Brief Reports

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Symmetry-forbidden laser-induced voltages in $YBa_2Cu_3O_7$

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We report the occurrence of potentials in the absence of applied currents up to several volts between 1-mm-spaced probes in the normal state of $YBa_2Cu_3O_7$ films when illuminated by a laser with intensities up to ~ 30 mJ/cm^2. For intensities ≤ 2 mJ/cm^2 these potentials disappear in the superconducting state but return, time delayed, at higher intensities. The mechanism is unknown, and the results are in contradiction to expectations based on symmetry arguments.

Numerous studies[1-5] of the change in resistance of the high-temperature superconductors with laser illumination have been made for samples carrying a transport current and, generally, at an ambient temperature below T_c. We report the observation of a transient voltage resulting from the illumination of $YBa_2Cu_3O_7$ thin films by laser illumination in the absence of a transport current, and at ambient temperatures corresponding to the normal and superconducting states. The magnitude of the voltage is not easily explained by the obvious possible phenomena, and its existence is forbidden by the presumed symmetry.

Measurements were made on 1-μm-thick films of laser-ablated c-axis-oriented $YBa_2Cu_3O_7$ (1:2:3) deposited on $SrTiO_3$ (100). Contacts were made using silver paste dabs fired on the films for 10 min at 900 °C and to which ultrasonically soldered In connections to Cu wires were made. Figure 1 shows the contact locations and film dimensions. The room-temperature resistivity ρ was $\sim 6\times 10^{-4}$ Ω cm, the four-wire potential probe resistance was ≈ 4 Ω, and the temperature coefficient, $dR/dT \approx 1.25\times 10^{-2}$ Ω/K, was nearly constant from 300 to 100 K. The resistive superconducting T_c was 90 (onset) to 82 K (completion) and the critical current density was $\sim 8\times 10^4$ A/cm^2 at 77 K. Illumination was made with the output of a pulsed Nd:YAG laser with most studies done using the second harmonic ($\lambda = 532$ nm). The full width at half maximum (FWHM) pulse time was $\sim$10–20 ns, the output energy densities were $E_{DL} \sim 1$–30 mJ/cm^2, and the beam profile was rectangular with a (Gaussian?) width $\sim$0.5–1 mm and a length exceeding the matching sample dimension. Measurements were made with a 50-Ω input oscilloscope having 2-ns resolution. Though not further reported in detail here, qualitatively similar effects to those described below have been seen at wavelengths of 1064 and 355 nm. We observed signal amplitudes of up to 2 V with the highest energy density reported and an extended beam profile. To preserve the film, we restricted our detailed studies to energy densities below 16 mJ/cm^2. We checked for changes in the film by resistance, x-ray diffraction, scanning electron microscopy (SEM), and profilometer measurements, and did not detect any alterations due to laser illumination.

Figure 2 shows the potential V_{CD} observed at 300 K with laser illumination level $E_{DL} \sim 16$ mJ/cm^2. The signal reaches its peak amplitude at the completion of the laser pulse and, in the absence of a transport current I_{tr}, decays in a time ~ 100 ns. With $I_{tr} = -0.05$ A the signal, whose resulting 200-mV dc negative offset has been re-

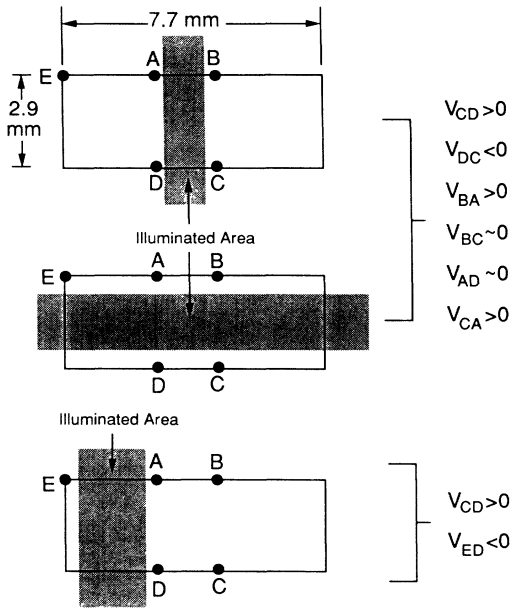

FIG. 1. Configuration of sample potential measurement locations, illuminated areas, and the observed potential polarities.

