PHYSICAL REVIEW B VOLUME 37, NUMBER 13 1 MAY 1988

Effect of substitution of Bi, Ga, and Fe on the structure and superconducting transition of $Y_1Ba_2Cu_3O_{6.5+\delta}$

J. Jung, J. P. Franck, W. A. Miner, and M. A.-K. Mohamed
Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2J1

(Received 8 October 1987)

High-temperature superconductivity was observed in the system $(M_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ where M = Ga, Bi, or Fe. Ga and Fe substituted for Y reduce the orthorhombic distortion in the $YBa_2Cu_3O_{6.5+\delta}$ tetragonal lattice. The changes in transition temperature at zero resistance are not related to gradual changes in the orthorhombic distortion. High-T_c superconductivity ($T_c^{R=0}=86$ K) can be maintained in an undistorted tetragonal lattice. Bi substituted for Y does not substantially change the lattice parameters of the $YBa_2Cu_3O_{6.5+\delta}$ compound.

The structure of $YBa_2Cu_3O_{6.5+\delta}$ consists of alternating CuO_2-(Ba,Y)O planes perpendicular to the c axis.[1] The copper ions sit in two crystallographically distinct and chemically dissimilar sites, one between a pair of Ba layers [Cu(1)] and the other between Ba and Y layers [Cu(2)].[2,3] The anisotropy of the oxygen occupation factor for Cu(1) planes induces the orthorhombic distortion of the $YBa_2Cu_3O_{6.5+\delta}$ structure and forms one-dimensional Cu(1)O chains. That anisotropy is believed to be essential for the high-temperature superconductivity in this compound. Substitution of Y by the series of rare-earth metal ions does not substantially change superconducting properties in this class of compounds.[4] However, partial substitution of Ba by Sr causes the reduction of the superconducting transition temperature of $YBa_{2-x}Sr_x$-$Cu_3O_{6.5+\delta}$.[5]

We report results on high-temperature superconductivity in systems of nominal composition $M_xY_{1-x}Ba_2Cu_3$-$O_{6.5+\delta}$, where the substitution was Ga, Bi, or Fe. This research was motivated by our success in observing high-temperature superconductivity in Al-substituted samples for $0 \leq x \leq 0.85$.[6] The trivalent ionic radii of Al and Ga are 0.51 and 0.62 Å, respectively. The ionic radii of Fe are 0.64 Å (trivalent) or 0.74 Å (divalent). These radii are much smaller than that of Y (0.92 Å). The chemistry of Al and Ga is similar to that of Y. We therefore have expected that the substitution of Y by these elements can modify the superconducting properties of the $YBa_2Cu_3O_{6.5+\delta}$ compound by substantial reduction of unit-cell dimension along c axis [i.e., by the reduction of the distance between Cu(2)O planes]. Fe substitution was also attempted to study the influence of the non-Jahn-Teller ion on the superconducting properties of $YBa_2Cu_3O_{6.5+\delta}$. Substituting Bi for Y was tried because of the similarity of its (trivalent) ionic radius (0.96 Å) to that of Y(0.92 Å).

The samples were investigated by resistance measurement as a function of temperature, and by room-temperature x-ray powder diffraction.

High-temperature superconductivity was observed in Ga-substituted samples for $0 \leq x \leq 0.50$, in Bi-substituted samples for $0 \leq x \leq 0.40$, and in Fe-substituted samples for $0 \leq x \leq 0.30$. The transition temperatures at zero resistance ($T_c^{R=0}$) decrease from 91 K for $x=0$ with increasing substitution levels. Changes in the x-ray spectrum take place and are qualitatively different for the three substituted elements.

