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Anomalous photovoltaic response in $YBa_2Cu_3O_7$

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Several experiments were carried out to study the origin of the anomalous photovoltaic effect in high-quality $YBa_2Cu_3O_7$ thin films. In particular, the issue of whether the signal is induced by thermal gradients was addressed. Using samples with well-characterized orientation and texture, and using low-power cw lasers, it was determined that the signal was proportional to the thermal gradient along the *c* axis. However the magnitude of the signal was more than 10 times larger than that produced by thermoelectric power. Additionally, the temperature dependence of this photovoltaic signal was found to be very sample dependent even for high-quality films where all the resistance-temperature curves were apparently the same. The photovoltaic signal may be related to the recently discovered time-dependent photoinduced changes in superconductivity.

I. INTRODUCTION

The observation of laser-induced voltages in $YBa_2Cu_3O_7$ (YBCO) by Chang *et al.*[1] has stimulated many studies on the origin of such signals.[2-7] Several conflicting results have been reported, especially regarding the thermal versus photovoltaic (PV) nature of these signals. We reported recently a study of this PV effect using low-intensity cw laser lights in a [110] oriented YBCO film.[4] The following facts have been established: (1) the signal is induced along the *c* axis only, (2) the signal is highly temperature dependent, (3) the signal is independent of the polarization of the laser, (4) there is no sign reversal of the signal with the laser incident from either the front or the back of the film, (5) the signal is only present in the orthorhombic YBCO material, and (6) a dc voltage can be induced with a cw light source.

Some of these observations are in direct contradiction with other published experimental results. Tate *et al.*[2] and Lengfellner *et al.*[7] claimed that the signal polarity was reversed if the laser irradiated the sample from the back instead of from the front. In another article, Tate *et al.* also claimed that the signal was dependent on the angle of incidence of the laser in a polycrystalline wafer.[3] More recently Li[6] and Lengfellner *et al.*[7] reported that voltages could be induced by simply placing a heat source in front of the sample. Lengfellner *et al.* also measured the PV signal carefully with laser pulses and concluded that the signals were due to an atomic thermopile. Therefore, the question still remains as to whether the signal is thermally induced or truly photovoltaic, and whether there is any tensorial effects.

In this paper, we shall show that even though the PV signal is in general proportional to the temperature gradient along the *c* axis, the magnitude of the signal is too large to be accounted for by conventional thermopower generation. It will also be shown that pulsed lasers are unsuitable for the investigation on the nature of this PV effect because the temperature increase in the sample is inevitably large (over tens or even hundreds of degrees Celcius). The PV signal is more clearly seen using low-power cw lasers. We shall show that the PV signal is only along the *c* axis of YBCO and is laser polarization insensitive. It is, however, highly dependent on the slight misorientation of the *c* axis. It will be shown that the sign reversal is only present with pulsed laser interactions. Finally, we report a peculiar temperature dependence of this PV signal which is somehow uncorrelated to the *R*-*T* characteristics of the films.

II. DEPENDENCE OF THE PV SIGNAL ON THE *c* AXIS MISALIGNMENT

All the samples in this investigation were high-quality pulsed laser deposited YBCO films.[8] The substrates used were either YSZ or $SrTiO_3$. All the YBCO films were characterized by rocking curve and pole figure texture analysis to determine their *c*-axis orientation and *a*- and *b*-axes alignment on the substrate.[8] The T_c's are all above 85 K. Most have higher T_c's near 89 K.

As reported in Ref. 4, by using a [110] substrate, the YBCO film will have a *c* axis at 45° to the substrate normal. And by detecting the signal as a function of the angle between the measuring electrodes and the projection of the *c* axis on the film surface, it can be confirmed that the PV signal is indeed along the *c* axis only. We have since found that [103] cut substrates provided a better way of orienting the *c* axis. In this case the YBCO film *c* axis is at 18.4° to the surface normal and is pointed in one direction only. Additionally, [100] substrates were also used in the present study. It was determined by x-ray analysis that the *c* axis of these substrates were tilted from the surface normal by a random small angle. This was presumably caused by mechanical polishing of the substrate during the manufacturing process. It provided a good set of data for measuring the dependence of the PV signal as a function of the *c* axis tilt angle θ.

