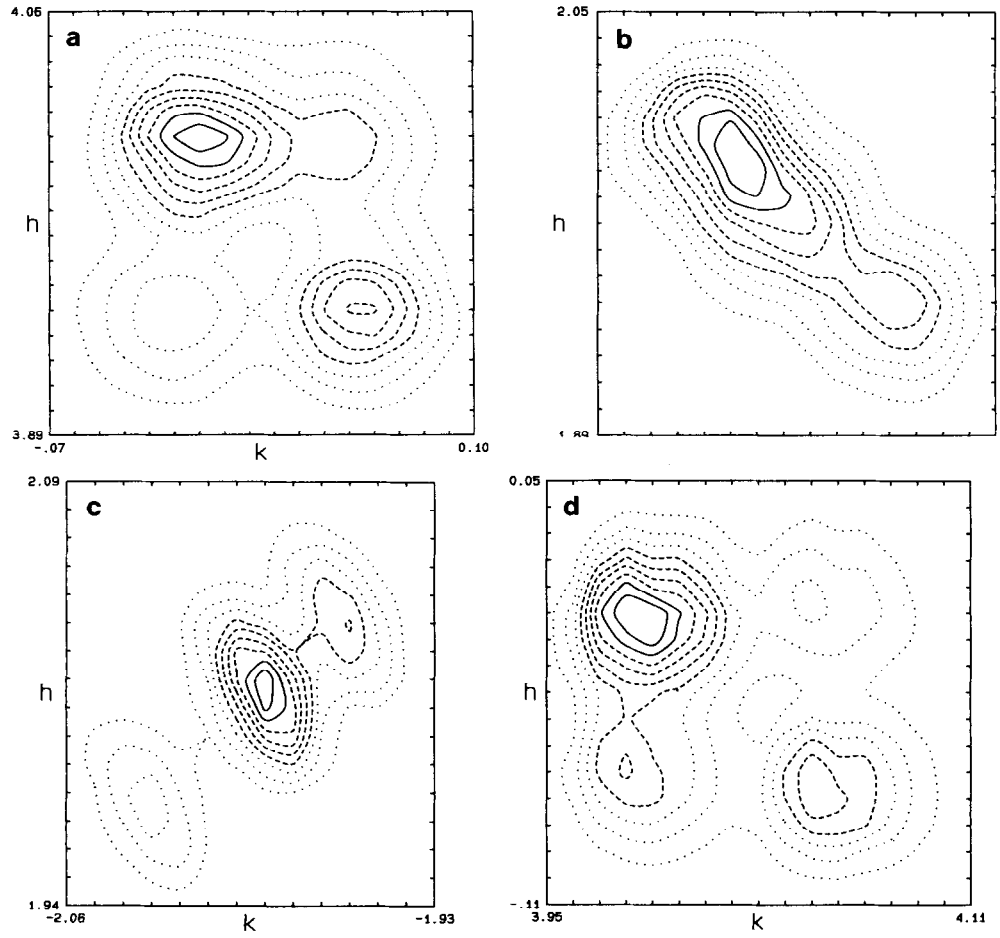

FIG. 1. Reciprocal space plots of (a) the observed (400) reflection, (b) the observed (220) reflection, (c) the observed ($2\bar{2}0$) reflection, and (d) the observed (040) reflection. In this and succeeding figures, contours are drawn every 10% of the maximum with dotted lines ≤30%, then dashed lines ≤ 70% and solid lines above 70%.

tion of the primary crystal. In the evaluation of the location of the various components relative to each other, differences in the a^* and b^* axial lengths and, hence, differences in the angles between the mirror plane(s) and the a^* and b^* axes were taken into account. Plots of the (400), the (220), and the ($2\bar{2}0$) reflections for the twinning modes are shown in Figs. 2–4. The plot of the ($2\bar{2}0$) reflection in twinning mode (2) is not shown since the reflection consists of a single peak. In all cases, it is evident that the third mode of twinning corresponds most closely to that which is observed and the poorest agreement is obtained if one assumes the first twinning mode.

