Stabilization of the tetragonal phase and superconducting behavior in $RBa_2(Cu_{1-x}Fe_x)_3O_y$ (R = Y, Gd; $0 \leq x \leq 0.15$)

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The structure and superconductivity for $YBa_2(Cu_{1-x}Fe_x)_3O_y$ and $GdBa_2(Cu_{1-x}Fe_x)_3O_y$ ceramics ($0 \leq x \leq 0.15$) have been studied by x-ray diffraction and resistivity measurements. In each family of materials (but more rapidly in the Gd ceramics), increasing Fe substitution leads to the stabilization of the tetragonal perovskite structure and suppression of superconductivity, apparently owing to pair breaking by the Fe moments. Anomalous behavior at higher Fe substitution is attributed to the combined influence of Gd and Fe moments.

The oxygen-deficient perovskites with composition $RBa_2Cu_3O_y$ ($y \sim 7$), where R is Y or one of a host of rare-earth ions including Nd, Sm, Eu, Gd, Ho, Er, Dy, Tm, and Lu,[1] show a superconducting transition ($T_c \sim 95$ K) which is essentially insensitive to the nature of the R ion, whether it be magnetic or nonmagnetic. A possible explanation of this impassive behavior may be sought in the crystalline structure. In the idealized perovskite $RBa_2Cu_3O_9$, the R and Ba ions alternate along the c axis in the sequence R-Ba-Ba... and each is surrounded by 12 oxygen atoms at the vertices of a cuboctahedron. In the oxygen-deficient structure $RBa_2Cu_3O_y$ there is a complete lack of oxygen atoms in the plane of the R ion,[2] reducing the coordination polyhedron about R to that of a cube. Additionally, high-resolution neutron scattering studies[2] on $YBa_2Cu_3O_y$ have established preferential ordering in the oxygen-deficient Cu$-$O planes. One Cu site [Cu(2), between Y and Ba planes] exhibits corrugated sheets (ab) of square-pyramidal coordination polyhedra, while the second Cu site [Cu(1), between planes of Ba ions] shows one-dimensional columns (b) of square-planar coordination polyhedra. Several theoretical mechanisms[3] for superconductivity in these oxygen-deficient ceramics invoke effects congenital to the reduced dimensionality of the two-dimensional Cu(2)$-$O sheets and the one-dimensional Cu(1)$-$O chains, and the insensitivity of T_c to the nature of the R ion is attributed to its relative isolation from either low-dimensional Cu$-$O network.[1-3] The actual details of the mechanism are, however, far from clear.

In an attempt to further elucidate structural trends and superconducting behavior in these materials, a detailed study of $YBa_2(Cu_{1-x}Fe_x)_3O_y$ and $GdBa_2(Cu_{1-x}Fe_x)_3O_y$ ceramics containing up to 15% Fe substitution has been undertaken. Considering the various ionic radii and the crystal chemistry, Fe is expected to substitute for Cu; and, since Y^{3+} carries no magnetic moment while Gd^{3+} possesses a large magnetic moment ($\sim 8\mu_B$), the magnetic structure is expected to be markedly different in the two materials. Indeed, direct evidence for both expectations is seen in Mössbauer spectra;[4] and resistivity data presented

here also argue for the important role of magnetism. Additionally, changes in the crystal structure on Fe substitution (*vide infra*) are significant. While increasing Fe substitution stabilizes the tetragonal phase in both compounds, higher symmetry is achieved at lower Fe concentration in the Gd-based ceramics than in the Y-based materials. In parallel, T_c falls rapidly as a function of increasing Fe substitution in both ceramics. Superconductivity is absent for concentrations larger than $\sim 10\%$ in the Gd-based materials, while the Y-based materials exhibit $T_c \cong 37$ K for 12% Fe, and possibly even 15% Fe substitution shows incipient superconductivity (at ~ 15 K) which is suppressed at lower temperatures.