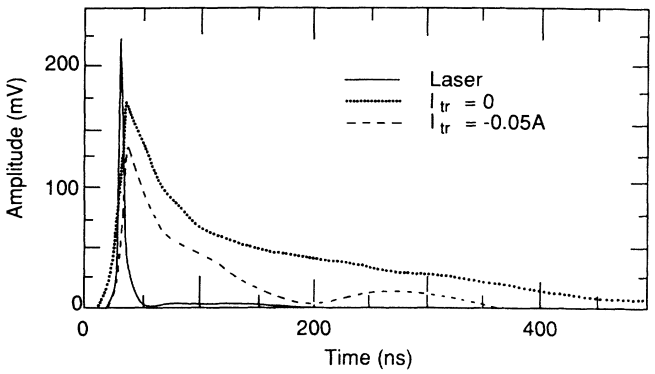

FIG. 2. Time signals corresponding to the laser output intensity (arbitrary units), and the sample potential V_{CD} (see Fig. 1) with and without transport current.

moved in the plot, shows a transient response which is $\sim 15\%$ smaller than the $I_{tr}=0$ case for the first 50 ns. The variations (with $I_{tr}=-0.05$ A) at $t\sim 200$–300 ns indicate another process with a characteristic lifetime at least this long, but the noise in the data and the questionable assumption of additivity of the I_{tr} contribution make it impossible to recover the time response of V_{tr} alone with accuracy. Such data, via the temperature dependence of the resistance, would provide suitable thermometry for the average film temperature. We have, however, thermally modeled the film's temperature response to the illumination and obtain the difference in the observed initial voltage changes between the current biased and unbiased states for an absorbed energy density $E_{DA}\approx 12$ mJ/cm^2, and a 300-ns decay time based on a thermal conductivity κ of ~ 30 mW/cm K in the film thickness (largely crystallographic "c" axis) direction.[6] The calculations also show that the initial average film temperature rises by ~ 45 K and remains constant (to within $\sim 5\%$) for 50–75 ns as the heat travels across the film. This causes the initial 15% voltage reduction (via dR/dT) which is maintained for that same time. These predictions are sufficiently close to observations to allow the thermal model to be used as a guide to the temperature environment of the film.

The signal amplitude with $I_{tr}=0$ was measured to be linearly dependent on the illumination energy density in the range $E_{DL}=2$–20 mJ/cm^2, also in agreement with calculations,[7] although some evidence indicates that a threshold intensity for this effect may exist.

The unexpected $I_{tr}=0$ signal disappeared when operating the laser but blocking the beam from the sample, demonstrating that it is an optically induced effect. The following results show that the signal voltage V_S does not originate from the electrical contacts: (i) the signal is little changed if the contacts are masked from the light, (ii) the signal is reduced by 95% when a restricted area beam is directed at each of the contacts, and (iii) moving the beam along the film's longer direction leads to a broad maximum in V_S when positioned between the potential probes, but no nulls or polarity reversals as the contacts are passed. The source impedance of V_S was estimated from the drop in signal with resistive loading at the scope input and found to be approximately the dc two-wire resistance ($\sim 10\ \Omega$) of the potential probes indicating, among other things, the absence of a large frequency dependence for this phenomenon out to at least $\sim 1/\tau\sim 10^8$ Hz.

