Observation of spontaneous polarization at a junction of a high-T_c superconductor with an insulator upon the phase transition to the superconducting state

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Quasiferroelectric phase transitions have been observed near T_c in dense ceramic samples of $YBa_2Cu_3O_{7-x}$ and $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_x$ by the method of thermally stimulated depolarization.

It was suggested in Refs. 1–3 that the high-T_c superconductors with the perovskite-like structure are quasiferroelectrics exhibiting an exciton superconductivity mechanism. It should be noted in this connection that absorption anomalies have been observed in the dispersion of an rf magnetic field stimulated by ultrasound near 90 K and also in the interval 150–180 K in an yttrium ceramic with the 1-2-3 composition.[4] A piezoelectric effect was later observed[5] in stressed single crystals of $YBa_2Cu_3O_{7-x}$ in the superconducting state. These crystals were oriented along the z axis.

In this letter we are reporting an effort to observe polarization effects in samples of high-T_c ceramics by the method of thermally stimulated depolarization (TSD). This method has been developed well for identifying ferroelectric transitions in insulating crystals, in which the TSD current stems from a reorientation of dipoles.[6] Another important advantage of the TSD method over the methods of Refs. 4 and 5 is that the samples are not subjected to any external agents other than temperature changes. Since the TSD is applicable in its classical form only for studying slow changes in charge, we have developed a technique[7] for carrying out measurements under conditions corresponding to spontaneous fluctuations of the charge.[8] For this purpose, and also to block charge leakage, we placed a thin ($h \sim 1$ μm) insulating film between the surface of the sample and the upper electrode (Fig. 1). This film, made of a copolymer of vinylidenefluoride and tetrafluoroethylene, followed the changes in the electric field which occurred at the surface of the sample.[7] The film thickness was chosen such that there would be no significant accumulation of the space charge which forms as the film is deformed during the temperature cycling.

The samples were cooled and heated in the temperature interval 78–250 K in a linear fashion. The cooling rate was 0.3 K/s, and the heating rate 0.1 K/s (Ref. 9). To avoid stray pickup associated with the adsorption of atmospheric gases and water vapor on the surface of the ceramics, we carried out the experiments in a vacuum of 10^{-6} Torr. The experimental layout is shown in Fig. 1. The polymer film (4) was deposited on a copper clamp electrode (2) from a dilute solution and then dried in vacuum at $T \simeq 473$ K. The electrode with the deposited film was baked in vacuum at $T = 300$ K after each experiment. Control experiments were carried out without superconductor samples (with the film alone).

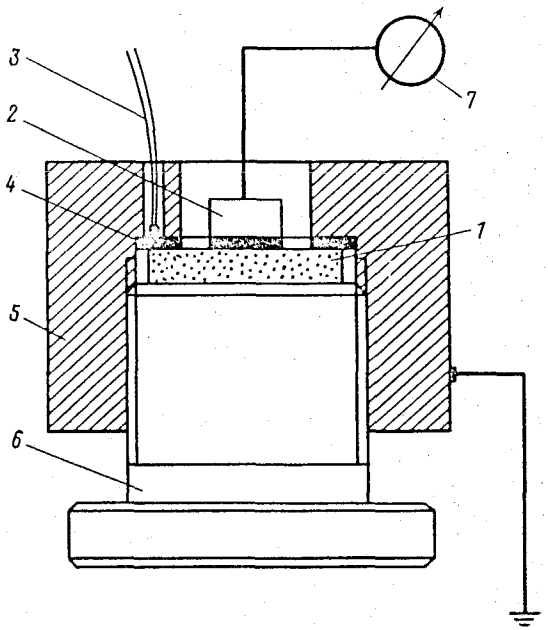

FIG. 1. Experimental layout for measuring the current of the thermally stimulated depolarization. 1—Sample of a high-T_c superconductor; 2—electrode; 3—thermocouple; 4—polymer film; 5—cryostat; 6—tightening screw; 7—U5-6 amplifying electrometer.

The experiments showed that the TSD spectrum of the film has a broad peak in the temperature interval 130–160 K. This peak is extremely small and has a negative polarity, during both cooling and heating. This peak is caused by the charge acquired by the film as it is deformed during the temperature changes (this peak was subsequently subtracted from the TSD spectra of the superconducting samples).

The test samples were ceramic samples of $YBa_2Cu_3O_{7-x}$ with $T_c = 92$ K (the transition width was $\Delta T \simeq 2$ K) and $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_x$ with $T_c = 110$ K ($\Delta T \simeq 9$ K). The samples were synthesized by the standard methods involving compaction at 5 kbar (these were textured samples). The resistive characteristics of these ceramic samples were measured by the four-probe method (see the insets in Figs. 2 and 3). As control samples we used samples of the same superconductors, annealed in vacuum at $T = 673$ K for 2 h. These control samples did not exhibit a superconductivity at $T > 77$ K.