The samples were prepared by the solid-state reaction methods from the metal oxides Ga_2O_3 (Johnson-Mathew Puratronic 99.999%), Bi_2O_3 (Alfa Products, Ventron Division, 99.8%), Fe_2O_3 (Fisher Scientific, 99.9%), Y_2O_3 (Morton Thiokol, Inc., 99.99%), CuO (Fisher Reagent Grade), and $BaCO_3$ (Baker Analyzed Reagent Grade). The powders were mixed, ground, and formed into a pellet of diameter 1.27 cm and approximately 1.5 mm thick. In order to avoid melting of samples, different reaction temperatures were used for Ga, Bi, and Fe substitutions. The compound of nominal composition $Ga_xY_{1-x}Ba_2Cu_3$-$O_{6.5+\delta}$ was reacted in air at 880 °C, $(Bi_xY_{1-x})Ba_2Cu_3$-$O_{6.5+\delta}$ at 810 °C, and $Fe_xY_{1-x}Ba_2Cu_3O_{6.5+\delta}$ at 895 °C for 24 h. After reaction pellets were reground, new pellets formed and sintered in flowing O_2 for 7 h at 925 °C. The product was furnace cooled for 12 h at an initial rate of 200 °C/h.

Resistance of samples was measured as a function of temperature using a four-terminal technique (pressed indium contacts) and measuring current densities between 5 and 150 mA/cm^2. Temperature was determined by a Pt thermometer calibrated to a precision of ±20 mK.

For Ga, Bi, and Fe substitutions, we studied the relationship between superconducting transition temperature (at zero resistance), orthorhombic distortion in YBa_2Cu_3-$O_{6.5+\delta}$ lattice, and substitution concentration.

Resistance data for Ga-, Ba-, and Fe-substituted samples as a function of substitution concentration are shown in Figs. 1–3, respectively. Introduction of foreign atoms into the Y-based compound has the effect of gradually raising the room-temperature resistance and decreasing the transition temperature at zero resistance. For the pure Y case $x=0$, the high-temperature resistance is exactly linear in temperature. Substitution of foreign elements gradually decreases the linear resistance region. For Ga- and Bi-substituted samples, the linear resistance behavior is not observed above $x=0.40$. However, for