Significant information, relevant for symmetry arguments to follow, is contained in the location and polarity of the observed potentials indicated in Fig. 1. The notation $V_{XY}>0$ means that an X positive to Y signal was observed with a similar time dependence to that in Fig. 2. Amplitudes were generally within a factor of 3 of each other except when indicated as "~ 0" where signals were reduced by more than a factor of 10. The results of Fig. 1 indicate that a polar asymmetry for this effect has been established in the plane of the film and along its longer dimension. Note that the findings $V_{CD}>0$ and $V_{BA}>0$ are not consistent with in-plane broken chiral symmetry, if such resulting handedness extends coherently for the separation between contacts.[8] The existence of a polar asymmetry is unexpected, and further discussion is given below.

On cooling from 300 to 100 K, V_S is reduced by roughly a factor of 3 and τ_S changes by less than 50% but detailed data were not obtained. On passing through the superconducting transition the signal disappeared ($>$ a factor of 20 reduction) if the laser energy density was $E_{DL}<2$ mJ/cm^2. It was possible to recover the signal from a starting temperature below T_c by increasing the laser intensity, but this recovered signal was time delayed relative to the normal-state signal. Figure 3(a) shows the signal observed at 99 K with $E_{DL}\approx 2$ mJ/cm^2 and which disappears below ~ 80 K. Also shown is the signal obtained at 57 K with the increased $E_{DL}\approx 4.5$ mJ/cm^2.

The absence of the signal with low-level illumination is consistent with the absence of electric fields in the superconducting state. At high E_{DL} the heating of the front surface will generate a normal/superconducting interface which propagates through the film thickness and may reach the substrate before returning to the front surface. It is this interface propagation time which is responsible for the delayed signal. We have calculated the temperature-time profile for a film under the conditions leading to the data of Fig. 3(a). Figure 3(b) shows the thermal model calculations of the film temperature versus time at 0.3 μm from the film-substrate interface[9] for $E_{DA}\sim 5$ mJ/cm^2 and with no thermal contact resistance at the latter interface. Similar results are obtained for $E_{DA}\sim 3.5$ mJ/cm^2 (approximately the experimental value) and with the small thermal contact resistivity of 6×10^{-4} K cm^2/W.

For the modeled absorbed energy density, the sample (at least the 30% of it adjacent to the substrate) remains superconducting for ~ 20 ns after laser firing (which occurs at time $=10$ ns) after which the normal state, and any electric fields, will return for the next 50 ns, followed by a return to the superconducting state roughly 120 ns after laser firing. This is in agreement with experiment. It should be noted, however, that while the magnitude of the film heating is controlled mainly by E_{DA}, which is probably known to $\pm 25\%$, the time to peak temperature (~ 50 ns after laser firing) in the calculation is determined mainly by C/κ where C, the temperature-

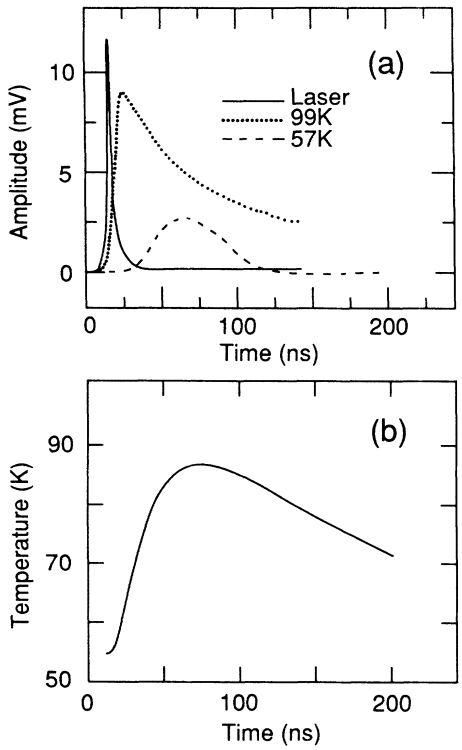

FIG. 3. (a) Laser output intensity (arbitrary units) and sample voltage (zero transport current) at ambient temperatures above and below T_c. The signal at 99 K is obtained with low intensity and disappears below T_c. The time-delayed signal at 57 K is obtained using higher laser intensities. (b) Calculated time dependence of the temperature for a position 0.3 μm from the film-substrate boundary, and using the experimental conditions leading to the 57-K data of (a).

