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# Relationship between superconductivity and lattice distortion in Y-Ba-Cu-O compounds

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The letter presents an explanation for the reversal of peak intensities in x-ray diffraction patterns of Y-Ba-Cu-O compounds with the same nominal compositions but distinctive properties of superconductivity due to different cooling conditions. Structural differences between the phases caused by different lattice distortions as well as the effect of these distortions on superconductivity are also discussed.

In our preceding paper,<sup>1</sup> we reported on the high  $T_c$  (onset 120 K) superconductors in the Y-Ba-Cu-O system. The superconducting phase was identified as  $Y_1Ba_2Cu_3O_{9-x}$ , which was supposed to be an orthorhombic layered structure of oxygen-deficient perovskite.<sup>2-5</sup> The multiphase compounds, followed by the single-phase ( $ABO_3$ ) compounds, will be considered here. It has been found that the samples with the same nominal composition and heat treatment temperature demonstrated different superconductive properties due to different cooling conditions. These samples superconducted either with a  $T_c$  near  $LN_2$  temperature or with a  $T_c$  below this, or they showed the resistive properties of a semiconductor near  $LN_2$  temperature. Yet in the high-resolution electron microscopic images and in the electron diffraction patterns no differences have been found in the crystal structures of these samples. The x-ray diffraction patterns of these samples at room temperature also show great similarities; the geometrical positions of diffraction peaks are almost identical to each other (see Fig. 1). This suggests that these allotropic compounds (different phases) can all be derived from the ideal orthorhombic layered perovskite. However, there exists a vital difference: the intensities of the three pairs of the main diffraction peaks gradually reverse with the properties changing from one extreme to the other (Fig. 1). In this letter, we present an explanation for this reversal as a result of lattice distortions and discuss the effect of the distortions on the phases.

It is usual to consider the typical displacement phase transitions in perovskite when accounting for this reversal. However, for simplicity and clarity, we shall ignore the specific displacements of ions in the unit cell. We are limited to the changes of position (Bragg angle  $\theta$  or interplanar spacing  $d$ ) of each ( $hkl$ ) reflection caused by changes in lattice parameters. Most of the diffraction maxima in Fig. 1(a), corresponding to the superconducting phase, can be indexed according to the results of Beyers *et al.* for single-phase compounds.<sup>6</sup> A least-squares fit of the observed  $d$  values gave the lattice parameters  $a = 3.823 \text{ \AA}$ ,  $b = 11.681 \text{ \AA}$ , and  $c = 3.892 \text{ \AA}$ . It is well known that the overlap of reflections of different indices but of (approximately) the same  $d$  value heightens the diffraction peak. Another fact is that due to the approximate cubic symmetry of the substructure of the layered perovskite, for each pair of the main peaks, three reflections have the similar structure factors:  $F_{031} \doteq F_{130} \doteq F_{101}$ , etc. (see Table I). Based on these two facts and

comparing with the results of Fig. 1(a), most of the peaks in Fig. 1(c), corresponding to the semiconducting phase, may be indexed in either of two possible ways: Case 1. (031)/(130), (101),..., (060), (002)/(200),..., (161), (132)/(231),...; Case 2. (031)/(101), (130),..., (002), (060)/(200),..., (132), (161)/(231),... These rearrangements of the ( $hkl$ ) reflections along the  $2\theta$  axis correspond to changes in lattice parameters. The preliminary values of  $a$ ,  $b$ , and  $c$  in both cases were used to calculate the  $d$  values. It is found that in Case 2 there were two conflicts between the observed and the calculated  $d$  values near the positions of (021), (120) and (122), (221) reflections, while the calculated results for Case 1 tended to coincide with those observed. Therefore, Case 2 was abandoned. Finally a least-squares fit for Case 1 gave the lattice parameters of the

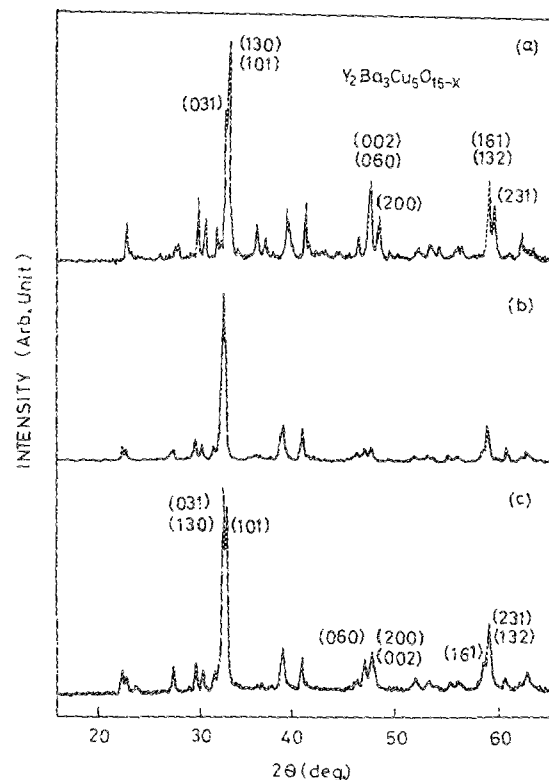


FIG. 1. X-ray diffraction patterns (at room temperature) of the multiphase samples (a) superconducting near  $LN_2$  temperature, (b) with  $T_c$  below this, and (c) showing the resistive property of a semiconductor near  $LN_2$  temperature.

TABLE I. Observed and calculated interplanar spacings for the superconducting and semiconducting phases.  $F_{031} \doteq F_{130} \doteq F_{101}$ ,  $F_{060} \doteq F_{002} \doteq F_{200}$ ,  $F_{161} \doteq F_{132} \doteq F_{231}$  (unit: angstrom).