Samples were fabricated by mixing appropriate amounts of Y_2O_3 or Gd_2O_3 with $BaCO_3$, CuO, and Fe_2O_3 and grinding, pressing, and sintering in flowing O_2 for 12 h. Attention was paid to thorough mixing to prevent clustering of Fe ions. This process was repeated at least three times to complete the solid-state reaction and to promote high oxygen content and single-phase materials. Thermogravimetric analysis (TGA) studies were carried out in flowing N_2 gas over the temperature range 50–950 °C at a rate of 1.5 °C/min. The x-ray diffraction data were obtained on a Phillips XRD 3100 powder diffractometer utilizing Cu $K\alpha$ radiation and scan speeds of 2 °/min for full spectra and 0.25 °/min for higher-resolution data. Temperature-dependent dc resistivity measurements were obtained on slab shaped samples, employing a standard four-probe geometry, silver paste contacts, and 1-mil gold wire leads. Measuring current densities were kept low (< 0.1 A/cm^2) in order to stay below the modest critical currents typically observed in this class of materials. Data were taken from 300 K down to as low as 1.4 K in some samples; the temperature was varied at 0.05 K intervals at a rate of 0.05 K/min through the superconducting transition region, on both cooling and warming.

X-ray diffraction patterns have been accumulated over the full range ($x = 0$–0.15) of $YBa_2(Cu_{1-x}Fe_x)_3O_y$ and $GdBa_2(Cu_{1-x}Fe_x)_3O_y$ ceramics. At all substitution levels, essentially (within 5%) single-phase polycrystalline samples were available. At low and intermediate Fe-

substitution levels, the now well-accepted orthorhombic ($b > a$), oxygen-deficient, perovskite structure[2] was ascertained. At higher Fe-substitution levels [near x =0.15 for $YBa_2(Cu_{1-x}Fe_x)_3O_y$ and near x =0.07 for $GdBa_2(Cu_{1-x}Fe_x)_3O_y$], a sharp (possibly first-order) transition to a tetragonal ($a = b$) phase is evident.

In Fig. 1, the variation in the lengths of the a, b, and c (shown as $c/3$) axes with Fe substitution for $YBa_2(Cu_{1-x}Fe_x)_3O_y$ is depicted. Clearly, both the b and c axes are relatively weakly dependent on percent Fe substitution, while the a axis increases smoothly and markedly with increasing Fe content. It is tempting to suggest that the rather weak dependence of the c-axis length on Fe content can be attributed to a moderate change in total oxygen content.[5] This notion is further quantified by the TGA results for samples from across the series which show a mean value for y near 7. While some variability in y was ascertained, these variations did not systematically correlate with Fe content. In a similar vein, the rather large difference in the lengths of the a [3.819(1) Å] and b [3.887(1) Å] axes at x =0 implies near full occupancy of the oxygen atom site $(0, \frac{1}{2}, 0)$ and near depletion of the oxygen atom site $(\frac{1}{2}, 0, 0)$.[2,5] Clearly, then, the smooth increase in the length of the a axis insinuates a monotonic renormalization of the occupancy of these oxygen atom sites with increasing Fe substitution, to the limit of equivalency in a tetragonal phase [$a = b = 3.873(2)$ Å] at x near 0.15.

Similar results were obtained for the series of $GdBa_2(Cu_{1-x}Fe_x)_3O_y$ ceramics. At x =0, there is a slightly smaller difference in the lengths of the a [3.842(1) Å] and b [3.898(1) Å] axes. The variation in total oxygen content is, however, similar across this series, as deduced from TGA, to that presented by the $YBa_2(Cu_{1-x}Fe_x)_3O_y$ materials. Again the a-axis length monotonically approaches that of the b axis, but the tetragonal limit is reached at a lower Fe-substitution level ($x \sim 0.07$).