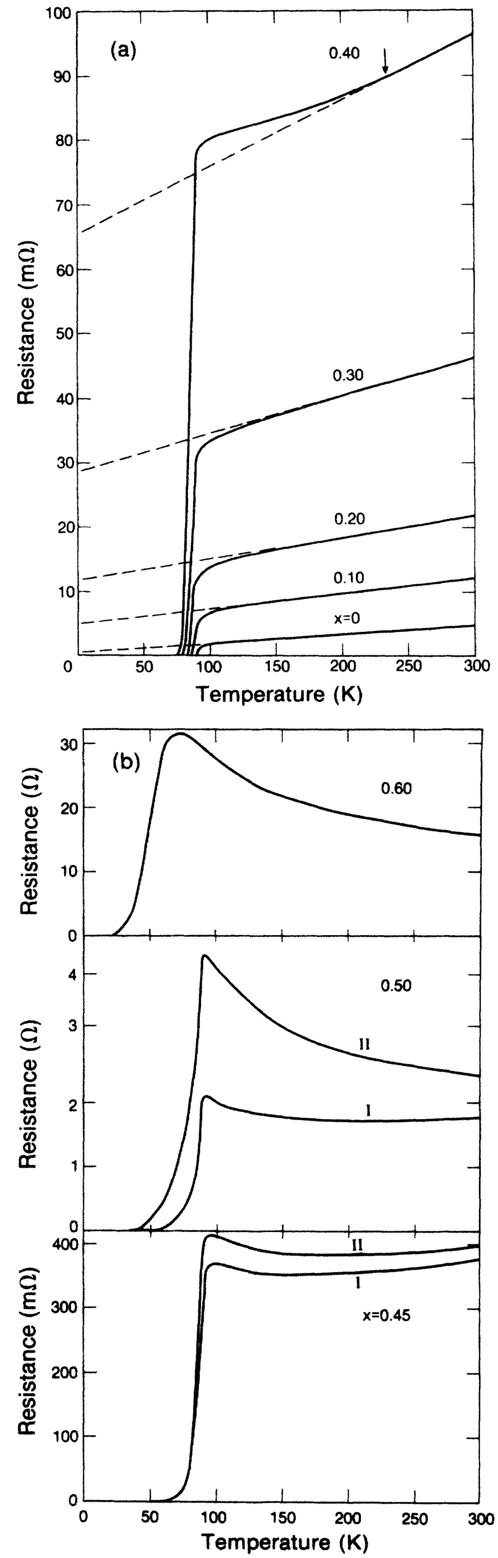

FIG. 1. Resistance of $(Ga_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ as a function of temperature and Ga concentration x. The high-temperature resistance is fitted to straight lines, the deviation from linearity is indicated by an arrow (resistance can be approximately converted to resistivity in Ω cm by multiplication with 0.07). (a) Resistance for $0 \leq x \leq 0.40$. (b) Resistance for $0.45 \leq x \leq 0.60$. Curve II is the resistance of the same sample measured after a few days.

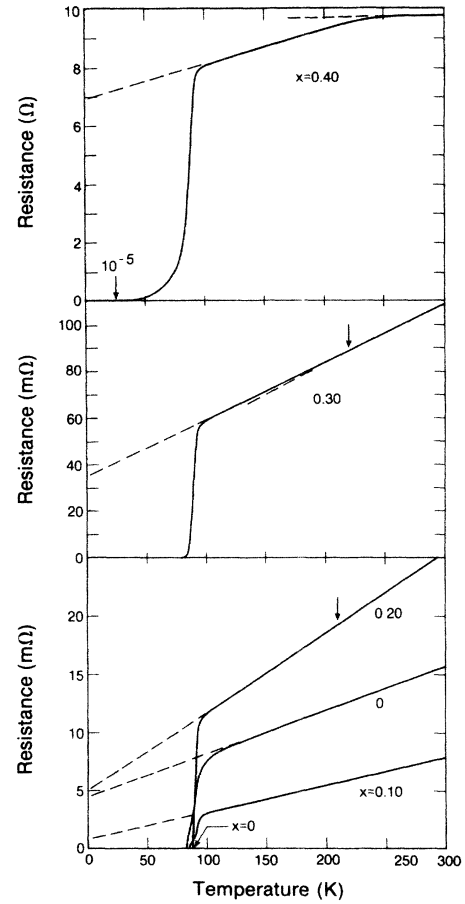

FIG. 2. Resistance of $(Bi_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ as a function of temperature and Bi concentration x. The high-temperature resistance is fitted to straight lines, the deviation from linearity is indicated by an arrow. (Resistance can be converted to resistivity in Ω cm by multiplication with 0.07.)

Fe-substituted samples, the linear resistance region disappears above $x = 0.20$. Above certain substitution levels, the samples show semiconductorlike resistance behavior; for Ga substitution above $x = 0.60$, for Bi substitution above $x = 0.40$, and for Fe substitution samples above $x = 0.30$. Resistance anomalies and instabilities are observed in the case of Ga substitutions. At $x_{Ga} = 0.60$ in spite of the resistance anomaly (resistance decreases by a factor of 300 between 75 and 25 K), the zero-resistance state is not reached. Instabilities of resistance behavior are observed (high-temperature resistance is not reproducible) at $0.40 < x < 0.60$ [Fig. 1(b)].

X-ray powder diagrams were taken from all samples on which resistance measurements were made, with a Rigaku Geigerflex diffractometer and Co $K\alpha_{1+2}$ radiation. The overall spectrum for $YBa_2Cu_3O_{6.5+\delta}$ is shown in Fig. 4. For Ga-, Bi-, and Fe-substituted samples, the typical x-ray spectrum of $YBa_2Cu_3O_{6.5+\delta}$ exhibited systematic and gradual changes with increasing Ga, Bi, or Fe content. The changes observed were in the splitting between lines of x-ray doublets and in the intensity of these lines.

