

X-ray photoelectron spectroscopy study of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$

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We have performed an x-ray photoelectron spectroscopy investigation on single-phase crystalline $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ ($x < 0.3$) samples, together with structural analysis and superconductivity measurements. It turned out that, in this series of samples, the density of states near the Fermi surface increased with increasing Fe content and that Cu^{3+} existed in both the valence band and the core levels. We also obtained experimental evidence that the low-binding-energy component of Ba $3d$ was related to that of O $1s$.

I. INTRODUCTION

It is interesting to investigate the structure and properties of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ samples. The substitution of Fe for Cu not only brings about much information about element substitution, but also helps reveal the influence of magnetism on high- T_c superconductivity. Much research work has already been done in this system.¹⁻⁶ It was found^{1,2} that the substitution of Fe for Cu would quickly lead to the orthorhombic to tetragonal phase transition, accompanied by the loss of superconductivity. Mossbauer spectrum analysis showed⁵⁻⁷ that Fe atoms mainly occupied Cu(1) sites, which would easily result in a random distribution of oxygen atoms in the Cu-O chains, and thus the orthorhombic-tetragonal phase transition. However, little is known about the electronic structure of the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ system. Owing to this fact, we performed an x-ray photoelectron spectroscopy (XPS) investigation of this system and obtained some meaningful results. We found that Cu^{3+} existed in both the valence band and the core levels, and that its concentration increased with increasing Fe content. We also had, for the first time, the experimental evidence that the low-binding-energy component of Ba $3d$ was related to that of O $1s$.

II. EXPERIMENTAL METHODS

Analytically pure BaCO_3 , Y_2O_3 , and CuO were mixed according to the nominal composition of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$. After careful grinding, the mixtures were preheated at 930°C in air for 24 h. Then they were pressed into small bars of dimension $12 \times 3 \times 2 \text{ mm}^3$,

and sintered in an oxygen atmosphere at 930°C for another 24 h, followed by slow cooling to room temperature within the furnace. The resistance-temperature relation of the samples was measured by a calibrated Ge resistance thermometer together with a Keithley 181 nanovoltmeter. The structural analysis was carried out on a RIGAKU D-Max-A² rotating-target x-ray diffractometer. The oxygen contents were measured using a SHIMADZA DT-30 thermal analyzer. An XPS study was performed on a ESCALAB MKII electron spectrometer. The surface of the samples was abraded just before they were introduced into the chamber. The basic pressure during measurement in this system was about 1×10^{-9} mbar. The x-ray radiation of magnesium (Mg $K = 1253.6$ eV) was employed as the excitation source. Both the spectra of the valence band and core levels of the components in the samples were collected.

A. Experimental results and discussions

1. Structure and superconductivity of the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ system

X-ray diffraction analysis showed that, when the content of Fe was increased, the sample's structure quickly changed from orthorhombic to tetragonal, and became tetragonal at the Fe concentration $x = 0.15$ (Fig. 1). A superconductivity measurement revealed that this structural transition was accompanied by a loss of superconductivity (Fig. 2). From Fig. 2 we can clearly see that, when $x = 0.025$ or greater, the sample at a normal state has a semiconductor-type conducting behavior. In the substitution of other elements for Cu, e.g., Zn, Ni, the decrease

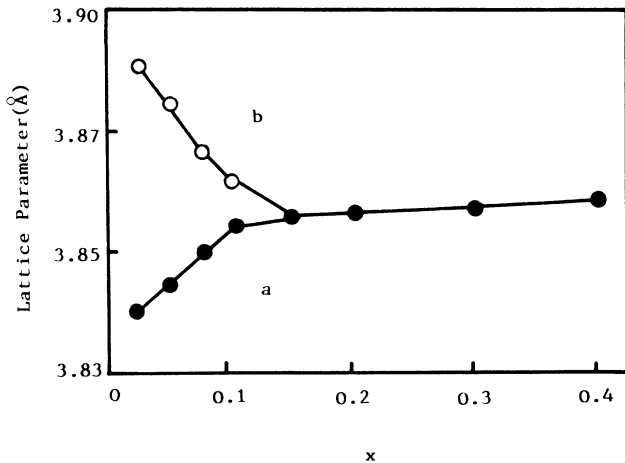


FIG. 1. Variation of the lattice parameters with Fe content x in the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ samples.