The combined diffraction results for the Y-based and Gd-based ceramics are presented in Fig. 2. There the degree of orthorhombic character is expressed in the form of
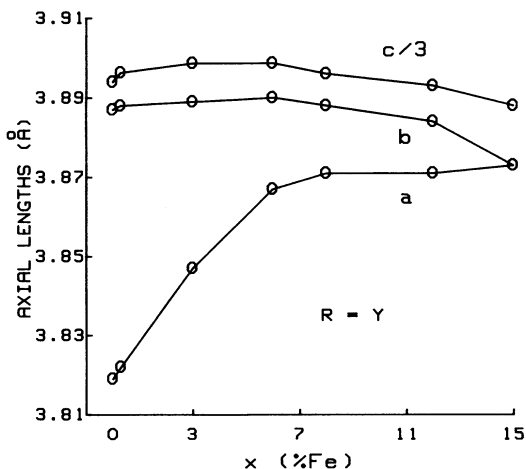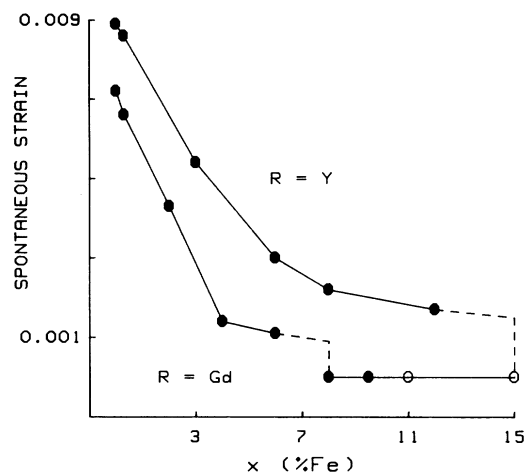

FIG. 2. Variation in the degree of orthorhombic character, defined as the spontaneous strain [$(b-a)/(b+a)$], with percent iron for $YBa_2(Cu_{1-x}Fe_x)_3O_y$ and $GdBa_2(Cu_{1-x}Fe_x)_3O_y$. Blackened data points correspond to superconducting samples.

the spontaneous strain [$(b-a)/(b+a)$].[6] Expectedly, this approach clearly shows the more rapid convergence to higher symmetry by the Gd-based compared to the Y-based ceramics. More importantly, the abruptness of the transitions, at $x \sim 0.15$ for Y-based and at $x \sim 0.07$ for Gd-based materials, is clearly evident.

In total, the x-ray results presented here as a function of percent Fe substitution are somewhat similar to those shown to arise from oxygen depletion.[7] There are, however, significant differences which suggest that the effect (either chemical or magnetic) of Fe substitution dominates that offered by a variation in oxygen stoichiometry. For example, while there is a nominally linear increase in the c-axis length in the orthorhombic phase and an abrupt increase in the c-axis length[7] at the orthorhombic-to-tetragonal (OT) transition ($y \sim 6.5$) on oxygen depletion, there is a monotonic decrease in the c-axis length in the orthorhombic phase and an abrupt decrease in the c-axis length at the (OT) transition with increasing Fe substitution. Finally, the very dramatic effect of Fe moments (see also Ref. 8) on the critical temperature (presented below) seems well in excess of that expected[5,7,9] from the nonsystematic variation in oxygen content as inferred from the x-ray results and confirmed by the TGA studies.

Room-temperature dc resistivities and the temperature dependence of the relative resistance, $R(T)/R(300 \text{ K})$, have been determined over the full range ($0 \le x \le 0.15$) for the $YBa_2(Cu_{1-x}Fe_x)_3O_y$ and $GdBa_2(Cu_{1-x}Fe_x)_3O_y$ ceramics described above. For the native (x =0) materials, the room-temperature resistivities are both ~ 1 mΩ cm, and the measured critical temperatures ($T_c \approx 93-94$ K) and transition widths ($\Delta T_c \approx 1.0-1.5$ K) (Ref. 10) are typical of well-prepared samples from other laboratories.[1] As the Fe fraction increases, the room-temperature resistivity is seen to steadily increase as well.