For Ga and Fe, there was no indication of a second

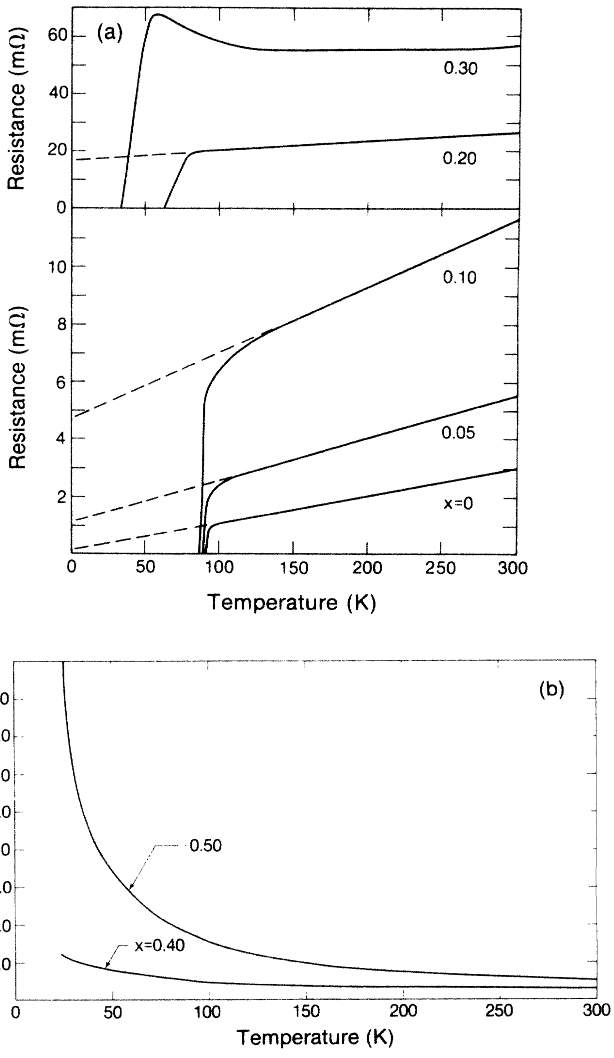

FIG. 3. Resistance of $(Fe_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ as a function of temperature and Fe concentration x. The high-temperature resistance is fitted to straight lines (resistance can be converted to resistivity in Ω cm by multiplication with 0.07). (a) Resistance for $0 \leq x \leq 0.30$. (b) Resistance for $x = 0.40$ and 0.50 showing semiconducting behavior as a function of temperature.

phase for $0 \leq x < 0.20$–0.30 although at higher substitution levels, samples are multiphase. For Bi-substituted samples, we found no solubility range of Bi in the Y-based lattice. (Samples are two phase and contain $YBa_2Cu_3O_{6.5+\delta}$ and $BiBa_2Cu_3O_{6.5+\delta}$ compounds at each substitution level.)

The change in the x-ray spectrum as a function of dopant concentration is most pronounced in the doublet at d spacings near 2.725 Å [$(hkl) = (103)$ and (110)] and 2.750 Å [(013)] (indexation is in the tetragonal cell). The highest-intensity doublet is shown in more detail in Figs. 5(a), 5(b), and 5(c) as a function of Ga, Bi, and Fe concentration, respectively. The splitting between the A line (2.725 Å) and the B line (2.750 Å) of this doublet which is caused by the orthorhombic distortion of tetragonal cell, is seen to change towards smaller splitting (less distortion) with increasing Ga or Fe content [Fig. 6(a) and 6(c)].

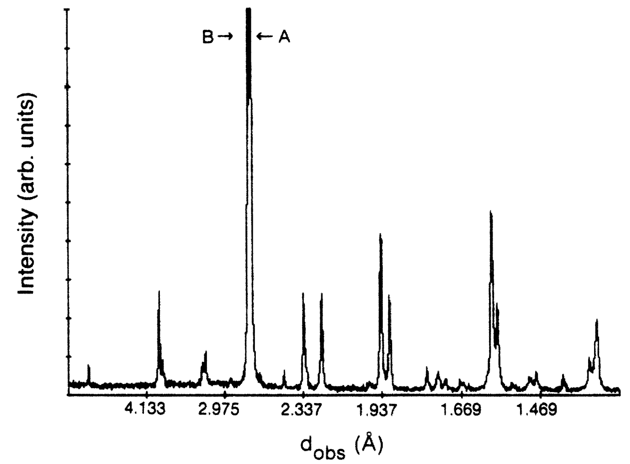

FIG. 4. X-ray powder diagram for $YBa_2Cu_3O_{6.5+\delta}$ compound.

