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Measurement of laser-induced voltages of superconducting Bi-Sr-Ca-Cu-O

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We report an experimental investigation of laser-induced voltages across point-contact junctions of Pt tips and superconducting Bi compounds. It has been observed that the laser-induced voltages of all 2:2:2:3 granular samples and 2:2:1:2 single-crystal samples are converted with increasing temperature from positive to negative sign, passing through a zero point. The signs for 2:2:1:2 granular samples and n-type $Nd_{1.85}Ce_{0.15}CuO_{4+y}$ sample are always positive. The temperature corresponding to the zero point is approximately the superconducting transition temperature (midpoint) of the measured sample.

Since the discovery of high-temperature superconductors there has been a great deal of interest in their optical properties—and their potential for device applications—including Raman spectroscopy, infrared spectroscopy, and other optical effects. Optical responses have previously been demonstrated in both granular bulk and thin-film superconducting samples.[1-5] In this paper, we report work in which laser-induced voltages were measured across point-contact junctions of metal tips and superconducting Bi compounds. We also discuss in detail the temperature dependence of these laser-induced voltages.

Measurements of laser-induced voltages were performed by means of a ROK 10-300 refrigerator-cooled cryostat and a BY1941 digital microvoltameter. Pb-doped sintered superconductors of nominal compositions of [Bi]:[Sr]:[Ca]:[Cu]=2:2:1:2 and 2:2:2:3 were prepared by the ordinary solid-state reaction method. A typical size of the samples was about $1\times5\times5$ mm^3 Besides, some single-crystal samples whose chemical composition was $Br_2Sr_2CaCu_2O_y$ ($1\times2\times0.1$ mm^3 in size) and an n-type high-T_c superconducting $Nd_{1.85}Ce_{0.15}CuO_{4+y}$ (Ref. 6) sample were also measured. A point-contact junction was formed using a metal Pt tip with a radius about 100 μm and a piece of superconducting Bi compounds which was cleaned prior to the experiment. The sample to be measured was fixed on the sample holder which was mounted on the flange of the 2nd stage of R210 cold head. The lowest temperature attained in this stage is ~10 K. Higher temperatures up to about 300 K can be achieved by heating the stages with or without using an electric heater. Temperature control by resistance measurement of the temperature sensors can be accomplished. To measure the temperature in the range approximately between 300 and 70 K a thermistor is used; and for lower temperatures, a carbon resistor. The laser beam passing through the window on the vacuum jacket of the cold head was directed at the junction of the sample. The lead from the metal probe was connected to the positive pole of the digital microvoltameter and the lead

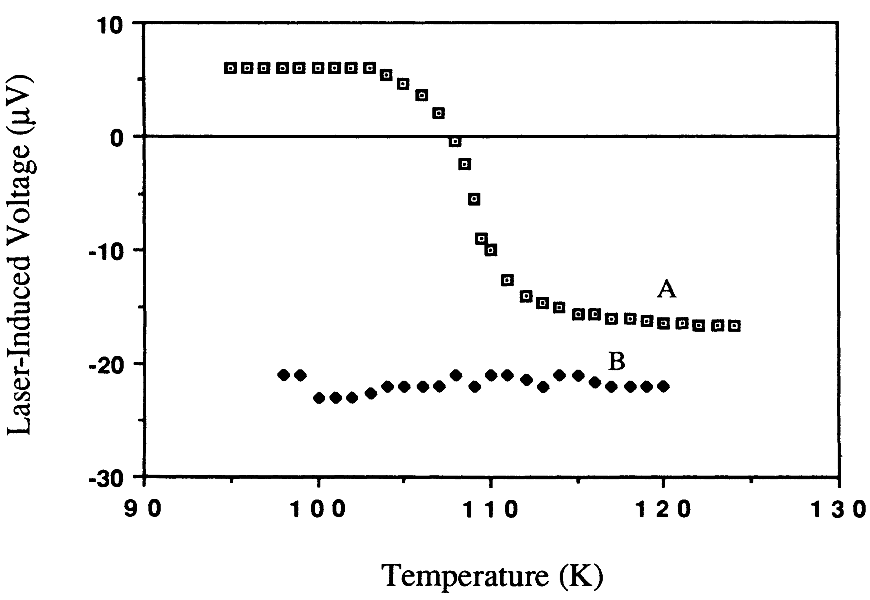

FIG. 1. A typical temperature dependence of laser-induced voltage for $Bi_2Sr_2Ca_2Cu_3O_y$ superconducting samples (curve A) and nonsuperconducting samples (curve B) with a Pt probe.

