EUROPHYSICS LETTERS 10 February 1994

Europhys. Lett., 25 (5), pp. 375-378 (1994)

Thermoelectric Effect in Normal-State $YBa_2Cu_3O_{7-\delta}$ Films.

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(received 15 November 1993; accepted 16 December 1993)

PACS. 73.60 – Electronic properties of thin films.
PACS. 74.75 – Superconducting films.
PACS. 86.40F – Storage in thermal energy (inc. solar ponds and tanks).

Abstract. – Signal pulses of several 100 volts and currents of several amperes have been obtained at lateral surface contacts on normal-state $YBa_2Cu_3O_{7-\delta}$ films in response to pulsed laser irradiation. The signals are shown to be of thermoelectric origin. Thermoelectric fields transverse to the laser-induced temperature gradient are due to the anisotropy of the thermopower in $YBa_2Cu_3O_{7-\delta}$ giving rise to non-zero off-diagonal elements $S_{ij} \propto \alpha$ of the Seebeck tensor for films prepared with a tilt angle α between the film c-axis and the film surface normal. Large–tilt-angle films (up to $\alpha = 20°$) could be grown on specially cut substrates and may be useful as almost wavelength-independent room temperature radiation detectors.

Large voltaic signals in response to laser irradiation of $YBa_2Cu_3O_{7-\delta}$ films in the normal-conducting state have been observed by several groups [1-4]. Earlier discussed phenomena for explanation of the signals, as tensorial photoelectric effects [5] and piezo- and pyroelectricity [6] can be ruled out meanwhile by experimental observations: the voltaic signals are independent of light polarization, and continuous voltages are obtained in case of continuous-irradiation experiments [3].

In this letter experiments are reported which proof that the voltaic signals are purely of thermoelectric origin. A comparison of signals induced by laser irradiation, or, alternatively, by a thermal heat source, shows that the signal strength is solely related to the flow of thermal energy through the film. Furthermore, it is shown that the voltaic signals are proportional to the tilt angle α between the crystallographic film c-axis and the film surface normal, in accordance with the tensorial Seebeck effect.

The thermoelectric field due to the Seebeck effect is given by

$$E = S \cdot \nabla T\,, \tag{1}$$

where S is the Seebeck tensor and ∇T the temperature gradient. With respect to the coordinate system defined in fig. 1, the Seebeck tensor for $YBa_2Cu_3O_{7-\delta}$, depending on the tilt angle α, and taking into account the values of main anisotropy of the thermopower S_c along the crystallographic c-axis and S_{ab} in the (a, b)-plane [7], is of the form

$$S = \begin{bmatrix} S_{ab}\cos^2\alpha + S_c\sin^2\alpha & 0 & (\sin 2\alpha/2)(S_{ab} - S_c) \\ 0 & S_{ab} & 0 \\ (\sin 2\alpha/2)(S_{ab} - S_c) & 0 & S_{ab}\sin^2\alpha + S_c\cos^2\alpha \end{bmatrix}. \tag{2}$$

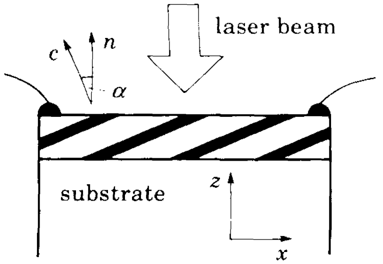

Fig. 1.

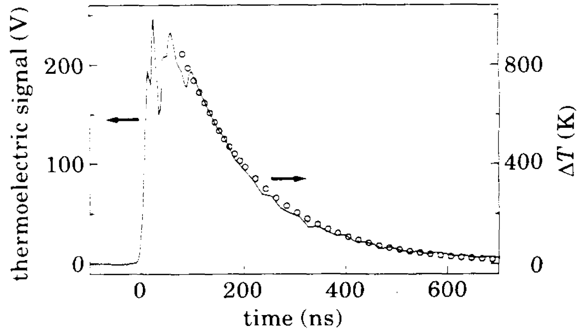

Fig. 2.

Fig. 1. – Schematic cross-section of a tilted $YBa_2Cu_3O_{7-\delta}$ film, consisting of CuO_2 layers (black) and intermediate layers, the c-axis is inclined by an angle α with respect to the surface normal n. Laser heating, electrical contacts and coordinate system used for calculations are also indicated.

