PHYSICAL REVIEW B VOLUME 48, NUMBER 22 1 DECEMBER 1993-II

Characterization of the pyroelectric effect in $YBa_2Cu_3O_{7-\delta}$

D. Mihailović, I. Poberaj, and A. Mertelj
Jozef Stefan Institute, University of Ljubljana, Jamova 39, Ljubljana, Slovenia

(Received 21 May 1993; revised manuscript received 23 August 1993)

Measurements of the pyroelectric effect in single crystals of $YBa_2Cu_3O_{7-\delta}$ are reported as a function of doping, external electric field, and temperature. The pyroelectric response of the material is found to be accurately described theoretically. The sign pyroelectric voltage $\mathbf{V}_p$ can be switched by an external field. Although poling was possible to some extent, a permanent switching of the direction of polarization could not be achieved at room temperature. A sign reversal of $\mathbf{V}_p$ is observed as a result of thermal cycling, presumably due to activated domain rearrangement. The magnitude of the spontaneous polarization $\mathbf{P}_s$ is found to increase with doping in such a way that the product $\rho\mathbf{P}_s$ remains approximately constant, where ρ is the resistivity. The origin of the polarization and the role of possible artifacts are discussed.

I. INTRODUCTION

The interplay of ferroelectricity and superconductivity has been a very important subject of research in the past, especially in $A15$ compounds.[1–3] Usually the conclusion has been that the two phenomena appear to be mutually exclusive, and that the appearance of a ferroelectric phase (often just above the superconducting transition temperature) in these materials prevented them from becoming superconductors. Alternatively, the onset of superconductivity prevented the phase transition to a polar structure from occurring.[1]

A number of experiments have recently suggested that the structure of high-T_c oxides could be noncentrosymmetric,[4–7] and so it appears that the issue of competition between superconductivity and ferroelectricity could also be raised in the high-T_c oxides. So far, there has been no indication of a polar structure from x-ray or neutron structural determinations and experiments suggesting ferroelectricity in high-T_c oxides thus seem to be in contradiction with the established structure. This contradiction is only apparent however, since small deviations from a centrosymmetric structure are not easily detectable in x-ray or neutron diffraction experiments. More recently, the observation of apparent *pyro*- and *piezo*electricity[7,8] in single crystals of $YBa_2Cu_3O_{7-\delta}$ (YBCO) seems to present more direct evidence for a polar structure. Although the origin of these effects (especially the microscopic origin) is not yet understood in detail, the consistent behavior from sample to sample as well as its appearance in La_2CuO_4 (Ref. 9) suggest the effects to be genuine.

In this paper we present pyroelectric effect measurements on single crystals of $YBa_2Cu_3O_{7-\delta}$ with different δ and as a function of temperature and applied external electric field. Rather than use the oscillating temperature method of Chynoweth,[10] we use an adaptation of the direct time-recording technique of the pyroelectric voltage originally developed by Simhony and Saulov.[11] We measure the pyroelectric coefficient $\mathbf{p}$ as well as determine the *sign* of the spontaneous polarization $\mathbf{P}_s$.

II. EXPERIMENTS

The high conductivity and highly nonlinear I-V characteristics of cuprate superconductors (paraconductivity) prevent us from performing the usual Tower-Sawyer bridge-type experiments[12] to investigate the polarization in these materials. Instead, we use the direct recording method of measuring the pyroelectric effect. We use a chopped laser beam as a heat source and record the resulting pyroelectric response as a function of time, bypassing somewhat the problem of paraconductivity, while still allowing the sign of the polarization to be determined.

All samples were etched in a 1% Br solution in methanol to remove the surfaces, which may either be contaminated or may have a different stoichiometry from the bulk. Gold or silver paste contacts were made to the samples immediately afterwards. The etching procedure is known from x-ray photoemission spectroscopy (XPS) measurements to result in a surface stoichiometry comparable to the bulk. The quality of the surface prepared in this way has recently been shown to be equivalent to low-temperature vacuum scraped surfaces.[13] No additional heat treatment was done on the samples to avoid diffusion of the contact paste material into the sample. The type of contact paste used for the contacts had no effect on the measurements. The sample resistance along the c axis, where a pyroelectric signal was measured, was always greater than the surface contact resistance (usually in the mΩ range), and so we have neglected the effects of contact resistance in these experiments.