TABLE I. T_{ε_0} (K) for three different samples for four measurements.

Sample No.	T_{ε_0}(K)			
I	108.4	110.4	108.5	109.8
II	107.6	108.8	107.7	107.8
III	103.6	83.6	100.0	103.0

from the superconductor was connected to the negative one.

A typical temperature dependence of the laser-induced voltage is shown in Fig. 1 (curve A). The measured superconducting material and metal probe were $Bi_2Sr_2Ca_2Cu_3O_y$ and a Pt tip, respectively. The output power of the He-Ne laser is 20 mW. The diameter of the laser spot is about 1 mm. For the sake of contrast, the temperature dependence of the laser-induced voltage of a nonsuperconducting sample with a Pt probe is also shown in Fig. 1 (curve B). Both the superconducting and nonsuperconducting materials had the same nominal composition; only the sintered conditions were slightly different. It is shown that curve A is different from curve B with increasing temperature, the laser-induced voltage for curve A is converted from a positive to negative sign, passing through a zero point. The temperature corresponding to the zero point is approximately equal to the sample's superconducting transition temperature. However, the laser-induced voltage for curve B is always negative and it fluctuates somewhat with increasing temperature.

Is the behavior in curve A characteristic of all superconducting Bi compounds? On the basis of measurements of a series of superconducting Bi compounds, we can now answer this question. All granular samples of the nominal composition 2:2:2:3, Pb-doped and undoped samples, were found that the temperature dependence of the laser-induced voltage was similar to curve A in Fig. 1. There is always a zero point on their voltage-temperature curves and this phenomenon recurs. Table I shows the results of the measurements at four different locations for three samples. Table II gives the temperature T_{ε_0} corresponding to the zero voltage and the three resistive transition temperatures from the normal state to the superconducting state, T_{on} (onset), T_{mid} (midpoint), and T_0 (zero resistivity), for six samples.

It is obvious that T_{ε_0} is approximately equal to T_{mid} for each sample. This is a common occurrence while the values of the laser-induced voltage signals increased with increasing output power of the He-Ne laser, the position of the zero point was unaffected. Then, we used a cw CO_2 laser which was attenuated to about 30 mW instead of the He-Ne laser, repeating the experiment under the same condition. The results were similar. There was not only a zero point but it also occurs at about the same temperature for each 2:2:2:3 sample. Single-crystal samples with the nominal composition 2:2:1:2 were also measured. The temperature dependence of the laser-induced voltage is shown in Fig. 2 (curve A). The temperature corresponding to zero voltage is 69 K, which is approximately equal to its superconducting transition temperature (67 K). However, curve A in Fig. 2 is different from curve A in Fig. 1. There is a maximum of the induced voltage on curve A in Fig. 2, with an extreme value observed in $YBa_2Cu_3O_{7+\delta}$ due to photovoltaic effects.[4] In addition, granular samples with the nominal composition 2:2:1:2 were measured. A typical induced voltage-temperature curve is shown in Fig. 2 (curve B). There is no zero point and the laser-induced voltage is always positive, rising slightly with increasing temperature.

In order to verify that the temperature dependence of the laser-induced voltage is related to the conductive mechanism of a superconducting sample, an n-type superconductor $Nd_{1.85}Ce_{0.15}CuO_{4+y}$, which had a critical temperature of approximately 22 K, was measured and the result is shown in Fig 3. Its behavior is similar to that shown by curve B in Fig. 2 and the induced voltage is always positive. But there is an obvious voltage increasing above the superconducting transition temperature.

Because the position of the zero voltage is about the same for both He-Ne laser and CO_2 laser, in our thinking, the origin of the above-mentioned laser-induced voltage is a photothermal effect. Therefore, the measured induced voltage may be taken as a thermoelectromotive force. From this point of view, we can estimate the value of the measured signal.

Figure 4 shows a schematic diagram of the circuit for measurement. There are five contact points a,b,c,d, and i in the circuit. Let their temperatures be T_a, T_b, T_c, T_d, and T_i, respectively. The lines ac and bd are two copper lead wires, ci is a metal probe, and id a bulk sample. Let the Seebeck coefficients of the copper wire, probe material, and superconducting sample be S_{Cu}, S_p, and S_s, respectively. If we take these Seebeck coefficients to be constant in the small region of variable tempera-

TABLE II. T_0, T_{on}, T_{mid}, T_{ε_0}, and $T_{\varepsilon_0}-T_{\text{mid}}$ for six different samples.