Increasing Ga content decreases the splitting by a factor of 2 at $x = 0.10$. At higher Ga-substitution levels, no substantial decrease of splitting can be seen; however, the A-B doublet is shifted to lower d spacings [Fig. 6(a)]. The intensity of the x-ray diffraction pattern for $YBa_2Cu_3O_{6.5+\delta}$ gradually decreases with increasing Ga concentration. At $x_{Ga} > 0.60$, there is no indication of the presence of the $YBa_2Cu_3O_{6.5+\delta}$ phase in the $Ga_xY_{1-x}Ba_2Cu_3O_{6.5+\delta}$ compound [Fig. 5(a)].

In the case of Fe substitutions, the splitting between the A and B line gradually decreases with increasing Fe content. At $x_{Fe} = 0.30$ the splitting is reduced by a factor of 20 [Fig. 6(c)]. At $x_{Fe} > 0.30$ no splitting can be observed [Figs. 5(c) and 6(c)].

In the case of Bi substitutions, the splitting does not change with increasing Bi content [Fig. 6(b)]. The intensity of the x-ray diffraction pattern for $YBa_2Cu_3O_{6.5+\delta}$ gradually decreases with increasing Bi concentration.

At $x_{Bi} > 0.60$ x-ray diffraction does not reveal the presence of the $YBa_2Cu_3O_{6.5+\delta}$ phase in the $Bi_xY_{1-x}Ba_2Cu_3O_{6.5+\delta}$ compound [Fig. 5(b)], suggesting the solubility range of Y in the Bi-based lattice.

In Fig. 6, we compare the splitting of the high-intensity doublet with the transition temperature as a function of Ga, Bi, and Fe concentration. In Fig. 7, the relationship is shown between lattice parameters (a,b,c) of $(M_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ compound and the concentration of Ga, Bi, and Fe dopants. It is clear that the lattice constant c decreases with increasing Ga and Fe content, suggesting the Ga and Fe may replace Y or Ba in the lattice. For Fe substitution, the structure becomes tetragonal at $x_{Fe} = 0.10$ but the superconducting transition temperature remains as high as 86 K. In the case of Ga substitution, the orthorhombic distortion is reduced by a factor of 5 at $x_{Ga} = 0.2$ corresponding to $T_c^{R=0} = 80$ K. Only substitution of Bi for Y does not substantially influence lattice parameters and no change of the orthorhombic distortion can be seen.