A. The pyroelectric response

Measurements of the pyroelectric effect rely on the fact that the change in polarization per unit area, $\delta\mathbf{P}_s$ resulting from a change in temperature δT of the sample is immediately compensated by the flow of charges from an external circuit which can then be measured. In our case a step heat transient is produced by exposing the front surface of the samples to a square laser pulse chopped mechanically from a 10–30 mW beam at 514.5 nm from an Ar laser. The magnitude of the temperature increase, δT, inferred from the measurement of the thermoelectric voltage at a gold-YBCO contact was kept below 20 K, and was usually in the range of $\sim$ 10 K. The resulting transient pyroelectric voltage V_P is amplified with a low-noise amplifier and recorded with a digital oscilloscope. The amplifier was normally dc coupled, except when an additional field was applied, in which case the ac coupling resistor and capacitor were introduced in the circuit. The charge compensating for the change in polarization accumulates only on the surface of the sample, and so the total charge is equal to the integral of the polarization over the sample surface,

$$q = \int_A \Delta \mathbf{P}_s dS. \tag{1}$$

The change in polarization is proportional to the change in temperature, $\Delta \mathbf{P}_s = \mathbf{p}\Delta T$, where $\mathbf{p}$ is the pyroelectric coefficient. The current around the exteral circuit is then

$$i = p \int_A \left(\frac{\partial T}{\partial t}\right) dS \ , \tag{2}$$

where p is the component of the pyroelectric coefficient perpendicular to the contact surfaces.

To calculate the time response of the pyroelectric signal, we need to calculate the time derivative of the temperature $\left(\frac{\partial T}{\partial t}\right)$. This can easily be done, using the thermal diffusion equation

$$\frac{1}{\kappa}\frac{\partial T(\mathbf{r},t)}{\partial t} = \nabla^2 T(\mathbf{r},t) + \frac{1}{\lambda}A(\mathbf{r},t), \tag{3}$$

where κ is the thermal diffusion constant, $\kappa = \lambda/\rho c_p$, $A(\mathbf{r},t)$ is the heat source, ρ is the density, λ is the thermal conductivity, and c_p is the heat capacity. In our case the heat source is a laser beam with intensity $I_0(1-\mathcal{R})$, where $\mathcal{R}$ is the reflectivity and I_0 is the incident laser power. We assume that the laser beam is incident along y, and is focused into a spot, small compared to the sample dimensions. To eliminate effects from thermoelectric voltages at the contacts, the laser spot was carefully positioned in the middle between the two contacts such that both contacts gave exactly equal and opposite thermovoltages, the sum being zero. We also neglect radiation losses, which we estimate to be small for the present experiments. We also suppose that the absorption length, $\alpha \sim 0.06$ μm at 514.5 nm is small compared to the thermal diffusion length, κ. For a square-wave incident laser wave form, the solution to the thermal diffusion equation under these conditions is[14]

$$\Delta T(\mathbf{r},t) = \frac{I_0(1-\mathcal{R})}{2\pi\lambda}\frac{1}{r}\operatorname{erfc}\left(\frac{r}{\sqrt{4\kappa t}}\right) , \tag{4}$$

where $\operatorname{erfc}(x)$ is the complementary error function, and r is the radial distance from the laser spot inside the sample. The time derivative is given by

$$\frac{\partial T(r,t)}{\partial t} = \frac{I_0(1-\mathcal{R})}{4\lambda\sqrt{\pi^3\kappa t^3}}\exp\left(-\frac{r^2}{4\kappa t}\right). \tag{5}$$

Integrating over the area of the sample of thickness l and area w^2, we obtain, for the compensating current,

$$i(t) = \frac{pI_0(1-\mathcal{R})\sqrt{\kappa}}{4\lambda\sqrt{\pi t}}\exp\left(-\frac{l^2}{4\kappa t}\right)\operatorname{erf}^2\left(-\frac{w}{\sqrt{4\kappa t}}\right). \tag{6}$$

The actual circuit used in the present experiments is shown schematically in Fig. 1(a). We assume the equivalent electrical circuit to consist of the sample as a current source shorted by the sample resistance and capacitance as shown in Fig. 1(b), where we have also taken into account the amplifier impedance, shown as C_A and R_A. The voltage V detected by the amplifier is given by the solution to