The experiments show that the TSD spectra of the control samples are the same as those of the polymer film. These samples thus do not contain intrinsic TSD currents which might be evidence of ferroelectric properties. On the other hand, two peaks are observed, during both cooling and heating, for the high-T_c ceramics, both the 1-2-3 ceramic and the 2-2-2-3 ceramic (BiPb) (Figs. 2 and 3). The most obvious TSD peaks are detected in "fresh" samples, which have not yet been subjected to temperature cycling. After a few such cycles, the TSD peaks shrink to the background level. This shrinkage is evidence that the texturing of the ceramics during the compaction is playing a role here, leading to a partial orientation of the ceramics (that a texturing occurs was verified by x-ray structural studies). Since the stress is relieved, and thus

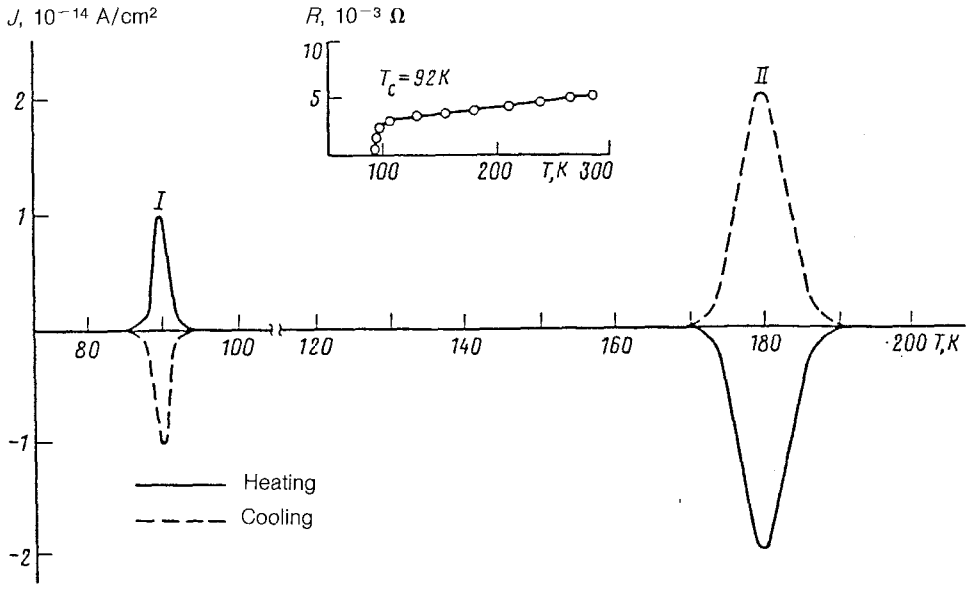

FIG. 2. Spectra of the thermally stimulated depolarization of samples of the high-T_c superconductor $YBa_2Cu_3O_{7-x}$ (the inset shows the temperature dependence of the resistance of these samples).

the orientation is lost, during repeated temperature cycling, it becomes impossible to observe depolarization currents. A possible additional cause of the gradual decrease in the TSD current may be a depletion of oxygen from a surface layer of the high-T_c superconductor during temperature cycling in vacuum.[9]

We see in Fig. 2 that the spectrum of the 1-2-3 sample has two peaks, which are detected during both heating and cooling. Peak I, with a crest near 90 K, has a negative polarity during cooling and a positive polarity during heating. This change in polarity during the temperature cycling indicates that the measured TSD currents cannot be attributed to thermoelectric power. The reason is that a change in the polarity of the thermoelectric current would imply a change in the sign of the charge carriers during the temperature cycling, but such a change is not observed in the case of the high-T_c superconductors.[10] The width of peak I is $\Delta T \simeq 2$ K and corresponds to the width of the superconducting transition (see the inset in Fig. 2). The total charge in the peak is $Q = 1.1 \times 10^{-13}$ C. The activation energy calculated for this peak by the Garlick–Gibson method is $E_I = 0.83$–0.05 eV. For peak II we have $T_{mII} = 180$ K, $\Delta T = 10$ K, $Q_{II} = 1 \times 10^{-12}$ C, and $E_{II} = 1.0 \pm 0.01$ eV. This peak is also observed during an incomplete cooling of the samples (to $T = 150$ K). In other words, this peak is not directly related to the onset of the superconducting state. On the basis of the data obtained, we can attribute peak II to the pyroelectric transition which is observed in yttrium ceramics of the 1-2-3 composition.[5,6]

In the case of the Bi ceramic (Fig. 3), the sign of the current for peak I ($T = 110$ K) is opposite the sign of the corresponding TSD signal for the 1-2-3 compound