The PV signal was measured as described previously.[4] A cw He-Ne or Ar ion laser was irradiated upon the sample and the dc PV signal was measured with a nanovoltmeter. In this study, all the samples were patterned into bridges with lengths of 2 mm and widths of 20 μm–1 mm. The expanded laser beam passed through a rectangular spatial filter and always covered the total width of the bridge.

It was found that the photovoltaic signal was independent of the width of the bridge but was proportional to the length of the bridge irradiated (D). Figure 1 shows the signal as a function of the tilt angle θ for [100] samples. The tilt angles were measured along the bridge lengths. The inset shows these data together with the one obtained with a [103] sample. The dashed curves in both Fig. 1 and its inset are a fit to all data points using

$$\Delta V = (AD/c)\sin\theta \,, \tag{1}$$

where ΔV is the PV signal, c is c-axis dimension, and A is a constant. For small θ, Eq. (1) implies that the signal is proportional to the number of c-direction unit cells irradiated. This inference is similar to the conclusion in Ref. 7. The reasonably good fit confirms indeed that the signal is generated only along the c axis and is proportional to the number of CuO_2 planes irradiated. The fact that the signal is independent of the width of the bridges but is proportional to D is consistent with this assertion.

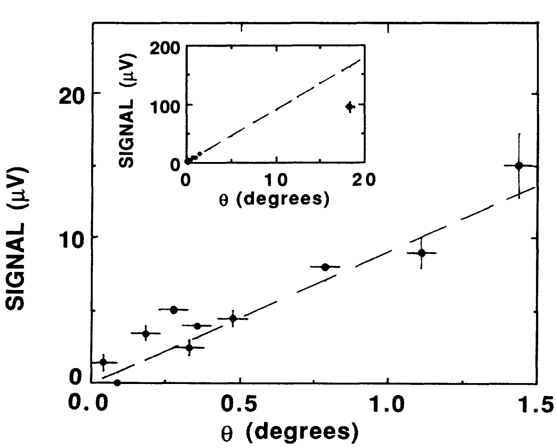

FIG. 1. PV signal as a function of the tilt angle between the YBCO *c* axis and the surface normal of the film, projected along the line of measurement. The point at 18.4° in the inset is from a [103] substrate. All other data points are from [100] substrates.

By changing the laser polarization and angle of incidence, it was confirmed that there was no significant changes in the PV signal. The major differences between our measurements and that of Tate *et al.* is that their sample had a random orientation of the *a*, *b*, *c* axes.[3] Moreover a pulsed laser resulting in a large temperature increase in the sample was used. In our experiment, it was ascertained that the laser induced only a small temperature increase. We believe that the huge temperature increases in all pulsed laser experiments render those data difficult to interpret.

III. THE QUESTION OF SIGN REVERSAL

In both Refs. 2 and 7, a reversal in the sign of the PV signal was observed when the laser pulse was incident from the back of the film. We did not see any reversal of sign in our measurements employing a cw laser. The explanation is quite straightforward and involves a discussion of heat diffusion in the sample.

The one-dimensional heat diffusion equation governing the temperature rise T, with the laser coming from the front, is given by

$$\frac{\partial T}{\partial t} - \kappa\frac{\partial^2 T}{\partial z^2} = \frac{\alpha I e^{-\alpha z}}{\rho C} \,, \tag{2}$$

where κ is the thermal diffusivity, I is the light intensity, α is the absorption coefficient, and ρ and C are the density and heat capacity of YBCO, respectively. It can be shown that the steady-state differential temperature rise between the top and the bottom of the film is independent of the substrate and is given by

$$\Delta T = \frac{I}{\alpha\rho C\kappa_f}(\alpha l + e^{-\alpha l} - 1) \,, \tag{3}$$

where l is the film thickness and κ_f is the thermal diffusivity in YBCO. When the laser is incident from the back, the heat diffusion equation has to be modified to

$$\frac{\partial T}{\partial t} - \kappa\frac{\partial^2 T}{\partial z^2} = \frac{\alpha I}{\rho C}e^{\alpha(z-l)} \,. \tag{4}$$