in T_c would not be any slower than for Fe; however, the doped superconductor does not have a semiconductor-type conducting behavior at a normal state for a relatively small value of impurity content. For example, the loss of superconductivity by substitution of Zn, Ni, and Fe for Cu all takes place at the impurity content about $x=0.15$; however, the semiconductor-type behavior at the normal state takes place at an impurity concentration of 7 at. % for the Fe-doped sample, but 15 at. % for the Zn-doped or Ni-doped sample.^{2,8} This indicates that the substitution of Fe for Cu would easily result in the localization of electrons. We shall refer to it again in our discussion of the valence band.

We have found in our experiment that, with increasing Fe content, the oxygen content is increased. This is in-

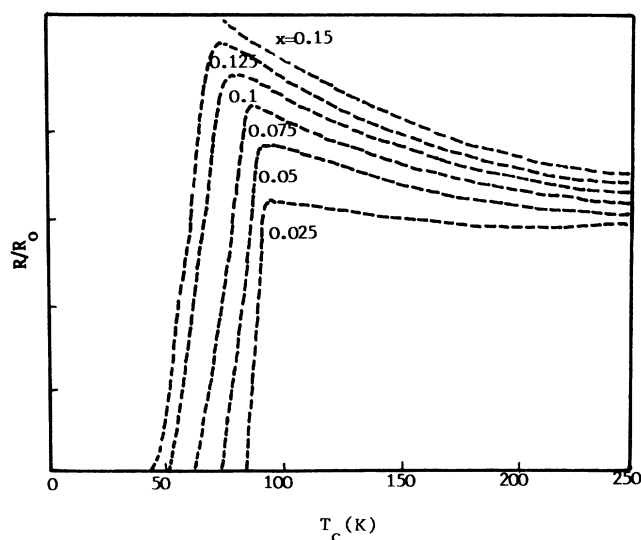


FIG. 2. The resistance-temperature relation of the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ samples.

consistent with the results of Tarascon *et al.*¹ and Westerholt *et al.*² The lattice parameters, oxygen content, and average valence of Cu in $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ are listed in Table I, from which we can see that the average valence of Cu in our superconducting samples has a maximum of 2.50, appreciably higher than 2.27, which is the case in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$. These results will shed light on our understanding of the XPS spectra.

2. Valence band of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$

The three $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ samples we used in the XPS experiment have x values of 0.125, 0.15, and 0.3, respectively, the former two are superconductors and the latter is a semiconductor. The valence-band spectra ranged from 0 to 18 eV. Regarding the contribution of $\text{Cu}^{3+}(3d^8)$ to the valence band at the binding energy of 11.7 eV, which is the result of calculation and experiment by Fujimori *et al.*⁹ and Frommer,¹⁰ respectively, we separate it into two parts, i.e., 0–8 eV and 8–18 eV, for discussions.

Figure 3 shows the valence-band spectra of the three samples. It is clearly shown that the density of states, which is within 1 eV above Fermi level, increases with increasing Fe content, and that the peak also shifts toward higher binding energy. From Fig. 4 we can see that the normal-state resistivity at a temperature of 233 K increases almost linearly with Fe content. Whether the increase in the resistivity is directly related to the increase in the density of states near the Fermi surface is still open to investigation. It is now commonly believed that the charge carriers in the Y-Ba-Cu-O system are holes in the O 2p band. Since Fe is trivalent, the excessive electrons may be neutralized by holes in the O 2p band, resulting in a decrease in the carrier concentration, or they may form with holes, the electron-hole pairs, thereby restricting the motion of the holes. Consequently the electronic states tend to be localized, and the resistance of the samples is increased.