dependent specific heat taken from the literature,[10] is probably known to $\sim$20% but $\kappa \sim 30$–40 mW/cm K is a fitted number for which no independent confirmation exists.[6]

These laser-induced voltages at room temperature have been observed in ten other thin-film samples of $YBa_2Cu_3O_7$. The films have been deposited on $SrTiO_3$, Al_2O_3, and MgO, and have varied in thickness from 1000 Å to 1.5 μm. The majority of these films are textured with the c axis perpendicular to the substrate, two films show no preferred orientation. Films with positive, negative, and approximately zero temperature coefficient of the resistivity in the normal state exhibit the laser-induced voltages. The signal has also been detected in a nonsuperconducting $PrBa_2Cu_3O_7$ thin film where the low resistance at room temperature allowed the observance of the fast signal. No measurement in insulating $YBa_2Cu_3O_6$ was done because the resistance is too high. On the other hand, we did not observe any effect in metal films, i.e., Al and Pt.

Some of these films showed vanishing longitudinal fields and nonzero transverse fields (a "rotated" symmetry version of Fig. 1), and evidence of metastable phases with lifetimes ~ 1 μs or longer. No films were found in which laser-induced potentials were absent.

We do not know the source of these normal- and superconducting-state signals but several features of the observations provide constraints for candidate mechanisms. The most immediate conclusion from Figs. 2 and 3(a) is that $V_S(t)$ is not proportional to the laser output intensity but, at least for short times, does scale with the time-integrated intensity. This result and the (only approximate) similarity of the observed and calculated (thermal) time constants for the data of Fig. 2 suggests that V_S could have a thermal origin. The time duration for these transient thermal effects would be determined by thermal diffusion through the film and therefore should be proportional to the square of the film thickness t. We have observed, however, that the electrical transients have approximately the same duration (to within a factor of 2) over a film thickness varying by a factor of 10. Thermal model calculations show, in addition, that both the average temperature and the average temperature gradient in the film-thickness direction have transient time decays which depend far more strongly on film thickness than is observed.[11] Thus, two explanations, pyroelectricity and thermoelectricity, which relate electric fields to temperature changes and temperature gradients, are precluded as the dominant mechanism. These effects are also forbidden[12,13] by conventional symmetry arguments if the reported point groups give a proper description of the microscopic state. This "symmetry problem" is endemic in that we have not found the symmetry-breaking element which selects the in-film plane direction for the resulting electric fields.[14]

In the absence of thermal effects, the time-integrated response noted above suggests an optically pumped excitation with a lifetime of $\sim 10^{-7}$ sec. Due to the low electrical impedance of this sample, an implied peak current flow up to $I_p \sim (1\text{ V})/(4\ \Omega) = 0.25$ A would result.[15] Direct evidence of the current flow has not been obtained, and no conclusion regarding the mechanism has been reached.

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[6]S. J. Hagan, Z. Z. Wang, and N. P. Ong [Phys. Rev. B **40**, 9389 (1989)] have found "c" axis thermal conductivities κ of $\sim$10–20 mW/cm K at 300 K which increase by $\sim$50% at 100 K, and "a-b" plane values which are about four times larger. Our films have strong "c" axis orientation but with a (200) line (a-b plane) intensity which is about 5% of the strongest (001). Our less accurate results for κ are therefore only in qualitative agreement with the direct measurements of κ. The thermal-model calculations are for a standard one-dimensional heat flow geometry with a constant thermal conductivity and a temperature-dependent specific heat over the calculated temperature variation. The calculations accounted for the optical absorption over a skin depth taken to be $\sim$500 Å but the results are insensitive to variations by a factor of 5 in this quantity. The specific heat was taken from various literature values and at 300 K is sufficiently close to the DuLong-Petit value (2.5 J/cm^{3}K) that large uncertainties are unlikely. We also estimated a 25% optical loss from laser output to film absorption due to windows and sample reflectance. For measurements made with a transport current, the corresponding modeling included the effect of transport current joule heating, but this did not produce significant changes.