It can be shown that the temperature rise in this case is given by

$$\Delta T = \frac{I e^{-\alpha l}}{\alpha\rho C\kappa_f}(e^{\alpha l} - 1 - \alpha l) \,. \tag{5}$$

Note that ΔT in both Eqs. (3) and (5) is always positive, meaning that the temperature is always hotter on the top than the bottom regardless of the direction of the laser. This is different from the case of pulsed heating where the interface between the film and the substrate can be hotter than the top of the film momentarily, thus giving rise to a sign reversal.[7]

Using known values of α and κ,[9] it can be calculated that the temperature differential in our experiment with a 1.4-W/cm^2 laser intensity was 2.2 mK. The front of the film had an absolute temperature rise of 9.26 K for the case of YSZ substrate and 1.24 K for $SrTiO_3$. These are rather moderate temperature increases as compared to pulsed laser heating. We believe that experiments per-

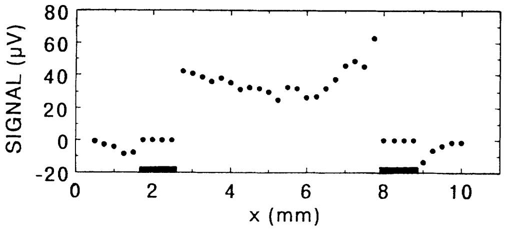

FIG. 2. PV signal as a function of the laser spot position. The sample was not patterned in this measurement. Positions of the electrodes are indicated.

formed with pulsed heating had temperature rises of hundreds of degrees.[3] Results from such large ΔT are difficult to interpret, not to mention the possibility of O_2 loss during the experiment.

IV. IS THE PV SIGNAL DUE TO THE OHMIC CONTACT?

We have verified that indeed a signal can be induced by placing a heat source in front of the sample. However, the magnitude is much smaller than that obtained with laser irradiation. We have also ascertained that the PV signal is not due to a differential between the two Ohmic contacts, though such an effect may exist under strong heating conditions.[6] This can be checked easily by scanning a weak laser between the two electrodes. Figure 2 shows the results. It can be seen that the signal remains positive as the laser spot scans between the electrodes. The laser spot size was 0.3 mm and were located at 2 and 8.5 mm in Fig. 2. As the laser scans past the electrodes, there is a small negative signal. This behavior is similar to the observations of Lengfellner *et al.*[7] and can be explained by the tilt of the c axis. If the signal was due to the differential temperature between the two electrodes, the sign should be reversed as the laser scans from one end to the other.

There is a qualitative difference between Fig. 2 and that of Lengfellner *et al.* though. In their results, there was a peak at the midpoint. Figure 2 is relatively constant throughout the scan. Again we attribute the difference to the large ΔT in their case.

V. IS THE PV SIGNAL DUE TO THERMOELECTRIC POWER?

If the signal is due to thermopower from atomic layer thermopiles, as suggested in Ref. 7, the Seebeck coefficient along the c axis can be calculated from the expression

$$S = \Delta V l / (D \sin\theta \Delta T) . \qquad (6)$$

Using the results in Fig. 1, the value of S is calculated to be 135 μV/K which is more than 10 times larger than the largest value published.[10,11] Therefore the PV signal cannot be explained by invoking conventional thermopower alone.

Another observation that may provide a clue to the nature of this PV signal is related to their peculiar temperature dependence. As reported in our previous study, the temperature dependence of the PV signal showed two thresholds near 90 and 200 K. We measured the temperature dependence of the PV signal for all the films studies here. It was found that they all had different temperature dependences. Even for the same film, different measurements could yield different T dependences in different runs even though the R-T curve remained the same and T_c did not change. Figure 3 shows some of the temperature dependence measured for the PV signal. Figure 4 shows the R-T curves of all the films studied. It should be emphasized that the resistance-temperature curves for all samples remained the same, showing a smooth linear drop in R as T was lowered. Yet the PV signal–T curves changed from run to run.

