

# Observation of superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_6\text{Cl}_x$

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(Submitted 20 July 1988)

*Pis'ma Zh. Eksp. Teor. Fiz.* **48**, No. 4, 225–227 (25 August 1988)

Ceramic samples with a composition close to  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , having a tetragonal structure and lacking any superconducting transition down to 0.35 K, were heat-treated in gaseous chlorine. The resulting samples turned out to be stable under standard conditions. They exhibited a superconducting transition beginning at 90–92 K, according to a jump in the magnetic susceptibility.

One possible direction for studying the crystal-chemistry aspects of the nature of high-temperature superconductivity in complex metal oxides might be experiments in which the oxygen is completely or partially replaced by atoms of other elements which manifest a negative valence in compounds. Some recent papers have reported attempts to substitute fluorine (Ref. 1, for example) and sulfur (Ref. 2, for example) for the oxygen in a Y–Ba–Cu–O system. These substitutions were achieved by synthesizing the desired compound from a mixture of the oxides of yttrium, barium, and copper, in which one of the oxides was replaced by a fluoride or sulfide in the required proportion. Structural features were observed above 100 K in the temperature dependence of the conductivity of the resulting  $\text{YBa}_2\text{Cu}_3(\text{O},\text{F})_x$  and  $\text{YBa}_2\text{Cu}_3(\text{O},\text{S})_x$  compounds and were interpreted as a superconducting transition.<sup>1,2</sup>

It appears that the samples synthesized by that procedure were unstable, since the effect disappeared when the measurements were repeated, and since attempts by other investigators to reproduce the results of Refs. 1 and 2 have been unsuccessful. Unfortunately, no evidence that some of the oxygen atoms were actually replaced by fluorine or sulfur was reported in Refs. 1 and 2. Furthermore, no information was given on the crystallographic positions of the atoms which were introduced.

In the present letter we report an attempt to use a different experimental procedure to replace some of the oxygen atoms in the Y–Ba–Cu–O system by chlorine. We also report low-temperature measurements of the magnetic susceptibility and structural characteristics of the resulting compounds. The idea underlying these experiments was to start with samples of a nonsuperconducting tetragonal phase of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  and to produce the compound  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{Cl}_x$  through a subsequent processing in gaseous chlorine.

The initial ceramic  $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$  samples, synthesized and annealed in oxygen, exhibited the following properties: A superconducting transition began at  $T_{c1} = 93$ –94 K, was centered at  $T_c \approx 90$  K, and had a width  $\Delta T_c \approx 6$  K. These figures were found through measurements of the ac magnetic susceptibility  $\chi_{ac}$  (the frequency of the modulating field was 111 Hz, and its amplitude was 0.5 G). The oxygen content  $O_y$  was measured by iodometric titration, and the composition was measured with a

Camebax x-ray microanalyzer. The crystal structure corresponded to an orthorhombic phase with the parameter values  $a = 3.81 \text{ \AA}$ ,  $b = 3.88 \text{ \AA}$ ,  $c = 11.64 \text{ \AA}$ . After their characteristics were determined, the samples were subjected to high-temperature annealing in vacuum. This annealing stripped the samples of their superconducting properties (no transition was detected as the samples were cooled down to 0.35 K). The temperature dependence of the electrical conductivity acquired a clearly expressed semiconducting nature. The oxygen content in the samples decreased to  $O_{6.0}-O_{6.1}$ . The crystal structure corresponded to tetragonal symmetry with the parameter values  $a = b = 3.864 \text{ \AA}$ ,  $c = 11.818 \text{ \AA}$ . At this point the samples were placed in a vacuum chamber and processed with pure gaseous chlorine at various temperatures.<sup>2)</sup> Chlorine from which traces of moisture were removed by passage through a solution of concentrated sulfuric acid was blown through the system continuously throughout the heat treatment. After the exposure to the chlorine, the samples were transferred (without making contact with air) into liquid nitrogen. Electrical and structural measurements were then carried out without heating above 120 K. Further experiments, however, revealed that these precautions (preventing contact with air and storage at low temperatures) were unnecessary.

Figure 1 shows the measurements of  $\chi_{ac}$  of a  $YBa_2Cu_3O_6Cl_x$  sample. There is a jump in the susceptibility, which we interpret as a transition to a superconducting state. The magnitude of the discontinuity (the magnetic-screening signal) constitutes 10–100%, for samples subjected to different types of heat treatment, of the magnitude of the diamagnetic response of a lead sample of approximately the same size and shape. The beginning of the transition corresponds to  $T_{c1} = 90-92 \text{ K}$ ; the middle of the transition varies from sample to sample over the interval  $T_c = 70-80 \text{ K}$ ; and the transition is spread out down to liquid-helium temperatures.