$$-i(t) = C\frac{dV}{dt} + \frac{V}{R} \ . \tag{7}$$

The solution to (7) is of the form

$$V(t) = V_0(t)\exp(-t/RC). \tag{8}$$

We thus obtain an expression for the voltage in terms of $i(t)$,

$$V(t) = -\frac{\exp(-t/CR)}{C}\int_0^t i(t')\exp(t'/CR)dt'. \tag{9}$$

If we assume that the thermal response of the sys-

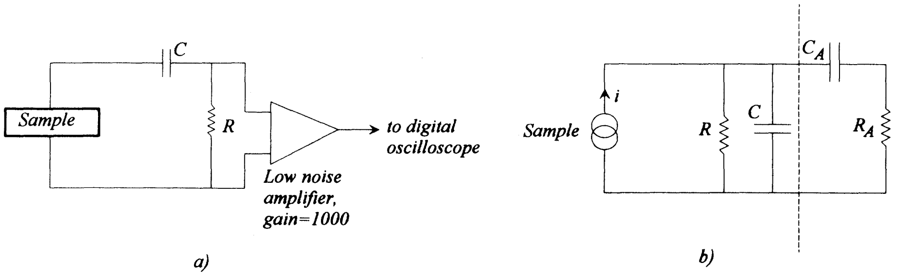

FIG. 1. (a) A schematic of the circuit used in the experiments, (b) the equivalent circuit used in calculating the pyroelectric signal. R and C are in the circuit only when a bias voltage is applied to the sample for electric field dependence measurement. Otherwise the circuit is dc coupled (i.e., R is removed and C is shorted). $\tau \simeq 2$ s.

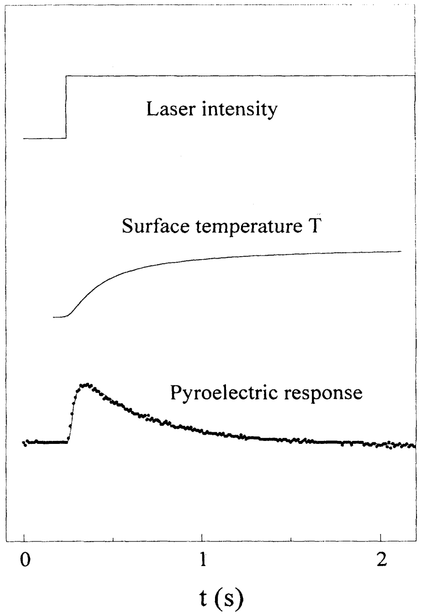

FIG. 2. The schematic trace of the laser intensity, the surface sample temperature, and a comparison of the theoretical pyroelectric response superimposed on the experimentally measured response.

tem is slow compared to the time constant RC, as is the case in our experiment, the measured voltage is $\Delta V(t) = -Ri(t)$, or

$$V(t) = \frac{RpI_0(1-\mathcal{R})\sqrt{\kappa}}{4\lambda\sqrt{\pi t}} \exp\left(-\frac{l^2}{4\kappa t}\right) \mathrm{erf}^2\left(-\frac{w}{\sqrt{4\kappa t}}\right) \times \exp\left(-\frac{t}{RC}\right). \tag{10}$$

The calculated curve (10) is plotted on top of the experimental voltage measured along the crystal c axis in Fig. 2. The measured pyroelectric response is seen to be accurately modeled by Eq. (10).

The peak in the voltage is at a short time t_0 after the onset of the pulse (i.e., when the rate of heating is greatest). For $w \gg \sqrt{4\kappa t}$, the erfc $\approx$ 1 and if we set our circuit time constant such that $RC \gg t_0$, the peak occurs at $t_0 = l^2/2\kappa$, and

$$V_p = \frac{RpI_0(1-\mathcal{R})}{4\rho c_p l}\sqrt{\frac{2}{e\pi}}. \tag{11}$$

The voltage is directly proportional to the pyroelectric coefficient and the laser intensity. The formula (11) thus gives a direct, accurate value for p simply by measuring the peak pyroelectric voltage V_p, the sample thickness l, and the amount of power dissipated in the sample $I_0(1-\mathcal{R})$. All other quantities in (11) are known or can be directly measured to a high degree of accuracy.

III. RESULTS

A. Doping dependence

First we report measurements on three different samples with different δ. The superconducting crystal ($\delta = 0.1$), showed a c-axis resistivity which was virtually constant from room temperature to 90 K, with $T_c = 90$ K and a resistive transition width of 0.3 K.[7] Susceptibility measurements show a single sharp drop in χ and full diamagnetism suggesting a homogeneous O distribution. To increase δ, the sample was reduced by annealing in an Ar atmosphere in the usual way. Annealing temperatures of 470 and 600 °C were used to reduce the oxygen content to $\delta = 0.6$ and $\delta = 0.8$, respectively. Annealing was performed for long periods (weeks) to ensure homogeneity of the O atoms. The O content was subsequently checked by the frequency of the apex O vibration in Raman spectroscopy, which is very sensitive to δ.[15]

The c component of the pyroelectric coefficient $\mathbf{p}$ for three different samples is given in Table I. The values of the constants used in the expression are $c_p = 300$ J K^{-1} mol^{-1}, $\rho = 6.38$ g cm^{-3}, $I_0 = 30$ mW, $\mathcal{R} = 0.3$, and $l = 0.5$ mm. No signal was found perpendicular to the c axis, suggesting that $p_a \sim p_b \sim 0$.

