Superconductivity above 100 K in the Bi–Ca–Sr–Cu–O system

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A superconducting transition in the temperature interval 100–130 K has been observed in addition to the primary superconducting transition at $T_c > 80$ K in the Bi–Ca–Sr–Cu–O system. A diamagnetic transition has been observed above 260 K; it may be caused by a new superconducting phase.

The discovery of superconductivity in the compound $Sr_2Bi_2Cu_2O_7$, which has no rare-earth elements,[1] has recently been followed by the observation of a superconducting transition in a sample of the bismuth ceramic $BiCaSrCu_2O_x$, with a transition temperature $T_c = 105$ K (Ref. 2). Since then there have been many reports of the observation of superconductivity in the Bi–Ca–Sr–Cu–O metal-ceramic system at temperatures below 120 K.

In this letter we are reporting a study of the superconducting transition temperature of samples of this system as a function of the composition and heat-treatment conditions. We studied two series of samples, with compositions described by the formulas $Bi_2Ca_ySr_{3-y}Cu_2O_x$ and $BiCa_xSr_yCu_3O_\delta$.

The samples were synthesized by the standard solid-phase powder procedure. The initial materials were oxides of bismuth and copper and carbonates of strontium and calcium ("extremely pure"). The powders were thoroughly mixed in the proportions required for the given composition and sintered in air at 850–850 °C for up to 50 h. The resulting powders were reground, pressed into tablets, and subjected to an additional heat treatment at 850–920 °C for up to 15 h. The time and temperature of the sintering were selected to suit the particular composition of the samples.

The resulting samples were subjected to an x-ray phase analysis, which indicated that the samples had a multiple-phase structure. The data from this analysis, in agreement with the data reported by other investigators,[3] indicate the presence of at least

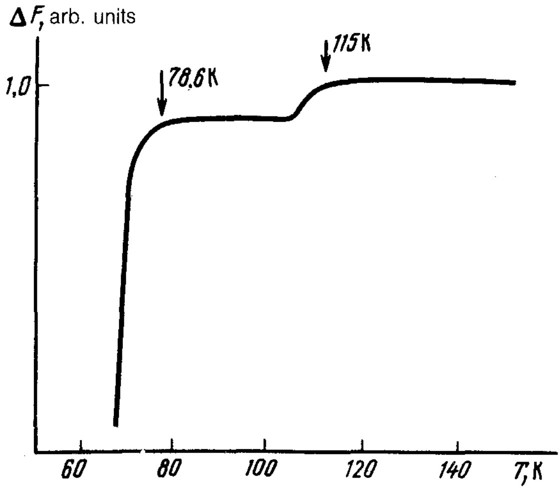

FIG. 1. Transition of a $Bi_2Ca_{1.5}Sr_{1.5}Cu_2O_x$ sample from the normal state to the superconducting state, according to the frequency shift of a tunnel-diode self-excited oscillator.

three tetragonal phases. We recorded curves of the superconducting transition, forward and backward along the temperature scale, in the geomagnetic field and in fields up to 1.5 kOe. The superconducting transition was detected from the frequency shift of a tunnel-diode cryogenic self-excited oscillator; the sample was in a coil in the oscillator circuit.[4] Figure 1 shows a typical transition curve for the bismuth ceramic samples studied. We see two transitions, near 80 K and 115 K, which correspond to two distinct phases with identical constants $a = 5.4$ Å and different values of c, 30 Å and 36 Å, respectively. Depending on the heat-treatment conditions, the value of T_c of the first main phase varies from 70 to 95 K, while T_c for the second phase lies between 100 and 130 K. The value of T_c of the first phase also depends strongly on the ratio Sr/Ca (Fig. 2). To verify that the structural feature at 115 K corresponds to specifically a transition to a superconducting state, rather than to some structural transition

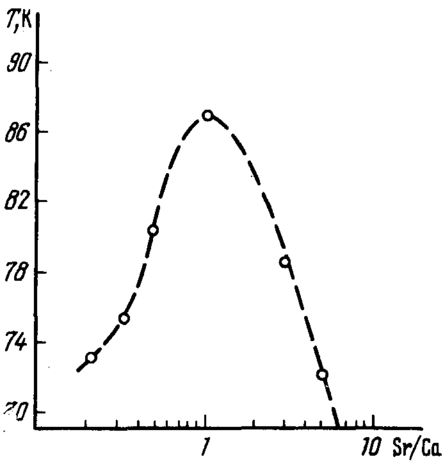

FIG. 2. The transition temperature T_c of a $Bi_2Ca_{3-x}Sr_xCu_2O_y$ sample for the low-temperature phase ($T_c \sim 80$ K) versus the Sr/Ca ratio.