Discussion

At high temperatures, this compound exists in the tetragonal space group $4/mmm$ having a fourfold rotation axis and mirrors

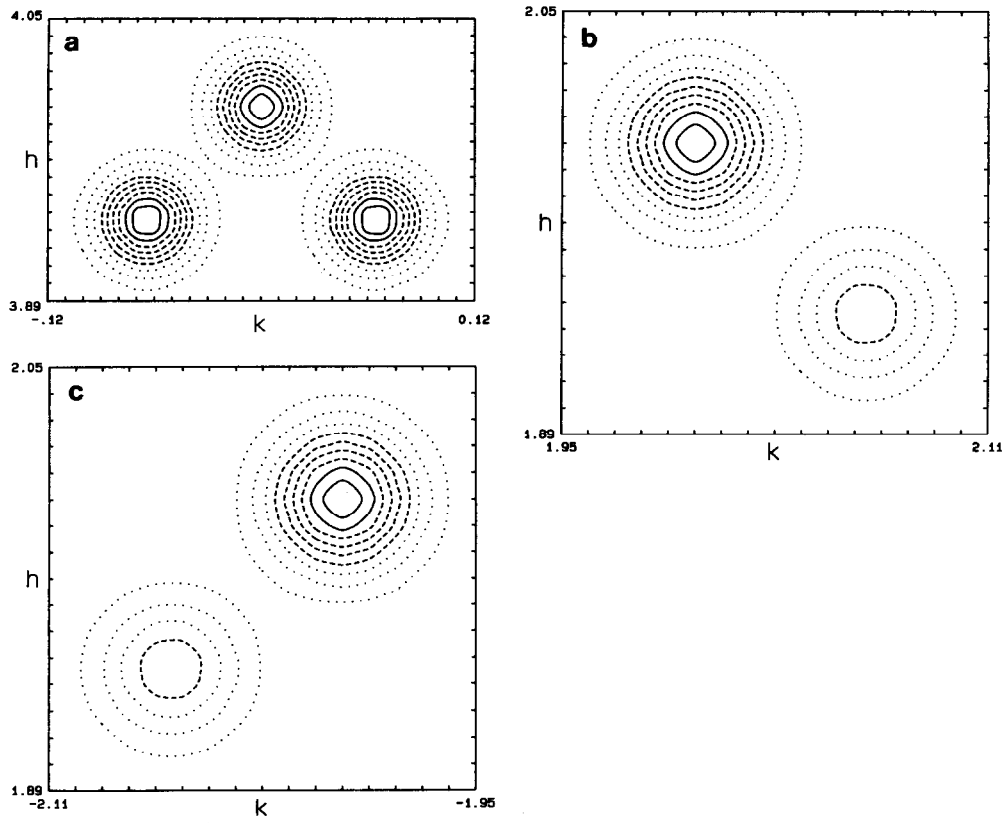

FIG. 2. Reciprocal space plots of (a) the calculated (400) reflection, (b) the calculated (220) reflection, and (c) the calculated ($2\bar{2}0$) reflection using twinning mode (1).

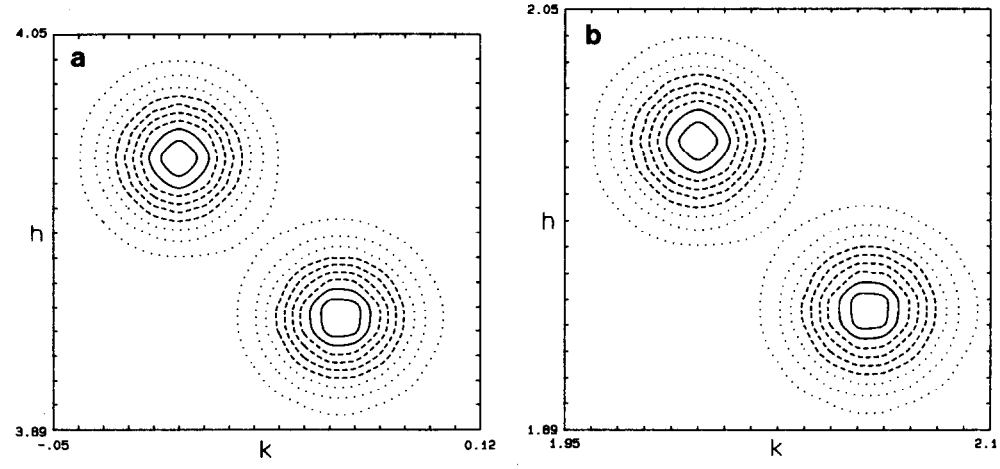

FIG. 3. Reciprocal space plots of (a) the calculated (400) reflection, and (b) the calculated (220) reflection using twinning mode (2).