Temperature-dependent relative resistances for the $YBa_2(Cu_{1-x}Fe_x)_3O_y$ series (up to x =0.12) are presented in Fig. 3. At low Fe content, the normal-state resistance

FIG. 1. Variation in the axial lengths a, b, and c (presented as $c/3$) with percent iron for $YBa_2(Cu_{1-x}Fe_x)_3O_y$.
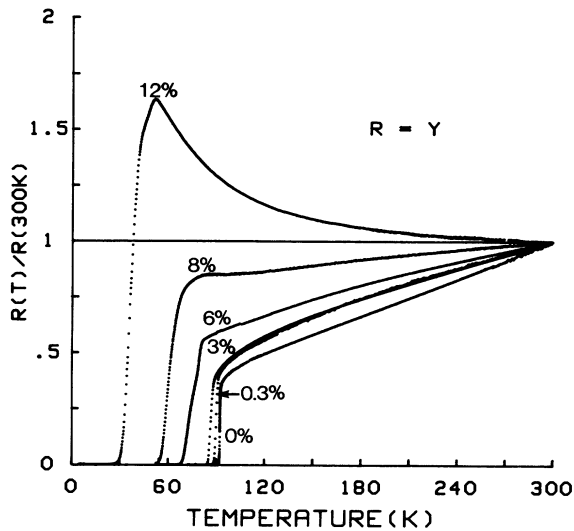
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FIG. 3. Temperature dependence of the relative resistance $R(T)/R(300 \text{ K})$ with percent iron for $YBa_2(Cu_{1-x}Fe_x)_3O_y$.

shows a positive temperature coefficient of resistance (TCR) and a nominally linear approach to the transition region. At intermediate Fe substitution ($x = 0.08$), the normal-state resistance exhibits a weakly positive TCR and a shallow minimum just prior to the critical region. At higher Fe content ($x = 0.12$), the normal-state resistance shows a negative TCR, culminating in a very rounded approach to the superconducting transition. In the normal state then, it is clear that increasing Fe content leads to a decreasing metallic conductivity (and eventually to a semiconducting behavior at $x = 0.15$, see below) showing the increasing localization of electrons. A very similar set of curves is obtained for the $GdBa_2(Cu_{1-x}Fe_x)_3O_y$ materials.

In both sets of ceramics, as the degree of Fe substituted for Cu increases, the critical temperature monotonically decreases as depicted in Fig. 4. Considering the meticu-
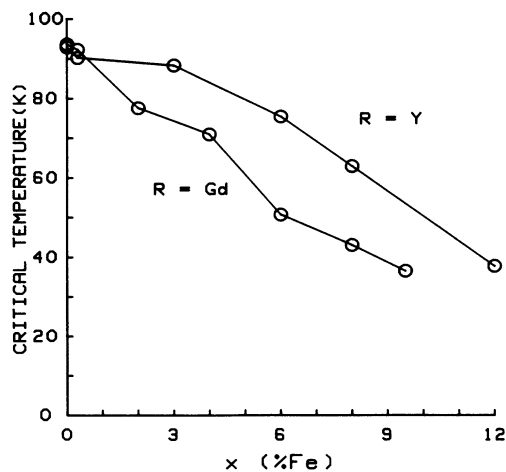
lous preparative procedure that yields single-phase materials and the small and nonsystematic oxygen variability, the decrease in T_c clearly follows from increasing Fe content as this is the only parameter which varies systematically across each series. For Fe percentages in excess of 12% in the Y system and in excess of 10% in the Gd system, superconductivity is not observed down to 1.4 K. As is clearly evident from Fig. 4, the decrease in T_c with increasing Fe content is more pronounced in the Gd-based ceramics than in the Y-based ceramics—a trend which parallels the tendency to the higher symmetry tetragonal structure as shown in Fig. 2.