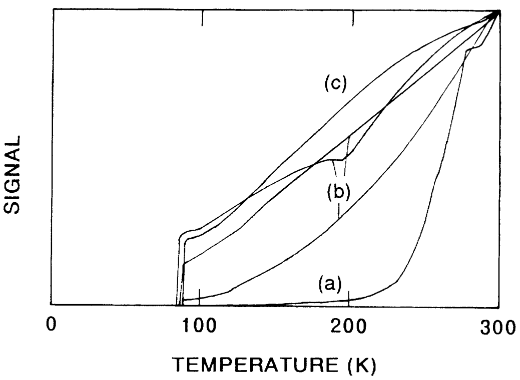

FIG. 3. Temperature dependence of the PV signal for several samples. (a) $SrTiO_3$ [110], (b) $SrTiO_3$ [100], (c) $SrTiO_3$ [103].

There seems to be no correlation between the T dependence of the PV signal (Fig. 3) and the regular behavior of R-T for these films (Fig. 4). However the PV signal at room temperature is always reproducible. Comparing with the thermopower measurements,[10,11] the temperature dependence of S is quite different from that of the PV signal reported here and shows less sample dependence.

We postulate that the PV signal is still thermal in origin. However, the Seebeck coefficients are modified in the presence of photoexcitation. This explanation is quite reasonable and is consistent with the fact that the PV sig-

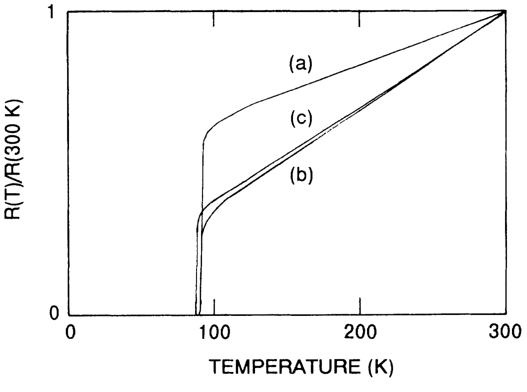

FIG. 4. R-T curves for the samples in Fig. 3. There is no correlation between the R-T curve and the PV signal.

nal is proportional to both the temperature gradient ΔT and the number of CuO_2 planes irradiated. The erratic temperature dependence may be related to the long-term time-dependent photoinduced changes of superconductivity in YBCO recently observed by Kudimov *et al.*[12] and Nieva *et al.*[13] We believe that the photoinduced changes in superconductivity should also produce changes in the normal-state property, specifically the thermoelectric power. Granted that the experiments in Refs. 12 and 13 were performed with the Ar ion laser at considerably higher laser power, similar changes should also be possible under the present conditions. It was postulated that the long-term changes involve photoinduced oxygen ordering the charge transfer. These physical changes should affect the thermopower coefficient also. Presumably this hypothesis can be checked by performing thermopower measurements under laser irradiation and searching for long-term changes in S.

VI. SUMMARY

We have reported some recent measurements of the PV signal in YBCO films. These films are well characterized which is a must in order to quantify the results. In particular the tilt angle of the c axis is intimately related to the magnitude of the signal and should be known. We have also shown that the sign reversal when the laser is incident from the back is due to the use of pulsed versus cw lasers.

Using low-power cw laser with very small temperature increases, it is possible to measure the temperature dependence of this PV signal. It was found that the magnitude of the signal and its temperature dependence distinguish the PV signal from ordinary thermopower. The PV signal is not due to conventional thermal effects. We believe that there is some unknown photoeffects that are responsible for the presence of this signal. This photoinduced effect may be similar to that responsible for long-term time-dependent changes in superconductivity recently observed.

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