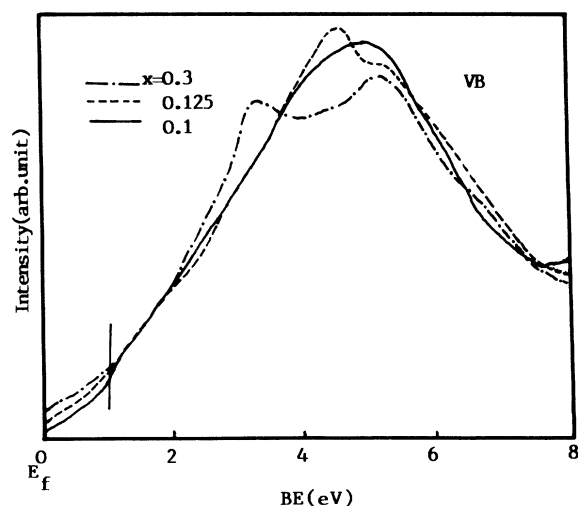


FIG. 3. Valence-band spectra between 0 and 8 eV of the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ samples.

TABLE I. The lattice parameters, oxygen contents, and average valence of Cu in the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ system.

x	a (Å)	b (Å)	c (Å)	Oxygen content	Average valence of Cu
0.025	3.841	3.880	11.650	7.02	2.35
0.05	3.844	3.874	11.621	7.08	2.40
0.075	3.849	3.866	11.612	7.10	2.42
0.10	3.854	3.861	11.637	7.16	2.47
0.125	3.854	3.858	11.631	7.17	2.48
0.15	3.855	3.855	11.634	7.18	2.50
0.20	3.857	3.857	11.615	7.20	2.53
0.30	3.859	3.859	11.633	7.20	2.57
0.40	3.862	3.862	11.623	7.19	2.60

In many XPS investigations of the Y-Ba-Cu-O system,¹¹ it has been pointed out that the $\text{Cu}^{3+}(3d^8)$ state is difficult to form since it is higher than the Fermi level by about 10 eV; instead, $3d^9\bar{L}$, where \bar{L} denotes a hole in the O $2p$ band, is easier to form. The actual state of Cu^{3+} is not purely $3d^8$, but a mixture of $3d^8$, $3d^9\bar{L}$, and $3d^{10}\bar{L}^2$. Fujimori *et al.* have calculated the valence-band structure of the atomic cluster $(\text{CuO}_6)^{10-}$ using configuration-interaction theory.⁹ They found that there is a contribution from $\text{Cu}^{3+}(3d^8)$ at a binding energy of 11.7 eV. The contribution from $3d^9\bar{L}$ at a binding energy of 4 eV, though large, is hard to identify for the reason that it coincides with the one from O $2p$. The experiment by Frommer supported the above speculation.¹⁰ Figure 5 shows the valence band between 8 and 18 eV of the samples studied. Two peaks are observed at 10 and 11.7 eV, which is in accordance with the calculation by Fujimori and the experiment by Frommer. And with increasing Fe content, the 10-eV peak diminishes whereas the 11.7-eV peak becomes more evident. Since iron and its oxides and hydroxides do not have any contribution at 10 and 11.7 eV,¹² we speculate that such a contribution is from $\text{Cu}^{3+}(3d^8)$. In addition, the concentration of Cu^{3+} increases with increasing Fe content. This is consistent

with the increase in the average valence of Cu with increasing Fe content as listed in Table I.

There is one thing in our experiment that is different from the result of Frommer.¹⁰ In Frommer's experiment, only the orthorhombic superconducting phase contributes to the valence band at 11.7 eV. In our experiment, however, the tetragonal nonsuperconducting $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ ($x=0.3$) also has a contribution at 11.7 eV, and it is even greater than from the superconducting samples. In view of the structure of a pure 1:2:3 superconductor (Fig. 6), the formation of the tetragonal phase is due to the random distribution of the oxygen atoms at $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, 0)$ sites. In such a sample, the oxygen content is relatively small (< 6.5), and the average valency of Cu is smaller than 2. However, in the Fe-doped samples, the oxygen content is greater than 7. From these results, we speculate that the existence of Cu^{3+} is only determined by the oxygen content, not by the sample's structure and whether it is a superconductor. Our present result confirms what we stated in our previous literature,¹³ i.e., the existence of Cu^{3+} is the result of charge balance.