The doping dependence of p_c is shown in Fig. 3. The magnitude of the pyroelectric effect is thus strongly dependent on O content, δ. The values of p that we measure would be the correct, intrinsic values if we were measuring a single-domain crystal. However, we will show later that actually the crystals are probably composed of many domains whose polarization may be in different directions, reducing the total polarization. This means that the values of p are probably somewhat greater than those listed in Table I. We do not expect the variation of domain size and the number of domains with δ to account for the observed behavior in Fig. 3, however. Note also that we find that the magnitude of p_c and possibly also of $\mathbf{P}_s$ appears to increase with increasing O content in such a way that the product,

$$p_c R \approx \text{const.} \tag{12}$$

The possible reasons for such behavior will be discussed later.

B. Electric field dependence

In a ferroelectric material, by definition, the direction of polarization can be switched by the application of an

TABLE I. Comparison of the magnitudes of the c-axis room-temperature pyroelectric coefficients in insulating and metallic samples of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ determined from Eq. (11). R is the sample resistance.

δ	$V_p \| c$ (μV)	R (Ω)	p_c (C m^{-2}K^{-1})
0.8 ± 0.1	15	6×10^5	5×10^{-6}
0.6 ± 0.1	5	180	6×10^{-3}
0.1 ± 0.05	10	0.1	20

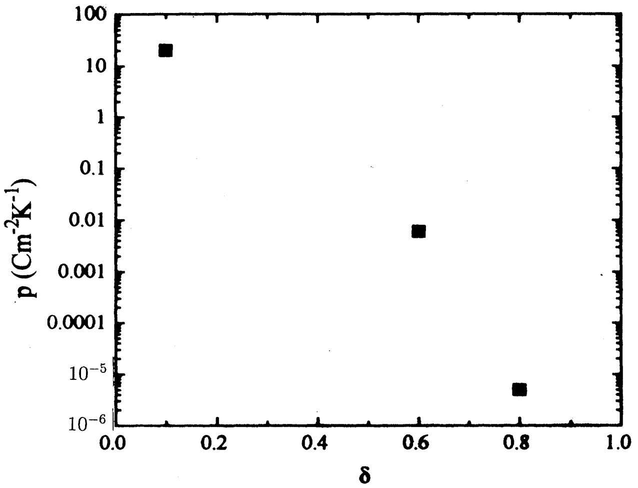

FIG. 3. A plot of the measured value of p versus doping, δ.

external field. Although it is not possible to apply a field of significant magnitude on conducting YBCO samples in the metallic range, i.e., with $\delta < 0.7$, we have found that fields in excess of 1 kV/m can be applied to the insulating sample with $\delta = 0.8$. By applying a dc bias on the sample, we have attempted to reverse the sign of the pyroelectric signal, which would indicate that the direction of polarization has been switched. A field was applied on the same set of contacts as for the normal pyroelectric measurements, but an ac coupling capacitor and resistor is switched into the amplifier input, to isolate the dc component but still allow through slow transient signals. ($\tau_{RC} \simeq 2$ s) (see Fig. 1). The signal was verified to be the same whether or not the power supply and additional circuit was connected. We were thus confident that the extra circuitry did not interfere with our measurment.

We have been able to observe a reversible change in sign of the pyroelectric voltage V_{p_c} which is switched by the direction of the electric field. The dependence of $\mathbf{V}_p$ on electric field is plotted in Fig. 4. At approximately $E = 500$ V/cm, the polarization shows signs of saturation and increasing the field further does not increase V_p. In all the samples tested, the nonlinear V_p versus E-field curve can be reproducibly traced and is completely reversible. Removing the field entirely did not leave the sample in the switched state, however, as would be expected for a ferroelectric; instead the pyroelectric signal showed that it had reverted back to its original polarization.

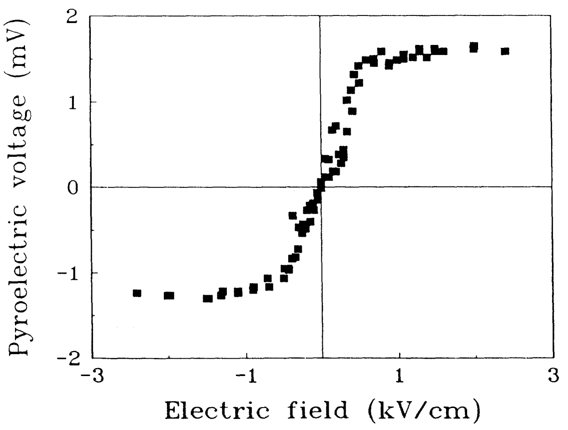

FIG. 4. Pyroelectric voltage on $YBa_2Cu_3O_{6.2}$ at 300 K as a function of applied external voltage.

