Motion of heavy ions in Y–Ba–Cu–O high-T_c superconductors and superconducting current

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(Submitted 28 November 1989)
Pis'ma Zh. Eksp. Teor. Fiz. **51**, No. 3, 132–134 (10 February 1990)

It is predicted on the basis of a symmetry analysis of the actual structure of a Y–Ba–Cu–O system that there may be a motion of heavy ions because of the low energy barrier between partially filled positions. An experiment has been carried out in order to observe the corresponding effect. The results of this experiment reveal a mass transfer at 4.2 K which is associated with the superconducting current.

The charge carriers in the high-T_c superconducting state of the Y–Ba–Cu–O oxide systems are known to have a positive sign.[1] Several hypotheses of a "copper scenario" or an "oxygen scenario" for high-T_c superconductivity have accordingly arisen; these hypotheses would require the presence of either O^{1-} or Cu^{3+} ions in the crystals. The formation of O^{1-} ions from O^{2-} ions would require an energy of 14 eV, and the formation of Cu^{3+} from Cu^{2+} would require 21 eV (Ref. 2). These energies are not at all comparable with, for example, the heat of fusion of an oxide per atom ($\sim$0.1 eV). However, in the Y–Ba–Cu–O structure the existence of a partially filled system of regular points means that there is, for example, a sublattice occupied by Cu^{2+}, for which the energy barrier for a transition of ions between partially filled positions should be low as long as the structure is stable. We know that structures of this sort promote a positive ion current and, as a result, a mass transfer and a degradation of the composition and properties of the structure itself. If a positive ion current is directly related to the superconducting current, it must also exist at liquid-helium temperatures. It would be manifested as a mass transfer or an accompanying effect characterized by a change in chemical composition. On the basis of general theoretical considerations, we would consider a mass transfer unlikely at liquid-helium temperatures. However, the arguments above concerning the particular structural geometry of the oxide high-T_c superconductors and also symmetry considerations incorporating the sizes of the atoms have motivated us to develop and carry out a special experiment to study possible mass transfer in the structures of oxide high-T_c superconductors at $T = 4.2$ K.

The test samples were polycrystalline films of the compound $Y_1Ba_2Cu_3O_{7-\delta}$ with a thickness of 1 μm, synthesized by a condensate-diffusion method on substrates of polycrystalline zirconium oxide stabilized by yttrium oxide.[3] The experimental method is a two-step method, including the successive formation of a multilayer composition ($\sim$10 layers) of the components of the high-T_c superconducting compound on the substrate (the substrate was Y_2O_3, BaO, or Cu; this was step 1) and a programmed annealing of this composition (step 2). The layers of the components were deposited by electron beam evaporation with condensation of the corresponding substances on the substrate at $T = 100°$ C in an oxygen atmosphere at a pressure of 5×10^{-5} torr. The resulting samples were annealed in flowing oxygen at atmospheric pressure, in accordance with a program optimized empirically for each type of substrate. The maximum annealing temperature was 925° C; the dimensions of a sample were 12×5 mm.

Four ohmic contacts, points 1 mm in diameter, were applied to the surface of the superconducting film in the direction parallel to the long side by rubbing on indium and then fusing it. The two outermost contacts, to which gold wires were soldered, were used to pass the transport current. Through one of two samples synthesized under identical conditions we passed a direct current for several days. Both samples were then studied by x-ray microspectral analysis, and the results were compared. For the current experiments the test sample was put in a holder which was placed in a cell with helium at atmospheric pressure as a heat-exchange medium in a vessel containing liquid helium. The apparatus made it possible to record a curve of the transition to the superconducting state and to pass a current through the sample at $T = 4.2$ K. In the latter case the electric circuit consisted of a galvanic element (emf = 1.12 V, internal resistance of 3.3 Ω), a dc milliammeter, a resistance box, and the test sample, all connected in series. The leads were made in an Nb–Ti alloy and had a resistance of 2 Ω at room temperature. A current of 45 mA was passed through a sample for 166 h at $T = 4.2$ K. The total charge passed through the sample was 2.7×10^4 C.

The curve of the transition to the superconducting state was monitored after the passage of the transport current; T_c was 86 K; and the width of the transition was $\sim$2 K. We found no substantial changes in the shape of the transition curve or in the transition temperature after the current was passed.

To determine more accurately any possible changes in the morphology or composition of the films, we studied them on a Camscan electron microscope with a Link energy-dispersion spectrometer for an x-ray spectral analysis. This apparatus made it possible to carry out an elemental and phase chemical analysis of the materials with a spatial resolution $\sim1\times1\times1$ μm. The spectra were analyzed by the *ZAF* program. The calculation of the oxygen concentration in this program was based on the difference between the concentration of Y, Ba, and Cu and 100%.

Here are the results of our study of the Y–Ba–Cu–O films after the passage of a current and also for a control sample, which we will call the "original" sample:

1. Morphological differences

In the original sample the phase contrast was uniform, and the surface smooth. After the current was passed, a "track" was formed between the electric contacts with the rough surface. The phase contrast was nonuniform, and there were flaky inclusions 1–20 μm in size, localized for the most part near the electric contacts. The morphological differences smoothed out at the periphery of the sample.

2. Composition irregularities

a. The overall composition of the films was determined on a 300×300-μm area in three regions: near the electric contacts and at the center of the film. The copper content of the original sample was 4–6% by weight higher than that in the sample after the passage of the current (the relative error of these measurements was 2%). The Ba concentration in the original sample was 2–3% by weight higher. In both films, on the other hand, the Y and O concentrations approached the stoichiometric values.

b. The local composition of the films was analyzed with a probe ~1 μm in diameter. In the original sample we found the composition to be highly homogeneous, indicating that these films were of good quality. After the passage of a current, we detected inclusions in the form of "dotted lines" (point inclusions arranged in lines), which bracketed regions with a stoichiometric composition. The quantitative composition of these inclusions corresponds to that of the $CuBaO_2$ phase. In addition, flaky inclusions rich in Y or Ba in comparison with the stoichiometry were observed near the electrodes.

A statistical analysis of the results of the local x-ray microspectral analysis for the homogeneity of the composition over a 300×300-μm area (we analyzed 25 points in a given area) showed that the electrode region with the negative polarity was rich in copper in comparision with the electrode region of positive polarity; the difference was 4% by weight. Near the negative electrode we found inclusions with a copper concentration up to 38% by weight. The oxygen concentration in the two films was typically the same according to the x-ray spectral analysis.

In summary, since a mass transfer accompanying a superconducting current (which would eliminate any other currents) is observed at 4.2 K, it is our interpretation that the superconducting current must be linked with a mass transfer.

These experimental results apparently constitute the observation of the lowest-temperature electrochemical reaction which occurs effectively in a solid phase.

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Translated by Dave Parsons