<i>hkl</i>	Superconducting phase		Semiconducting phase	
	$d_{\text{obs}}$	$d_{\text{cal}}$	$d_{\text{obs}}$	$d_{\text{cal}}$
021	3.2337	3.2391	3.2314	3.2271
120	3.1984	3.1989	3.2314	3.2255
040	2.9237	2.9204	2.9284	2.9393
031	2.7485	2.7529	2.7485	2.7504
130	2.7273	2.7281	2.7485	2.7494
101	2.7273	2.7276	2.7192	2.7291
121	2.4694	2.4714	2.4707	2.4754
041	2.3392	2.3360	2.3421	2.3387
050	2.3392	2.3363	2.3617	2.3514
131	2.2333	2.2340	2.2413	2.2396
060	1.9446	1.9469	1.9713	1.9595
002	1.9446	1.9463	1.9286	1.9305
200	1.9117	1.9116	1.9286	1.9291
061	1.7446	1.7413	1.7427	1.7473
201	1.7149	1.7159	1.7263	1.7257
122	1.6625	1.6627	1.6576	1.6565
221	1.6507	1.6463	1.6576	1.6558
161	1.5820	1.5844	1.5945	1.5917
132	1.5820	1.5847	1.5801	1.5799
231	1.5690	1.5702	1.5801	1.5794

semiconducting phase  $a = 3.858 \text{ \AA}$ ,  $b = 11.757 \text{ \AA}$ , and  $c = 3.861 \text{ \AA}$  (pseudotetragonal structure). The observed and calculated results are shown in Table I. It seems that the lattice distortion is the predominant factor for the reversal of peak intensities. In fact, the substitutions of different ions in the unit cell have minor effects on the diffraction patterns. Similarly, for the case that each pair of the main peaks merges completely to form single peaks (this corresponds to a critical phase), the lattice parameters were calculated as  $a = 3.878 \text{ \AA}$ ,  $b = 11.634 \text{ \AA}$ , and  $c = 3.878 \text{ \AA}$  (tetragonal structure). This critical phase can be treated as the ideal orthorhombic layered perovskite ( $a = c = b/3$ ). In our experiment the single-phase compounds were also investigated and the situation found to be similar to that of the multiphase compounds. The lattice parameters corresponding to the three phases mentioned above (superconducting, semiconducting, and critical) were also calculated from x-ray diffraction patterns in the same way. These results are listed in Table II, in which the percentages of lattice distortions of superconducting and semiconducting phases relative to the critical phases have been calculated both for multiphase and single-phase compounds. It should be noted here that the single-phase compounds are much less stable than the multiphase compounds. As a result of aging the single-phase compounds in vapor, the pairs of the main diffraction peaks gradually joined together to form single peaks and the superconductivity easily vanished near  $\text{LN}_2$  temperature.

The structural differences between the superconducting and semiconducting phases can be seen very clearly from Table II. The length of the shortest axis  $a$  of the superconducting phase decreased the most, while for the semiconducting phase the length of the longest axis  $b$  increased the most. In Fig. 1 (a), when the space between each pair of the main peaks, such as (031) and (130)/(101), broadens, the interplanar spacing  $d_{031}$  increases and the length of  $a$  decreases drastically compared with the changes in  $b$  and  $c$ .

TABLE II. Distortions of the three axes of the superconducting and semiconducting phases relative to the critical phase. For single-phase compounds, the calculated lattice parameters are (1)  $a = 3.830 \text{ \AA}$ ,  $b = 11.702 \text{ \AA}$ ,  $c = 3.892 \text{ \AA}$ , for the superconducting phase; (2)  $a = 3.856 \text{ \AA}$ ,  $b = 11.784 \text{ \AA}$ ,  $c = 3.868 \text{ \AA}$ , for the semiconducting phase; (3)  $a = 3.879 \text{ \AA}$ ,  $b = 11.638 \text{ \AA}$ ,  $c = 3.879 \text{ \AA}$ , for the critical phase.

	Multiple compounds			Single compounds		
	$\Delta a/a$	$\Delta b/b$	$\Delta c/c$	$\Delta a/a$	$\Delta b/b$	$\Delta c/c$
Super. phase ( $a < b/3 \doteq c$ )	-1.4%	0.4%	0.4%	-1.3%	0.6%	0.3%
Semi. phase ( $b/3 > a \doteq c$ )	-0.5%	1.1%	-0.4%	-0.6%	1.2%	-0.3%

This perhaps indicates that there are much more oxygen vacancies in the  $a$  axis than in the  $c$  axis. Combined with the experimental results it seems that the shorter the  $a$  axis, the more partial the aggregation of oxygens between the  $a$  and  $c$  axes and the higher the  $T_c$ . Perhaps the oxygen vacancies have a direct effect on the values of  $T_c$ . Experiments also showed that when the two branches in each pair of the main peaks were nearing together,  $T_c$  dropped continually to lower temperatures. In this case the oxygen ions become more and more equally distributed in the  $a$  and  $c$  axes until the critical phase is reached in which no orthorhombic distortions exist. On the other hand, when the lower branch appeared on the other side of each pair of the main peaks, which was caused by another form of distortion, the semiconductive properties near  $\text{LN}_2$  temperature occurred. Because of its stronger polarization field,  $T_c$  of this phase may drop even more, and it might behave as a semiconductor over the whole temperature range. We conclude that small distortions of the crystal lattice can cause great changes in  $T_c$  in the Y-Ba-Cu-O system. The partial aggregation of oxygen ions along different axes in the Cu-O plane, as well as the intensities of polarization caused by the displacements of cations vertical to the Cu-O plane, may be critical to the superconductive properties.

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