It seems unlikely that the reduction of $T_c^{R=0}$ for Ga, Bi,

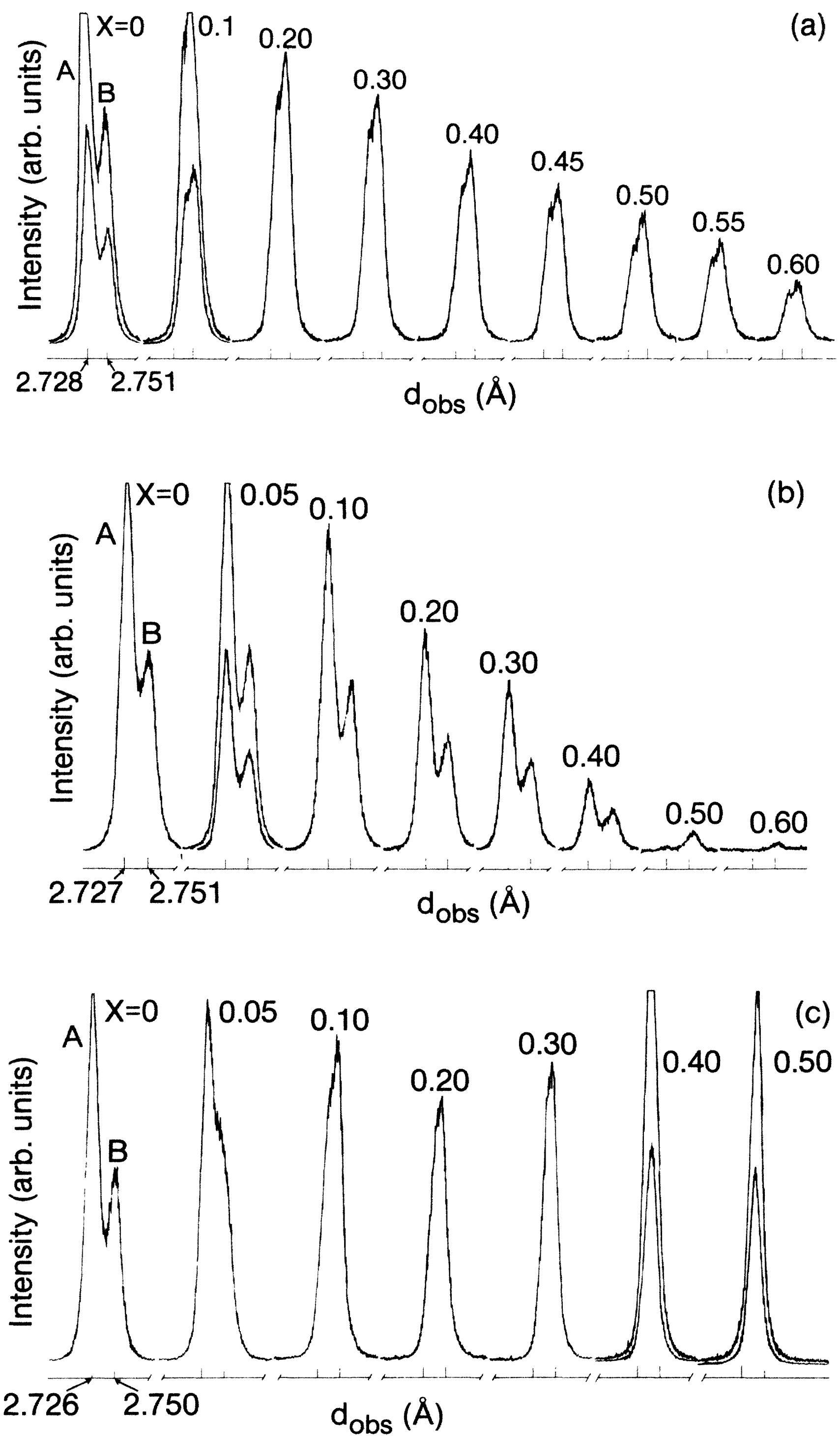

FIG. 5. High-resolution x-ray powder diagram of the *A* and *B* lines near 2.725 and 2.750 Å, as a function of foreign element concentration *x*: (a) Ga; (b) Bi; and (c) Fe.

and Fe substitutions is caused by oxygen deficiency, since there is no correlation between $T_c^{R=0}$ and orthorhombic distortion (oxygen deficiency in the $YBa_2Cu_3O_{6.5+\delta}$ compound causes the reduction of $T_c^{R=0}$ and the orthorhombic distortion[7]). For $x_{Fe}=0.30$, $\delta=0.2$ as confirmed by chemical analysis (iodide titration).

It appears that the orthorhombic splitting of the tetragonal lattice of $YBa_2Cu_3O_{6.5+\delta}$ is not necessary to keep high-T_c superconductivity in this compound. However, the decrease of the intensity of the x-ray diffraction pattern with the increasing concentration of foreign elements suggest that the reduction of the amount of the YBa_2-