Sample No.	T_0 (K)	T_{on} (K)	T_{mid} (K)	T_{ε_0} (K)	T_{ε_0}-T_{mid} (K)
I	79.2	125.4		108.4	
II	81.0	113.8	109.8	107.7	−2.2
III	80.3	114.0	102.0	103.0	1.0
IV	100.6	108.0	104.0	102.0	−2.0
V	86.6	112.6	102.7	104.0	1.3
VI	94.6	112.8	105.8	103.0	−2.8

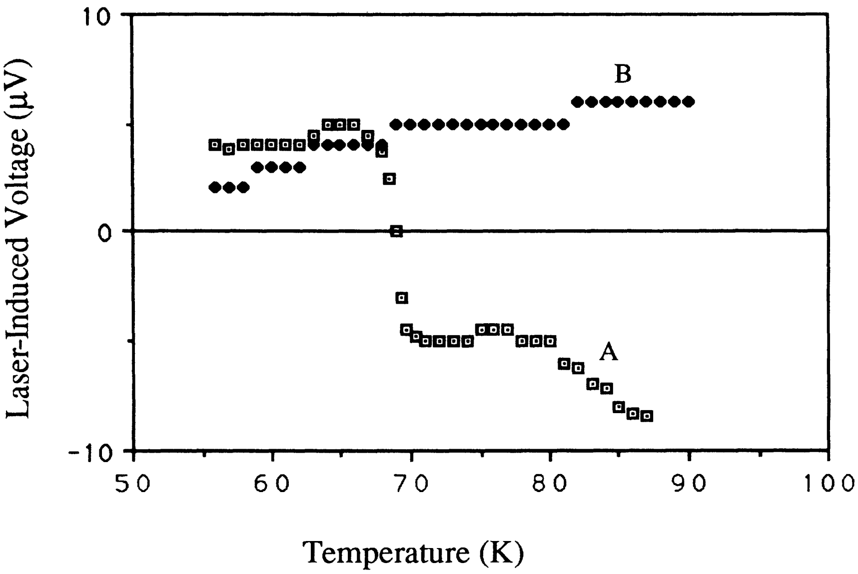

FIG. 2. The temperature dependence of laser-induced voltage for the single-crystal sample (curve A) and granular sample (curve B) of nominal composition 2:2:1:2 with a Pt probe.

ture, a thermoelectromotive force

$$\varepsilon_{ab} = \int_{T_d}^{T_i} (S_{\mathrm{Cu}} - S_s) dT + \int_{T_i}^{T_c} (S_s - S_p) dT$$
$$= (S_{\mathrm{Cu}} - S_s)(T_i - T_d) + (S_s - S_p)(T_c - T_i) \quad (1)$$

is obtained. When point i is irradiated by a laser beam, an increment ΔT_i arises. Our measurement is performed at that instant. Roughly, the changes of T_c and T_d caused by thermal conduction, which is due to $T_i + \Delta T_i > T_c$, T_d, can be neglected. The value

$$\varepsilon'_{ab} = (S_{\mathrm{Cu}} - S_s)(T_i + \Delta T_i - T_d)$$
$$+ (S_s - S_p)(T_c - T_i - \Delta T_i) \quad (2)$$

is obtained. So that the measured signal is approximately

$$\Delta \varepsilon_{ab} = \varepsilon'_{ab} - \varepsilon_{ab} = (S_{\mathrm{Cu}} + S_p - 2S_s)\Delta T_i \ . \quad (3)$$

It is well known that the Seebeck coefficient of a superconductor is equal to zero (i.e., $S_s = 0$), when the temperatures are below T_0. Thus we have

$$\Delta \varepsilon_{ab} = (S_{\mathrm{Cu}} + S_p)\Delta T_i \ , \quad T < T_0 \ . \quad (4)$$

In the temperature region of our experiment, 10–130 K, we have $S_{\mathrm{Cu}} = 0.34-1.15$ μV/K, $S_{\mathrm{Pt}} = 1.81-3.56$ μV/K,[7] and $S_s \approx 10$ μV/K[8,9] for 2:2:2:3 Bi-Sr-Ca-Cu-O samples. From Eqs. (3) and (4), consequently, the values of $\Delta\varepsilon_{ab}$ are positive when the temperatures are below T_0, and negative above T_{on}, and zero always corresponding to a point between T_0 and T_{on}. It is well consistent with our experimental results for the 2:2:2:3 superconducting samples. However, for 2:2:2:3 nonsuperconducting sample with $S_s \neq 0$ in the region of measured temperatures, the $\Delta\varepsilon_{ab}$ is always negative. That is also consistent with our experimental result.

