

Observation of superconductivity in a bromine- and iodine-doped Y-Ba-Cu-O ceramic

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A transition to a superconducting (diamagnetic) state has been observed in nonsuperconducting tetragonal samples of a $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$ ceramic heat-treated with gaseous bromine or iodine. The transition begins at $T_{c0} \approx 75$ K or $T_{c0} \approx 50$ K, respectively.

The role played by Cu-O planes as a common structural element possibly the reason for the high-temperature superconductivity of complex metal oxides has recently been discussed widely. Central questions here are the bonding of the Cu-O planes with other structural elements, which determine both the appearance of charge at the planes (holes in the $2p$ shell of oxygen) and the stability of the crystal as a whole.¹ It is accordingly important to study the consequences of a complete or partial substitution of the elements in the cationic and anionic sublattices of the superconductors.

In a recent paper² we suggested a method for replacing oxygen in Cu(I)-O planes by other oxidants through the use of the reaction $\text{YBa}_2\text{Cu}_3\text{O}_6 + \text{gas}$. In particular, we demonstrated the appearance of a superconducting transition beginning at $T_{c0} \approx 90-92$ K in initially tetragonal samples of a $\text{YBa}_2\text{Cu}_3\text{O}_6$ ceramic heat-treated with gaseous chlorine. A corresponding study³ has been reported on an oxygen \rightarrow fluorine replacement in a Y-Ba-Cu-O ceramic.

In the present letter we are reporting experiments on the doping of a Y-Ba-Cu-O ceramic with bromine and iodine, carried out by the procedure proposed in Ref. 2.

In the experiments we studied samples of a nonsuperconducting ceramic with a composition of approximately $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$. The oxygen concentration was determined by iodometric titration. The crystal structure was studied with an TIR M-62 x-ray diffractometer. The temperature dependence of the ac susceptibility χ_{ac} was measured by a contactless inductive method (the frequency of the modulating field was 111 Hz, and its amplitude was 0.5 G). After preparation, the samples were treated with gaseous bromine at 200-300 °C or iodine at 300-500 °C (oxygen was excluded).

Figure 1 shows results of the measurements of $\chi_{ac}(T)$ for samples heat-treated with bromine at 230 °C and iodine at 450 °C. We interpret the significant change in χ_{ac} as a transition to a superconducting (diamagnetic) state. The beginning of the transition, T_{c0} , corresponds to ≈ 75 K in the case of bromine and ≈ 50 K in the case of iodine. Note the sharp jump in the susceptibility at 50-55 K on the curve of $\chi_{ac}(T)$ for the Br-doped sample. In all cases, the overall transition stretched down to liquid-helium temperatures. The beginning of the transition lay in the interval 70-75 K (for

χ_{ac} , arb. units

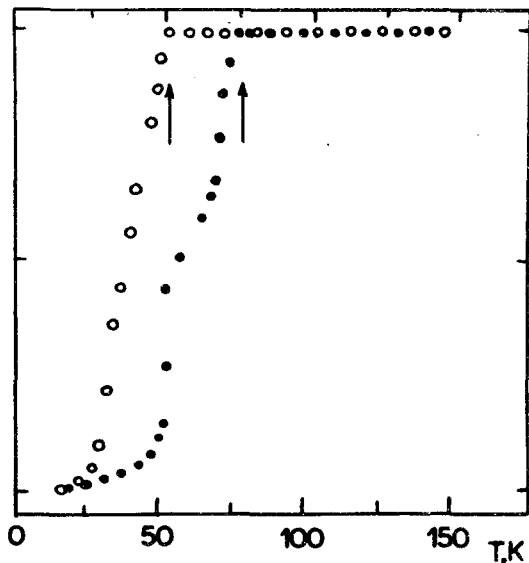


FIG 1. Temperature dependence of the magnetic susceptibility, $\chi_{ac}(T)$, of samples of a $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$ ceramic doped with (*) bromine and (o) iodine.

Br) and 35–55 K (for I) for the various samples. A transition to a diamagnetic state was noted for all samples (more than 40 of them) which were heat treated in this interval.²⁾ The magnitude of the magnetic screening signal was usually 5–10% of the diamagnetic response of a lead sample of similar size and shape.