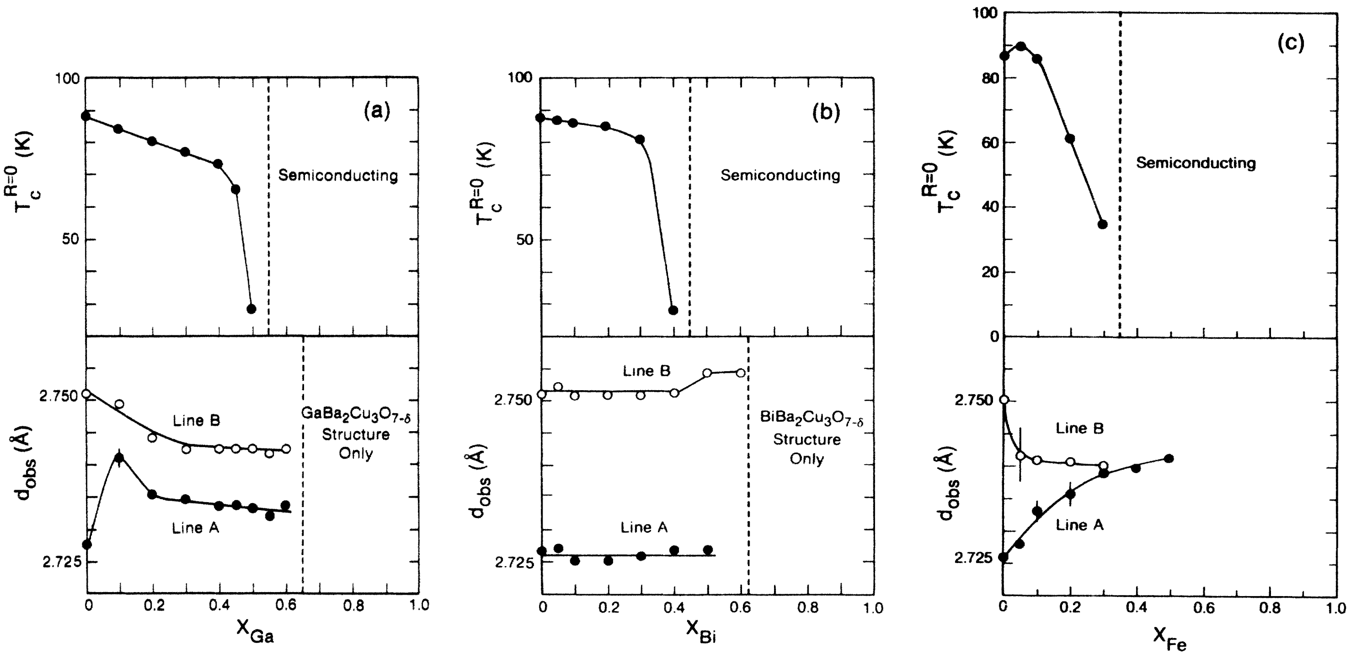

FIG. 6. Superconducting transition temperature (zero resistance) $T_c^{R=0}$ as a function of foreign element concentration (upper figure). Observed planar spacing of the high-intensity doublet (lower figure) (A line [(103) and (110)] and B line [103)], indexed in the tetragonal cell): (a) Ga; (b) Bi; and (c) Fe.

$Cu_3O_{6.5+\delta}$ phase in the $M_xY_{1-x}Ba_2Cu_3O_{6.5+\delta}$ compound may be responsible for the decrease of $T_c^{R=0}$.

The effect of Ga and Fe substitutions on superconducting properties of $YBa_2Cu_3O_{6.5+\delta}$ has also been studied by Maeno *et al.*[8] in the system $YBa_2(M_xCu_{1-x})_3O_{6.5+\delta}$, and by Kimball *et al.*[9] in the system $YBa_2Cu_{3-x}Fe_xO_{6.5+\delta}$. The substitution of Ga and Fe on copper site reduces the orthorhombic distortion but leaves lattice parameter c unchanged.

Maeno reported that the tetragonal structure was induced by doping with Fe at $x = 0.033$ corresponding to T_c (midpoint) around 60 K. The tetragonal structure remains down to 77 K. T_c is not sensitive to the orthorhombic-tetragonal phase transition induced by impurities. It was suggested that superconductivity along one-dimensional Cu-O chains is unlikely.

This conclusion is in agreement with our results (for Fe substituted for Y) since we can see qualitatively similar changes in T_c and structure (orthorhombic-to-tetragonal transition).