Forro *et al.*[10] and Pekala *et al.*[11] reported the Seebeck coefficients of 2:2:1:2 single crystals. All the S values are

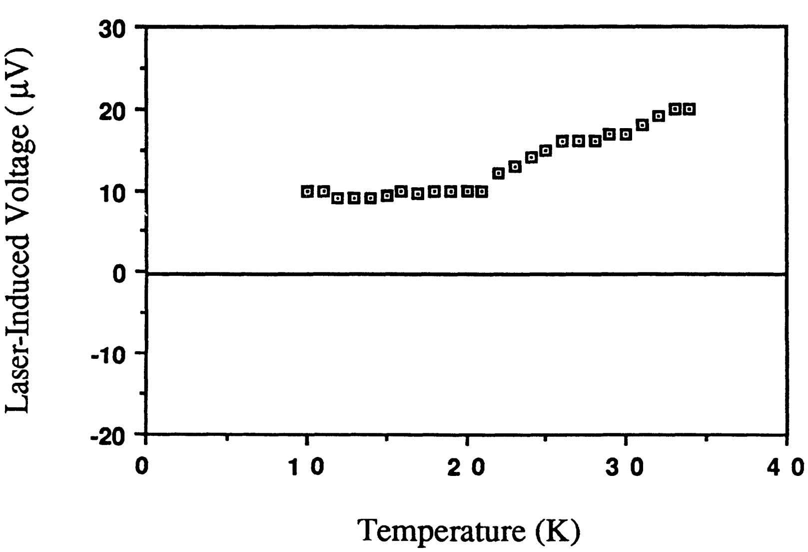

FIG. 3. The laser-induced voltage-temperature curve of the n-type superconductor $Nd_{1.85}Ce_{0.15}CuO_{4+y}$ with a Pt probe.

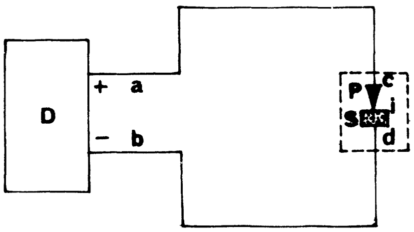

FIG. 4. The schematic diagram of the circuit for the measurements: D, digital microvoltameter, P, Pt tip, and S, sample.

positive within the whole temperature interval with exception for temperatures below the transition temperature, where S vanishes. So the behavior of the induced voltage temperature is similar to that of the 2:2:2:3 superconducting sample. The reported Seebeck coefficient of the granular superconducting samples with nominal composition 2:2:1:2 is negative[12] but smaller. Thus the $\Delta\varepsilon_{ab}$ is always positive as seen in curve B of Fig. 2. As for the n-type superconductor $Nd_{1.85}Ce_{0.15}CuO_{4+y}$, Rao *et al.*[12] and Lopez-Morales *et al.*[13] reported that the sign of the thermopower remained negative from room temperature down to T_c and the slope of S-T plot is negative above T_c. From Eqs. (3) and (4) it can be seen that the value of $\Delta\varepsilon_{ab}$ is always positive. It is also well consistent with our experimental result shown in Fig. 3.

In conclusion, the laser-induced voltages were measured across point-contact junctions of Pt tips and superconducting Bi compounds. The temperature dependence of the induced voltage is different for different kinds of superconducting material. The induced voltages of all 2:2:2:3 granular samples and 2:2:1:2 single-crystal samples change from a positive to negative sign, passing through a zero point in the temperature range under study. However, the induced voltages of 2:2:1:2 granular samples and the n-type $Nd_{1.85}Ce_{0.15}CuO_{4+y}$ sample are always positive. It seems that the induced voltages are nearly thermoelectromotive forces as a result of the local heating by absorbed laser radiation. Clearly, this measurement can be used as a method to determine the signs of the Seebeck coefficients of these kinds of superconducting material and their approximate superconducting transition temperature. We add one final comment: why we failed to find photovoltaic effects in granular superconduction Bi compounds, as had been observed in $YBa_2Cu_3O_{7+\delta}$ samples[4] and $Bi_2Sr_2CaCu_2O_y$ single-crystal samples, remains an intriguing issue to be resolved.

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