Figure 2 shows typical fragments of x-ray powder diffraction patterns of (a) the initial $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$ samples and of samples doped with (b) iodine and (c) bromine. The initial ceramic has a tetragonal structure with constants $a = b = 3.861 \text{ \AA}$, $c = 11.791 \text{ \AA}$. The doped samples correspond to an orthorhombic symmetry with the constants³⁾ $a = 3.840 \text{ \AA}$, $b = 3.881 \text{ \AA}$, $c = 11.733 \text{ \AA}$ in the case of iodine and $a = 3.850 \text{ \AA}$, $b = 3.877 \text{ \AA}$, $c = 11.736 \text{ \AA}$ in the case of bromine. In all cases, most of the sample (at least 90% of it) is a single phase; in some of the samples we observed small amounts of unknown phases (no more than 5%), but none of these unknown phases appeared regularly. In some of the bromine-doped samples we observed a partial disordering, but to a considerably lesser extent than is characteristic of the chlorine-treated ceramic. A distinctive feature of the samples with iodine is the highly anisotropic shape of the particles which are formed when the samples are crushed. This anisotropy was detected from the pronounced tendency toward the formation of textures, and it was manifested on the diffraction patterns as a sharp intensification of the (00 l) basal reflections.

It can thus be asserted that when a tetragonal Y–Ba–Cu–O ceramic is doped with iodine and bromine, we observe a transition to a superconducting state with $T_{c0} \approx 50 \text{ K}$ and $T_{c0} \approx 75 \text{ K}$, respectively, and a change in structure from tetragonal to orthorhombic.

At this point we do not have direct proof that the observed effects are a conse-

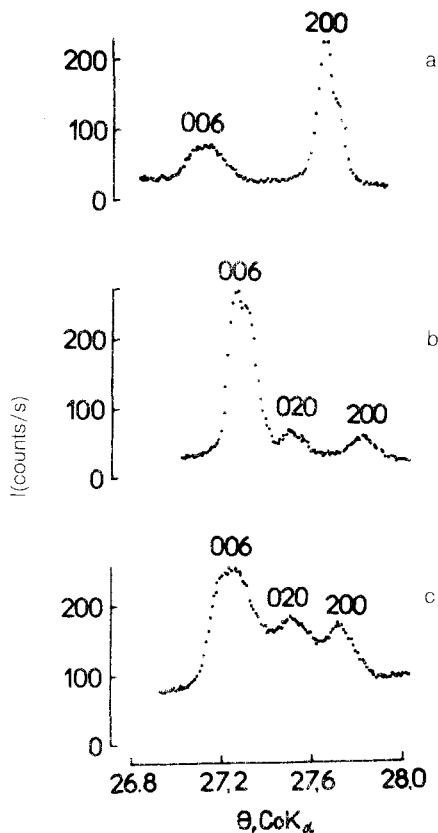


FIG. 2. Fragments of x-ray powder diffraction patterns, a—Original $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ sample; b—after treatment with iodine; 3—after treatment with bromine.

quence of a filling of vacant oxygen positions in the Cu(I)–O plane by bromine or iodine atoms. There is the further possibility of a more complicated process in which the lattice of the Y–Ba–Cu–O ceramic assimilates bromine or iodine in different positions, in a process accompanied by a displacement of oxygen atoms into Cu(I)–O chains.

In order to explain the various aspects of the appearance of a high-temperature superconductivity in the Y–Ba–Cu–O system doped with bromine and iodine (and also chlorine), one will have to answer the following basic questions:

1. Which crystallographic positions are occupied by the Cl, Br, and I atoms, and what valence do they exhibit?
2. What are the sign and magnitude of the charge at the Cu(II)–O plane and the carrier density in these cases in comparison with $\text{YBa}_2\text{Cu}_3\text{O}_7$?
3. Which basic differences in the structures and phonon spectra of the Y–Ba–Cu–O ceramic doped with Cl, Br, and I can lead to the different values of T_c (90, 75, and 50 K).

At this point we have obtained preliminary results by Mössbauer spectroscopy

and neutron diffraction in a doped Y-Ba-Cu-O ceramic which also point to an entry of iodine and bromine atoms into the lattice and which support the validity of posing these questions.

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²⁾ Detailed information on the kinetics and parameters of the heat treatment in bromine and iodine and their effect on the structure and properties of the Y-Ba-Cu-O ceramics will be published separately.

³⁾ These are average values; the variations in the values of a and b are significant (0.002–0.004 Å). The results of a detailed analysis of the structural features of the orthorhombic phase which arises will be published separately.

¹⁾ V. J. Emery and G. Reiter, *Phys. Rev.* **B38**, 4547 (1988).

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³⁾ P. K. Davies, J. A. Stuart, S. White *et al.*, *Solid State Commun.* **64**, 1441 (1987).

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