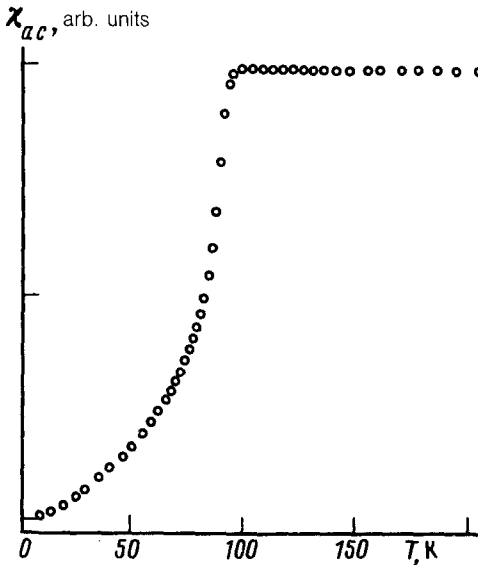


FIG. 1. Temperature dependence of the ac magnetic susceptibility,  $\chi_{ac}(T)$ , of samples of the compound  $YBa_2Cu_3O_6Cl_x$ .

The x-ray microanalysis demonstrates that there is a significant amount of chlorine in the samples, but we were not able to distinguish chlorine which had become a direct part of the composition of the chemical compound from adsorbed atoms or molecules of chlorine in pores, microscopic cracks, and so forth. For this reason, we do not state a specific value for  $x$  in the formula  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{Cl}_x$ .

Our study of the crystal structure of the chlorine-treated samples yielded the following results. The lattice parameters for the various samples are  $a = 3.83\text{--}3.84 \text{ \AA}$ ,  $b = 3.87\text{--}3.88 \text{ \AA}$ ,  $c = 11.65\text{--}11.75 \text{ \AA}$ ; i.e., the resulting structure is orthorhombic, but with a smaller difference between the parameters ( $b-a$ ) than would be characteristic of a  $90^\circ$  superconducting orthorhombic "oxygen" phase. The exposure of the tetragonal-phase samples to chlorine thus led to a phase transition and a transition to an orthorhombic structure in our samples.

Heating the chlorine-treated samples to room temperature and holding them under standard conditions usually resulted in no significant degradation of the superconducting properties or change in structure. These results may indicate that the  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{Cl}_x$  system is stable at least at 300 K. In some cases we did observe a slight decrease (3–5 K) in  $T_c$  after the samples were held for a day at 300 K, but thereafter there was no change in  $T_c$ .

Summarizing these experimental results, we can assert that treatment of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  samples with gaseous chlorine has produced a compound  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{Cl}_x$  which has an orthorhombic structure but whose lattice parameters differ from the corresponding values for an oxygen orthorhombic phase.

This compound is superconducting with  $T_{c1} = 90 \text{ K}$ ; i.e., its  $T_c$  is essentially the same as that of the compound  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

With regard to an interpretation of the crystal-chemistry aspects of this result, we find the following two models to be the most obvious ones:

- 1) Chlorine which has entered the crystal structure of the initial  $\text{YBa}_2\text{Cu}_3\text{O}_6$  compound, which is present in certain lattice sites, possibly becoming ordered, and which itself participates in chemical binding, gives rise to superconducting current carriers (paired holes). In this case the orthorhombic nature is determined by the ordering of the chlorine atoms.
- 2) Chlorine replaces some of the oxygen in the  $\text{YBa}_2\text{Cu}_3\text{O}_6$  structure and displaces this part of the oxygen to other crystallographic positions (to positions where the oxygen is in a region of a higher oxygen concentration, close to  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ). In this case the orthorhombic nature results from an ordering of the oxygen which is in excess of  $\text{YBa}_2\text{Cu}_3\text{O}_6$ . The formation of a superconducting electron subsystem (paired holes) in this case, as in all  $\text{MeBa}_2\text{Cu}_3\text{O}_y$  cases, is associated with the crystal chemistry of the excess oxygen (chains of  $-\text{Cu}-\text{O}-$ , etc).

New experiments on these samples are obviously required in order to decide between these two models. The formulation of many such experiments is already clear, and work has already begun. Experiments have also been undertaken to determine the crystallographic positions of the chlorine atoms and their dynamics and to more accurately determine the total chlorine concentration in the samples.

Perrin *et al.*<sup>3</sup> have attempted to treat samples of the Y–Ba–Cu–O system with gaseous fluorine. They also noted the appearance of a diamagnetic response in nonsuperconducting samples after treatment with fluorine. That result could apparently correlate with the data of the present study. Furthermore, after we submitted this letter for publication we learned that Suzuki *et al.*<sup>4</sup> have measured the static magnetic susceptibility in the normal state of a  $\text{YBa}_2\text{Cu}_3\text{O}_y$  ceramic processed in an atmosphere of gaseous HCl. Suzuki *et al.*<sup>4</sup> suggest that some of the oxygen atoms may be replaced by chlorine in the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  samples under certain conditions.

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<sup>2</sup>Detailed information on the parameters of the heat treatment in chlorine (the temperature, the pressure, the kinetics, and so forth) will be published in a following paper.

<sup>3</sup>S. R. Ovshinsky, R. T. Young, D. D. Allred *et al.*, Phys. Rev. Lett. **58**, 2579 (1987).

<sup>4</sup>K. N. R. Taylor, D. N. Matthews, and G. J. Russell, J. Cryst. Growth **85**, 628 (1987).

<sup>5</sup>C. Perrin, O. Pena, M. Sergent *et al.*, Phys. C: **153-155**, 934 (1988).

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Translated by Dave Parsons