Fig. 2. – Full line, left ordinate scale: voltage signal of a $YBa_2Cu_3O_{7-\delta}$ film with 20° tilt angle obtained by pulsed laser irradiation with energy density close to the damage threshold of the film. Note the peak voltage of ~ 250 V. Circles, right ordinate scale: calculated laser-induced temperature difference between film surface and film bottom.

Assuming heat flow from the film into the substrate to be essentially parallel to the film surface normal (*i.e.* $\nabla T = \nabla_z T$), a thermoelectric voltage

$$U = \Delta T \Delta S \frac{l}{2d} \sin 2\alpha \tag{3}$$

is expected upon film heating from eqs. (1) and (2), where l is the diameter of the heated spot on the film surface, d is the film thickness, ΔT the temperature difference between film surface and film bottom, and $\Delta S = S_{ab} - S_c$.

Epitaxial $YBa_2Cu_3O_{7-\delta}$ films were grown by laser ablation on $SrTiO_3$ substrates of $(10 \times \times 10)$ mm^2 area. The substrates were cut with one face (substrate bottom) parallel to the (100) crystallographic planes, and the opposing face (substrate surface) with a tilt angle α between (100) planes and surface. Substrates were prepared with $\alpha = 0$, 5, 10, 15 and 20 degrees. Under identical conditions, $YBa_2Cu_3O_{7-\delta}$ films were grown on the substrate surface by laser ablation. Film growth with a tilt angle α between the film c-axis and the surface normal as expected from lattice matching has been confirmed by X-ray diffraction measurements. Epitaxial film growh with unaltered c-axis orientation across low-angle steps on (100) $SrTiO_3$ substrates has been reported recently [8] indicating parallel alignment of $YBa_2Cu_3O_{7-\delta}$ and $SrTiO_3$ (100) planes independent of α.

In fig. 2, a thermoelectric signal pulse is shown for a $YBa_2Cu_3O_{7-\delta}$ film grown on a substrate with a tilt angle $\alpha = 20°$. The film was irradiated at room temperature with radiation of a pulsed UV laser (energy density 1 J/cm^2, pulse duration 20 ns, wavelength 308 nm). This energy density was close to the damage threshold of the film. At the end of the laser heating process, a maximum voltage of about 250 V was generated by the film. The signal then decayed within several 100 ns, due to the decay of the temperature difference ΔT between the film surface and the film bottom by heat diffusion into the substrate.

The structures in the signal slope immediately after the energy deposition are only observed for large laser energies and are possibly due to dielectric breakdown within the film caused by the large electric fields or film damaging by the laser irradiation. In addition to the thermoelectric signal (solid line and left ordinate scale) the calculated decay $\Delta T(t)$ is also shown in fig. 2 (circles and right ordinate scale). This calculation has been performed using a heat transfer model [9] and published data on thermal properties $YBa_2Cu_3O_{7-\delta}$ [10]. Similar slopes of $\Delta T(t)$ and the voltaic signal, also observed in other experiments [4, 11], suggest a process related to heat. From a comparison of the experimental and the calculated curves a sensitivity ~ 100 mV/K for the signal-generating mechanism is estimated.

In fig. 3, the height of the voltaic signal is shown for a large range of laser power, using continuous and pulsed laser sources with wavelengths from far-infrared to UV. In case of continuous sources, the laser power was measured with calibrated power meters, in case of pulsed sources, the power was calculated from a measurement of the pulse energy and the pulse duration. For a given source (one set of symbols in fig. 3) the voltaic signal is linear in laser power. Small differences in signal height for different sources are partly due to the wavelength-dependent light absorption in the $YBa_2Cu_3O_{7-\delta}$ material, and also to slightly different spot diameters of the light beams from the different sources. The break between the curves obtained by continuous and pulsed sources is due to a principal difference between continuous- and pulsed-heating methods. The temperature gradient in a film is proportional to the energy delivered within the thermal time constant τ_{th} of a film. From the signal decay observed in fig. 2, a time τ_{th} of several 100 ns can be derived. To compare continuous- and short-pulse-heating experiments with laser pulse duration $\tau_l < \tau_{th}$, the laser pulse power should be multiplied by a factor τ_l/τ_{th}, with values $\simeq 0.1$ in our experiments. Taking into account this correction would shift the curve obtained from pulsed measurements by one order of magnitude to smaller laser powers and thus fit to the continuous-heating experiments.