[7]The peak signal magnitude in the thermal model, which occurs at the completion of the laser pulse, depends upon the specific heat (which is nearly temperature independent above 300 K) but not the thermal conductivity.

[8]Some handedness patterns comprised of two simple in-plane vortices appear to be contradicted by other findings in Fig. 1, but a complete exclusion of this possibility has not been made. No evidence regarding transverse-plane vortex flow has been obtained directly, but such currents could give rise to in-plane potentials, as observed.

[9]The behavior at the interface itself is controlled by the unknown thermal boundary condition there. Further into the film the results depend less on the boundary condition and, in view of the speed of the moving interface, allow estimates of the quenching time for superconductivity. It should be noted that at least two complicating factors have been ignored in these calculations: (i) finite frequency effects on the motion of the N/S interface and the quenching of superconductivity, and (ii) if real currents are flowing, their compaction into the vanishing superconducting cross section may lead to the destruction of superconductivity by exceeding the critical current density before the normal/superconducting interface reaches the sample/substrate interface, and to voltages due to the movement of the N/S interface in the self-B field of the current.

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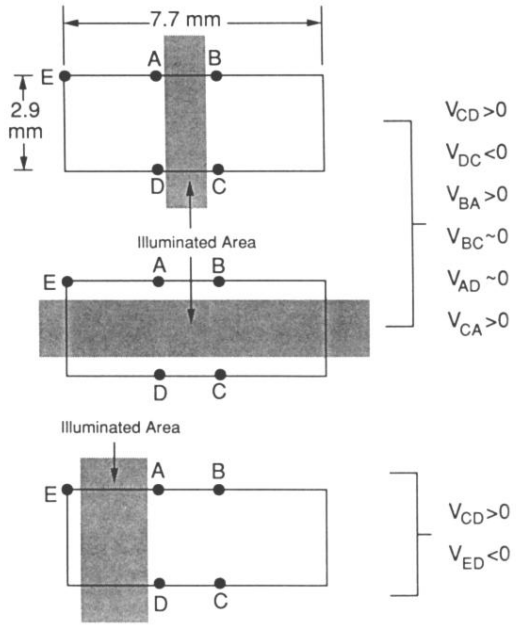
[11]Using thermal conductivities between 0.02 and 0.04 W/cm K, and specific heats within 50% of those given in Refs. 6 and 10, we find in our calculations that the average film-temperature increase would have a time duration (FWHM) ranging from 15 ns (which arises mainly from the FWHM of the laser pulse—a part of the input model) for the thin films to over 400 ns for the thickest films.

[12]If the material is homogeneous and isotropic in the plane of the film, no thermoelectric voltages can occur no matter what the temperature profile or value of S_{XX} ($=S_{YY}$) except that associated with the temperature difference of the contacts and the S corresponding to contact (123)/In. These voltages are far less than those observed.

[13]For the pyroelectric effect case, the problem lies in that the pyroelectric coefficients vanish for the reported 123 point groups, and exist only in the c-axis (our Z) direction for all orthorhombic and tetragonal point groups.

[14]We searched for a symmetry-breaking element in the intensity of the light beam by introducing a convex lens at a distance twice its focal length from the sample. The resulting in-plane inversion (the only symmetry change tested) of the intensity profile produced (roughly) the same signal amplitude and with the same sign. We also checked for a polarization dependence of V_S by physically rotating the beam. Both horizontally and vertically polarized laser beams produced the same signal.

[15]For thermoelectric phenomena these currents are offset by charge transport due to heat flow, and no net current would result.



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