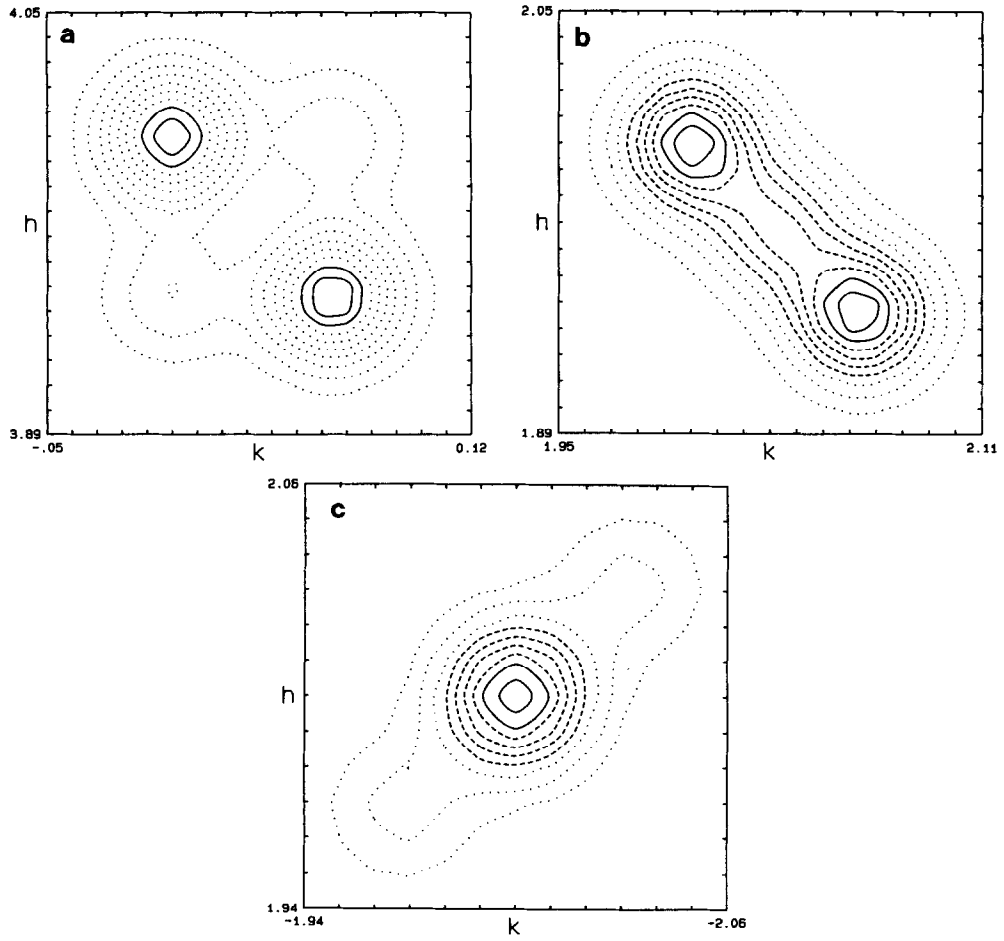

FIG. 4. Reciprocal space plots of (a) the calculated (400) reflection, (b) the calculated (220) reflection, and (c) the calculated ($2\bar{2}0$) reflection using twinning mode (3).

along $hh0$ and $h\bar{h}0$. As it cools, it undergoes a transformation to an orthorhombic phase. The accepted space group for this phase is *Pmmm*.

Since this orthorhombic space group contains mirror planes along each axis, one would expect that if a twinning mode utilizing a mirror along $hh0$ occurs, then it is equally likely that a twinning mode utilizing a mirror along $h\bar{h}0$ would also be present. In such a twinning mode, the (220) and the ($2\bar{2}0$) reflections should have the same shape. However, examination of the observed (220) and ($2\bar{2}0$) reflections clearly indicates that the two are quite different from each other. Also as shown in Fig. 2a, the (400) reflection should have three major components for this twinning mode, but the observed reflection only has two major components.

The twinning model which provides the best agreement to the structure of the observed reflections is mode (3): a main crystal and a satellite crystal, each containing a mirror along $h\bar{h}0$, with the satellite crystal rotated 90° relative to the main

crystal. It is not unexpected that a rotated satellite should be found, as this could easily be a result of the loss of the fourfold rotation axis. It was also noted that the intensity of the satellite reflections relative to the primary reflections showed some variation from crystal to crystal.

The most surprising result of our study is that the twinning model only contains one mirror. This may indicate that the correct space group is not *Pmmm* but is of lower orthorhombic symmetry, or that there is some type of long-range "memory" effect occurring so that once twinning begins in one direction, that direction becomes the preferred twinning direction.

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