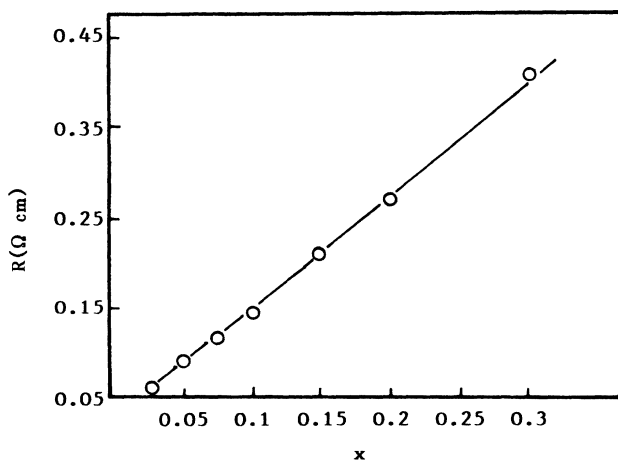


FIG. 4. The relation between Fe content and the resistivity of the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ samples at a temperature of 233 K.

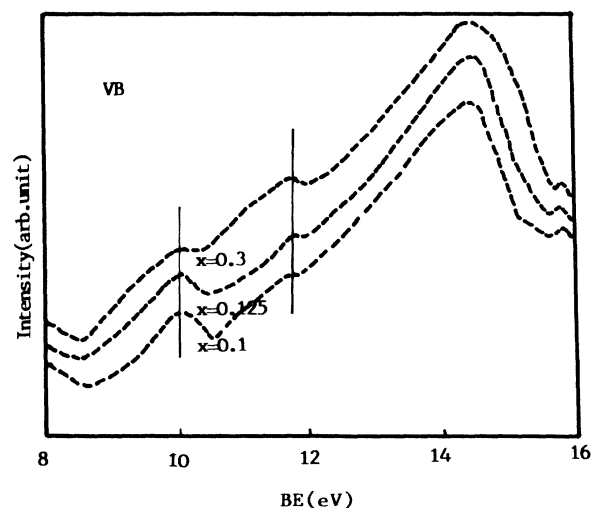


FIG. 5. Valence-band spectra between 8 and 18 eV of the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ samples.

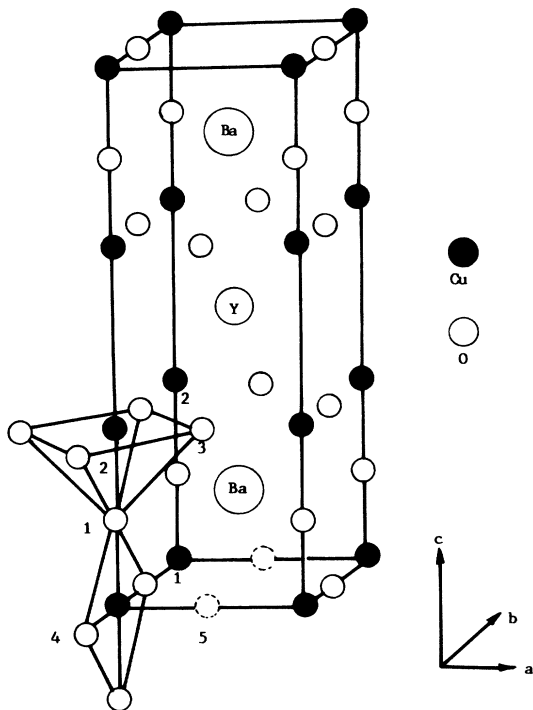


FIG. 6. Crystalline structure of the 1:2:3 phase.