to a diamagnetic phase, we recorded transition curves in magnetic fields up to 1.5 kOe. The effect of the magnetic field on the diamagnetic anomaly could be observed better in a sample with the composition $Bi_2Ca_{1.5}Sr_{1.5}Cu_2O_x$, with a superconducting transition of the main phase beginning at $T_c^{beg} = 78.6$ K and with an approximately 5% content of diamagnetic phase at a temperature $T_c \sim 115$ K. The diamagnetic transition of this sample had a width $\Delta T \sim 7$ K. In a magnetic field of $-$ 1.5 kOe, the beginning of the transition was lowered by less than 0.4 ± 0.1 K. We can thus estimate $dH_c(T)/dT$ to be 4 kOe/K within an error of 25%, in agreement with measurements by other investigators.[5]

In another bismuth ceramic sample with the composition $BiCaSrCu_3O_{6.5+x}$, the superconducting transition was fairly slow, beginning at $T_c^{beg} = 86$ K.

Upon the first cooling of the sample from room temperature we observed, in addition to the superconducting transition described above, a change in the oscillator frequency at $\sim$264 K, which corresponded to the appearance of a bulk diamagnetism in the sample, with a magnitude $\sim$5% of the limiting value. A study of this diamagnetic structural feature revealed that it disappears completely upon heating in a fairly narrow temperature interval, but at a generally higher temperature than during cooling. This hysteresis was also observed during subsequent cooling-heating cycles. Figure 3 shows temperatures at which the transition begins (0) and ends (Δ), along with its width $\Delta T(\bullet)$, for several (N) successive thermal cycles during the cooling of the sample. During heating we observed a similar behavior, but some 5–10 K further up the temperature scale. A common feature of these curves is a gradual shift of the diamagnetic anomaly up the temperature scale during the thermal cycling, with a simultaneous broadening of the transition. A similar effect has been observed previously[6] in La–Sr–Nb–O films at temperatures above 255 K.

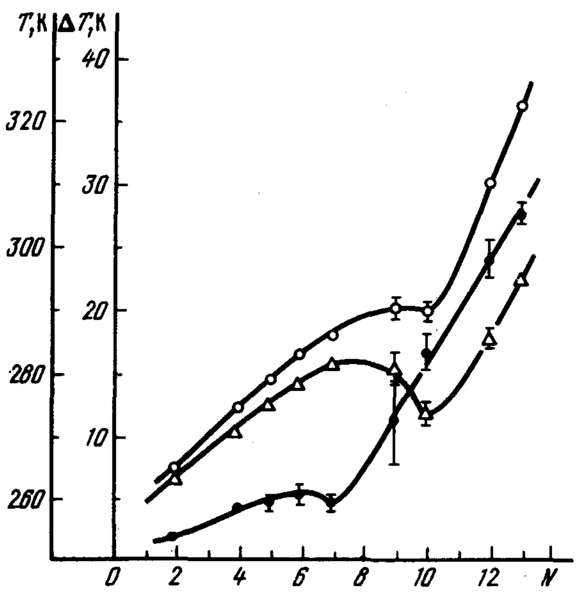

FIG. 3. Temperature at which the transition to the diamagnetic phase begins (O) and ends (Δ), and the width of the transition, $\Delta T(\bullet)$, of a $BiCaSrCu_3O_{6.5+x}$ sample versus the number of thermal cycles during the cooling of the sample.

These results were obtained in the geomagnetic field. Unfortunately, after several thermal cycles without an external magnetic field the curves of the diamagnetic transitions broadened significantly, and a magnetic field up to 1.5 kOe in the apparatus caused no noticeable decrease in the transition temperature. In an applied field of 1.5 kOe we observed only a further broadening of the transition curves, which in this case could not be unambiguously attributed to the influence of the magnetic field.

In summary, a superconducting transition in the temperature interval 100–130 K has been observed in addition to the main superconducting transition at $T_c \approx 80$ K in several samples of a bismuth ceramic. In addition, we have observed a diamagnetic transition at temperatures above 260 K, which may be due to the existence of a new high-temperature superconducting phase. We believe that the diamagnetism observed at room temperatures deserves a very careful study.

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