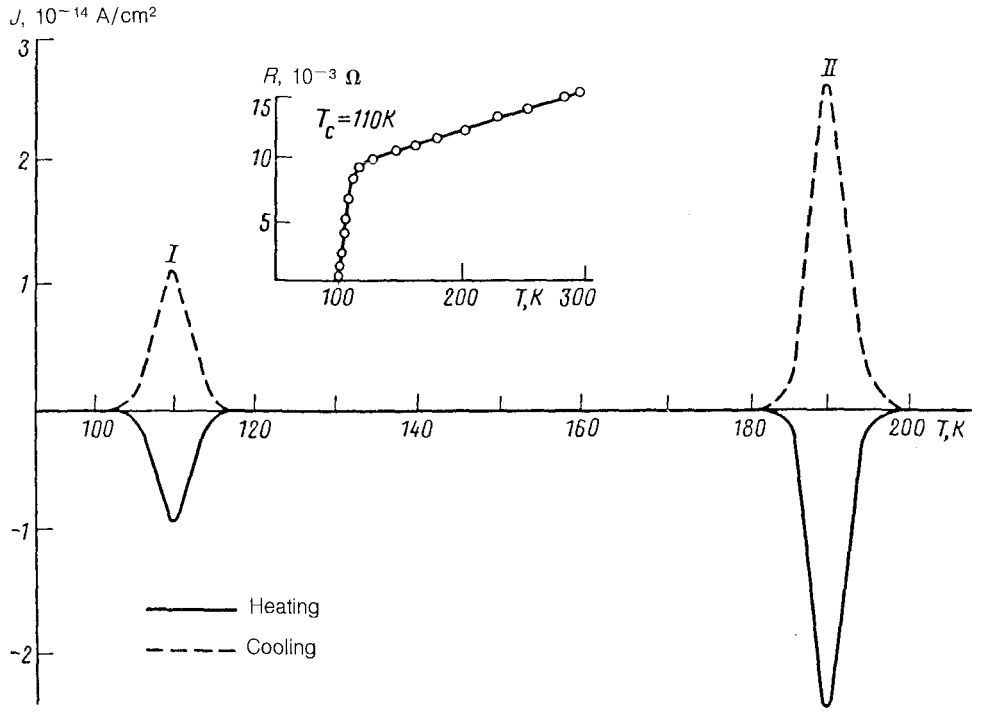

FIG. 3. Spectra of the thermally stimulated depolarization of samples of the high-T_c superconductor $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_x$. The inset shows the temperature dependence of the resistance of these samples.

(Fig. 2), but the activation energy is nearly the same, $E_I = 0.85 \pm 0.05$ eV ($Q_I = 1.5 \times 10^{-13}$ C). The average width of peak I in this case is $\Delta T = 6$ K, slightly smaller than ΔT of the superconducting transition (see the inset in Fig. 3). In certain cases, however, we find two peaks (a splitting) in the interval 100–115 K. This splitting is evidence that the 2-2-2-3 samples contain at least two phases. This conclusion is also implied by the diffuse resistive transition (see the inset in Fig. 3). The reason why the sign for the Bi ceramic is the opposite for that of the 1-2-3 ceramic may be the presence of an electron component of the carriers at a grain boundary in the 2-2-2-3 ceramics[10] (in contrast with the 1-2-3 ceramics). This circumstance would in turn change the sign of the TSD signal. Peak II for these ceramics is similar to peak II for the 1-2-3 compound, but it occurs at a point 10 K higher ($T_{mII} = 190$ K, $\Delta T = 6$ K, $Q_{II} = 1.2 \times 10^{-12}$ C, $E_{II} = 1.5 \pm 0.1$ eV).

The generation of TSD currents is thus observed in compressed samples of high-T_c superconductors during temperature cycling over the range 78–250 K. The resistive superconducting transitions are accompanied by quasiferroelectric phase transitions near T_c. Consequently, the detection of TSD currents at a junction of a high-T_c superconductor with an insulator might serve as a new method for identifying the high-T_c superconducting phase transition.

A direct estimate of the polarization, with allowance for the electrical resistance of the superconductors at $T > 92$ K, $r \sim 10^{-3}$ Ω (1-2-3), yields implausibly high values $\Delta P \sim 10^2$–10^4 C/cm^2. However, since the superconductor makes contact with the polymer film through the insulating surface of the samples (degradation occurs at this surface because of defects and contact with air), and in view of the high resistance of this nonsuperconducting region, of size L ($r \sim 10^4$–10^5 Ω for $L \sim 10$–100 Å; Ref. 11), we conclude that the spontaneous polarization at the junction is 10^{-6}–10^{-5} C/cm^2. Such values are typical of perovskite-like ferroelectrics. It follows that the TSD currents that are detected reflect processes which are occurring in nonsuperconducting surface regions of the superconductor. On the other hand, these processes are evidently a consequence of electronic transitions which are occurring at the boundaries of superconducting grains, since the TSD currents are not detected on nonsuperconducting samples of these high-T_c materials (annealed samples) or on superconducting samples with a degraded texture (after the temperature cycling). In view of the data of Refs. 2–5, the polarization effects which are observed may thus be an indirect reflection of fluctuations in charge[8] which occur when regions near the junction of the superconducting and nonsuperconducting phases of the superconductor undergo a transition to a regime of dynamic polarization. Reaching a detailed understanding of the mechanism for the effects observed here will require further research.

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