3. XPS spectra of the core levels in the $YBa_2Cu_{3-x}Fe_xO_{7+y}$ system

According to Ref. 10, the binding energy of Cu^{3+} has a peak centered at 934.5 eV, and because the Cu^{3+} state is a mixture of $3d^8$, $3d^9\bar{L}$, and $3d^{10}\bar{L}^2$, the peak is broadened. Figure 7 clearly shows this feature. If the Fe content is increased, the peak which is associated with Cu^{3+} shifts toward a higher binding energy. According to the calculation and experiment by O'Keeffe *et al.*,¹⁴ the average valence of Cu(2) is 2.29 and of Cu(1) is 2.42. Pauling¹⁵ suggested that Cu^{3+} is in the Cu(1) site. Since the oxygen content is greater than 7 due to Fe substitution, $(\frac{1}{2}, 0, 0)$ sites must be partially occupied by oxygen

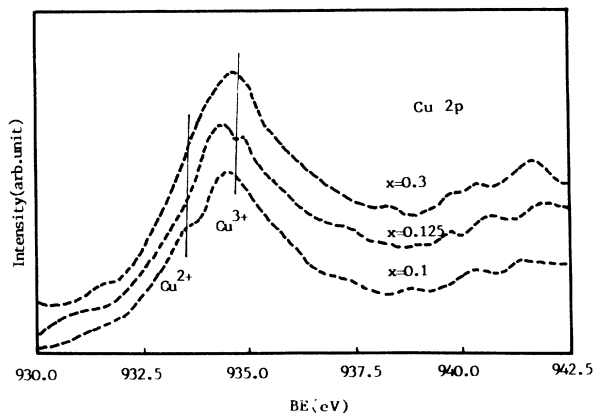


FIG. 7. XPS spectra of Cu 2p in three samples: Cu^{2+} , 933.4 eV; Cu^{3+} , 934.5 eV.

atoms if we presume that all $(0, \frac{1}{2}, 0)$ sites have been occupied. Therefore, the oxygen atoms around Cu(1) form an octahedron instead of a parallelogram, and, because the valence of an atom is the sum of all bond valences connected to it, the sixfold-coordinate Cu(1) will have a higher valence than that of a fourfold-coordinate one. Assuming the valence of Cu(2)-O(1), which is the smallest in all Cu-O bonds, to be 0.2, our estimation according to Ref. 14 gives the result that the additional two Cu(1)-O(5) bonds will have a total valence of 0.4. Hence, the valence of Cu(1) will be 2.82, very close to 3. Of course, not all Cu(1), actually only a small portion, have such octahedron-coordinated oxygen, the main contribution to the XPS spectra comes from $3d^9\bar{L}$.

4. Correlation of the electronic states of Ba_{3d} , O_{1s} , and Cu_{3d}

In the XPS spectrum of the pure Y-Ba-Cu-O system, there is a low-binding-energy component of Ba 3d centered at 778.2 eV. Although it is generally believed that the two states of Ba, which have not yet been very well understood, have something to do with oxygen content, little experimental evidence is available. We have found some in our experiments on the $YBa_2Cu_{3-x}Fe_xO_{7+y}$ system. From Fig. 8 we can clearly see that the low-binding-energy component of Ba is gradually reduced

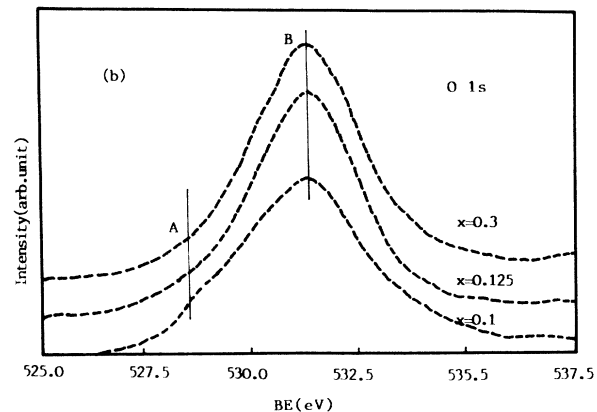
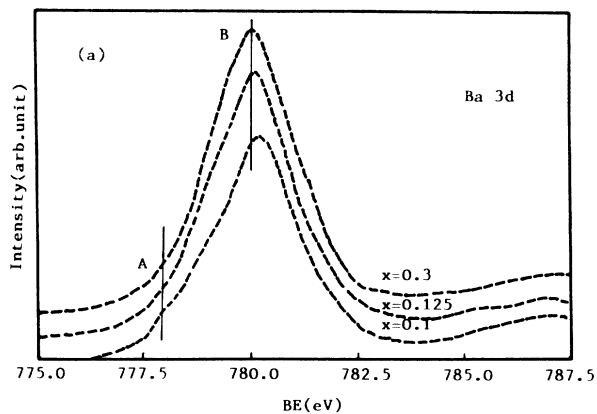


FIG. 8. XPS spectra of O 1s and Ba 3d.