Instead of directly irradiating the $YBa_2Cu_3O_{7-\delta}$ film with a laser source (empty squares in fig. 3), a thin slab of mica coated with graphite for complete absorption of light was placed onto the film and irradiated with the same source (full squares, fig. 3). The thermal contact between mica and the $YBa_2Cu_3O_{7-\delta}$ film was improved by a drop of oil between the contact areas. Then a voltaic signal even slightly larger than in the direct-irradiation experiment was obtained. This experiment clearly shows that the voltaic signal is purely due to film heating. The observation of continuous electric-potential differences and currents in case of continuous-heating experiments furthermore proves the thermoelectric nature of the reported effects.

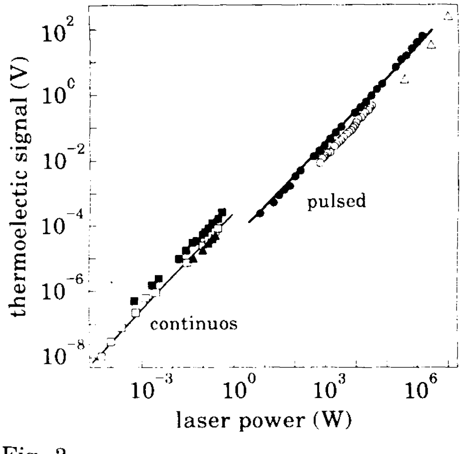

Fig. 3.

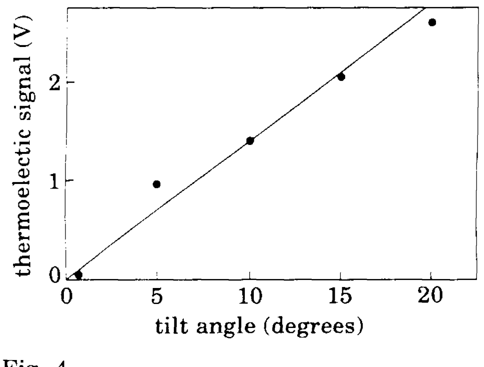

Fig. 4.

Fig. 3. – Thermoelectric signal *vs.* laser power, for several continuous and pulsed laser sources (△ 308 nm, ● 10 μm, ○ 230 μm, □ 488 nm, ■ mica absorber (488 nm), ▲ 360 nm) obtained by direct film irradiation, and also using a light absorber placed on top of the film (full squares).

Fig. 4. – Thermoelectric signal as a function of the tilt angle for constant irradiation intensity.

In fig. 4, the height of the voltaic signal is shown, for a constant laser energy of ~ 10 mJ per pulse (pulse duration ~ 100 ns, wavelength $\simeq 10\,\mu$m) for five samples prepared with different tilt angles. With $\sin 2\alpha/2 \approx \alpha$, a linear dependence of the voltaic signal on tilt angle is found within the accuracy of the measurement. The linear dependence was also found in a continuous-irradiation experiment by Kwok *et al.* [3] performed mainly in the range of small tilt angles $\alpha = 0 \ldots 1.5$ degrees.

The described experimental results agree quantitatively with the thermoelectric effect described by eq. (3). Large signal voltages of several 100 V are easily reproduced: inserting values $\Delta T = 800$ K, $l = 10$ mm, $\alpha = 20°$, $d = 1500$ Å and $\Delta S \simeq 10\,\mu$V/K [7], corresponding to the experiment shown in fig. 2, into eq. (3) leads to a signal voltage $U \simeq 200$ V.

The dependence $U \propto \Delta T$ has been verified by the linear dependence of the voltaic signal on laser power of a power range of 12 orders of magnitude (fig. 3). By indirect film heating via an optical absorber, it has been shown that the signal is purely due to film heating. Also film heating by other thermal sources [11] leads to a voltaic signal consistent with eq. (3).

Finally, we would like to note that it seems to be an outstanding property of $YBa_2Cu_3O_{7-\delta}$ films to grow with large tilt angles adjustable by a properly cut substrate. Thin $YBa_2Cu_3O_{7-\delta}$ films of large tilt angle may become useful as almost wavelength-independent room temperature radiation detectors. From our experiment (fig. 3), a responsivity of the order of 10^{-3} V/W in the far-infrared to the UV spectral range is estimated.

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The work was supported by the Deutsche Forschungsgemeinschaft (HL), and the Bayerische Forschungsstiftung (WP and KFR) through the Forschungsverbund Hochtemperatur-Supraleiter (FORSUPRA). HL gratefully acknowledges helpful discussions with L. R. TESTARDI (Florida State University).

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