Two particular results, however, provide a more definitive differentiation between the Y- and Gd-containing materials. First, the transition to a nonsuperconducting material and the achievement of tetragonal symmetry appear to be essentially coincident in the Y materials. In contrast, for the Gd ceramics the structural data indicate tetragonal symmetry by ~7% Fe substitution, whereas superconductivity remains attainable (although at severely reduced values for T_c) up to at least 10% Fe content. Second, at the highest level of Fe substitution studied ($x = 0.15$), the temperature dependence of the resistance is markedly different for $YBa_2(Cu_{0.85}Fe_{0.15})_3O_y$ and $GdBa_2(Cu_{0.85}Fe_{0.15})_3O_y$ (Fig. 5). It is clearly evident from Fig. 5 that 15% Fe substitution in the Gd sample causes a smooth, monotonic increase in resistance with decreasing temperature, until at low temperatures the resistance is some 20 times that at room temperature. For the Y sample at 15% iron content not only is the rise in resistance with decreasing temperature less steep, but at approximately 15 K there is a break in the curve which might indicate an incipient superconducting state, consistent with the trend shown in Fig. 4, or perhaps signals a magnetic or structural phase transformation.

The latter of these two effects seems to be clearly traceable to the magnetism associated with the Gd sublattice, assuming the magnetism associated with the Fe sublattice
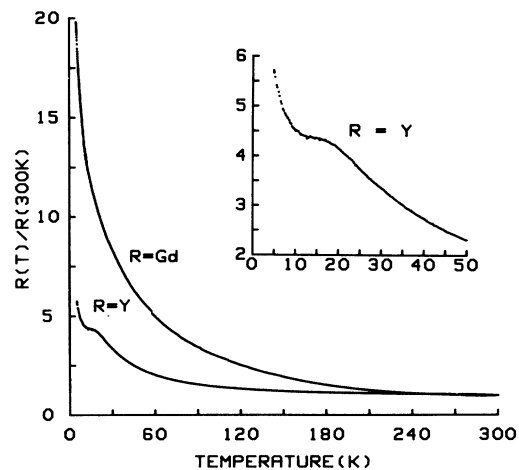

FIG. 4. Variation in critical temperature (T_c) with percent iron for $YBa_2(Cu_{1-x}Fe_x)_3O_y$ and $GdBa_2(Cu_{1-x}Fe_x)_3O_y$.

FIG. 5. Temperature dependence of the relative resistance for $YBa_2(Cu_{0.85}Fe_{0.15})_3O_y$ and $GdBa_2(Cu_{0.85}Fe_{0.15})_3O_y$. The inset highlights the low-temperature anomaly in the Y-based ceramic.

is nominally equivalent (no clustering) in both samples. Apparently, there is sufficient pair breaking owing to the presence of the Gd moments (interacting with the Fe sublattice) for superconductivity to be completely suppressed in $GdBa_2(Cu_{0.85}Fe_{0.15})_3O_y$. In any event, it is clear that while the effects of the magnetism of the Fe sublattice alone in $YBa_2(Cu_{0.85}Fe_{0.15})_3O_y$ are sufficient to repress pair condensation, the level of pair breaking may be insufficient to completely suppress the tendency to a superconducting state.

Finally, the retention of superconductivity at 8% and 9.5% Fe substitution in $GdBa_2(Cu_{1-x}Fe_x)_3O_y$ in spite of the apparent achievement of tetragonal symmetry is perhaps even more surprising. This unusual behavior does not appear to be structurally related, since the more readily achieved tetragonal symmetry in the Gd ceramics (Fig. 2) is consistent with the less distorted orthorhombic struc-

ture at $x = 0$. It is possible that minor differences in oxygen content between the Y- and Gd-containing materials in this composition range may in some way allow the retention of superconductivity at 8% and 9.5% Fe substitution in the Gd samples. But more likely is the existence of a magnetic interaction between the Gd and Fe sublattices at these intermediate substitution levels which stabilizes the superconducting phase in the tetragonal structure *via* coupling to local spin configurations.[3] Temperature-dependent Mössbauer and magnetization measurements on both series are currently underway which should shed some light on this subject.

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[10]The critical temperature T_c is defined as the midpoint between the temperature at which the sample reaches 90% and 10% of its onset resistance, and ΔT_c is defined at the temperature difference between the 90% and 10% points.