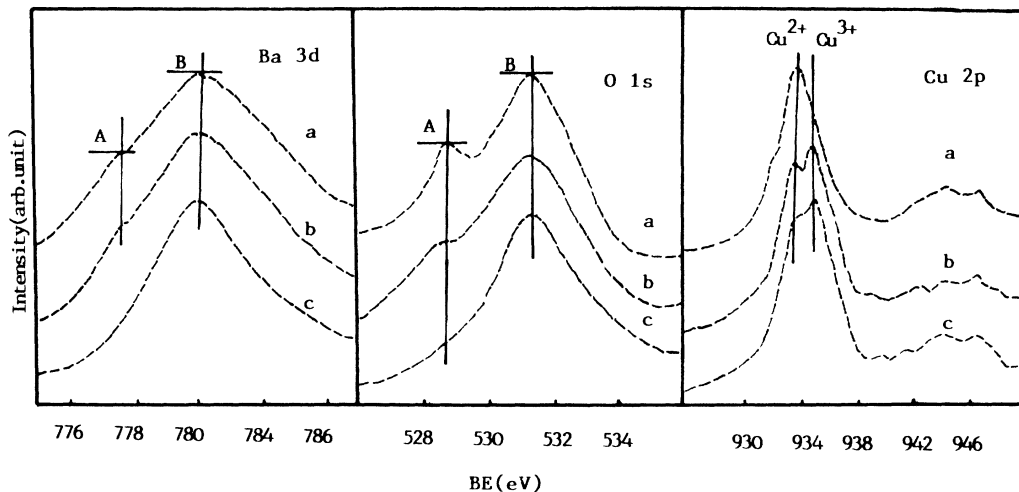


FIG. 9. Comparison of the XPS spectra of three systems. (a) $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, (b) $\text{YBa}_2\text{Cu}_{2.9}\text{Al}_{0.1}\text{O}_{7.1}$, (c) $\text{YBa}_2\text{Cu}_{2.9}\text{Fe}_{0.1}\text{O}_{7.16}$.

with increasing Fe content and completely vanishes for $x=0.15$; at the same time, the low-binding-energy component of O 1s also diminishes. According to Zhang *et al.*,¹³ the low-binding-energy component of O 1s is related to the existence of Cu^{3+} . In the sample without Cu^{3+} , the two peaks of O 1s are clearly seen; however, in the presence of Cu^{3+} the contribution from the low-binding-energy component, although it still exists, is reduced, and thereby the two peaks become blurred. In the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ system, where Cu^{3+} is found, the two peaks of O 1s are hardly distinguishable, and the low-binding-energy component of Ba disappears, so does that of O 1s (Fig. 9). In other words, the low-binding-energy component of Ba is related to that of O 1s, and the two states of Ba 3d are caused by different Ba-O relations. In view of the crystal structure of the 1:2:3 phase superconductor, there are ten oxygen coordinations about one

Ba ion: four above, four in plane, and two below. Owing to the inhomogeneous distribution of the oxygen atoms, an electric field gradient, which, in the case of Sn's occupancy of a Ba site, will cause a quadruple splitting in the Mossbauer spectrum,¹⁶ is established in the vicinity of Ba ions. Maybe the two different states of Ba are due to such an electric field gradient. If Fe occupies a Cu(1) site, the oxygen content will be increased. The occupancy of $(\frac{1}{2}, 0, 0)$ sites by oxygen atoms adds to the coordinations of oxygen below Ba ions; thereby the electric field gradient diminishes and the two states of Ba become one.

ACKNOWLEDGMENTS

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