In conclusion, we studied the effect of the substitution of Y by Ga, Bi, and Fe on the structure, and the supercon-

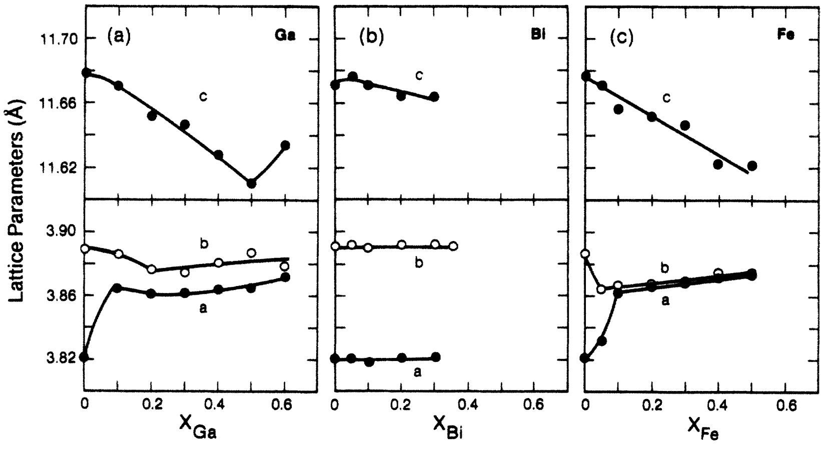

FIG. 7. Lattice parameters (a,b,c) at room temperature for the $(M_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ compound as a function of foreign element content: (a) Ga; (b) Bi; and (c) Fe.

ducting transition of $YBa_2Cu_3O_{6.5+\delta}$. We found that Ga and Fe substitutions reduce the orthorhombic distortion in the $YBa_2Cu_3O_{6.5+\delta}$ tetragonal lattice. The changes in transition temperature are not related to gradual changes in the orthorhombic splitting. High-T_c superconductivity can be maintained in an undistorted tetragonal lattice. Bi substituted for Y does not substantially change the lattice parameters of $YBa_2Cu_3O_{6.5+\delta}$ suggesting that there is no solubility range of Bi in the Y-based lattice.

We would like to thank Dr. B. Kratochvil for making the chemical analysis of oxygen content. This research was supported by grants from the Natural Sciences and Engineering Research Council of Canada.

---

[1] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1976 (1987).

[2] W. I. F. David, W. T. A. Harrison, J. M. F. Gunn, O. Moze, A. K. Soper, P. Day, J. D. Jorgensen, D. G. Hinkes, M. A. Beno, L. Soderholm, D. W. Capone II, I. K. Schuller, C. U. Segre, K. Zhang, and J. D. Grace, Nature **327**, 310 (1987).

[3] F. Izumi, H. Asano, T. Ishigaki, E. Takayama-Muromachi, Y. Uchida, N. Watanabe, and T. Nishikawa, Jpn. J. Appl. Phys. **26**, L649 (1987).

[4] P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987).

[5] B. W. Veal, W. K. Kwok, A. Umezawa, G. W. Crabtree, J. D. Jorgensen, J. W. Downey, L. J. Nowicki, A. W. Mitchell, A. P. Pawlikas, and C. H. Sowers, Appl. Phys. Lett. **51**, 279 (1987).

[6] J. P. Franck, J. Jung, and M. A.-K. Mohamed, Phys. Rev. B **36**, 2308 (1987).

[7] H. Oyanagi, H. Ihara, T. Matsubara, M. Tokumoto, T. Matsushita, M. Hirabayashi, K. Murata, N. Terada, T. Yao, H. Iwasaki, and Y. Kimura, Jpn. J. Phys. **26**, 348 (1987).

[8] Y. Maeno, T. Tomita, M. Kyogaku, S. Awaji, Y. Aoki, K. Hoshino, A. Minami, and T. Fujita, Nature **328**, 512 (1987).

[9] C. W. Kimball, T. M. Matykiewicz, T. Giapintzakis, A. E. Dwight, M. B. Brodsky, M. Slaski, B. D. Dunlap, and F. Y. Fradin, in *Yamada Conference XVIII on Superconductivity in Highly Correlated Fermion Systems, Sendai, Japan, 1987,* edited by M. Tachiki, Y. Muto, and S. Maekawa [Physica B **148**, 309 (1987)].