However, the application of an external dc field (500 V/cm) for 2 days did increase the value of V_p by 2–3 times, showing that the pyroelectric coefficient can be changed, implying that the spontaneous polarization can be changed; i.e., the material can be poled to some extent even at room temperature.

C. Temperature dependence

The pyroelectric voltage $\mathbf{V}_p$ as a function of temperature for two different types of samples (δ=0.1 and δ=0.8) is shown in Fig. 5. Two types of behavior were generally observed: Either the signal was reasonably temperature independent, or it appeared to swing between two extreme values, of approximately similar magnitude. In the superconducting sample ($\delta = 0.1$), the signal dissappears ($V_p < 10^{-6}$ V) at T_c . Virtually all samples showed some kind of an anomaly in $\mathbf{V}_p$ (a sign change or increase in magnitude) in the region 200–240 K (Fig. 5). The anomaly in this temperature range is believed to be due to the onset of O ordering.[16] In Fig. 6 we show the signal V_p as a function of time during one such polarization reversal. The pulses with a time constant $\sim$ 0.5–1.5 s are the pyroelectric signal. The origin of the fast response which is visible in some traces is not entirely clear at present, but it is believed to be related to Barkhausen pulses:electric pulses which appear when domains fuse to-

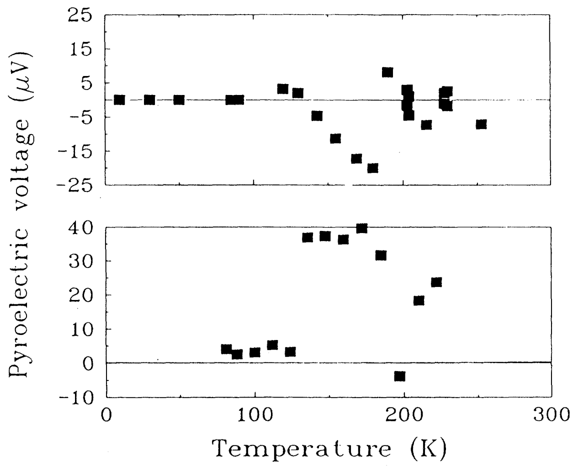

FIG. 5. Examples of the temperature dependence of the peak pyroelectric voltage in $YBa_2Cu_3O_{7-\delta}$ for δ=0.1 (top) and δ=0.8 (bottom). In the superconducting sample, the signal disappears at T_c.

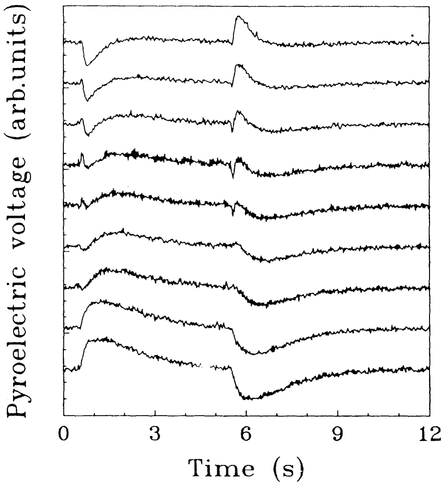

FIG. 6. Time dependence of the pyroelectric signal at different temperatures during a polarization reversal. The laser heat pulse timing is shown in the top of the figure. The traces are in the temperature range from 192 K (top) to 240 K (bottom), taken at approximately 6 K intervals.

gether. (The elimination of a domain wall releases energy and this is observed in the form of a voltage pulse.)

We interpret the change in the magnitude and sign of V_p to be primarily due to temperature-activated domain rearrangement. Repeated temperature cycling often tends to reduce the number of sign reversals of V_p between 90 and 300 K. Because of the lack of any systematic behavior in repeated temperature cycling, we were not able to extract an intrinsic temperature dependence for p from measurements on the present set of samples. Although insulating samples can be poled to some extent, it is not clear whether a single-domain structure could be achieved—a clear necessity for reproducible temperature dependence measurements.

IV. DISCUSSION

A. Discussion of artifacts

Although the measured pyroelectric response is observed to be described extremely well by the theoretical calculation, a discussion of possible artifacts in these experiments is still in order. We have previously eliminated possible artifacts due to (a) photovoltaic and (b) thermoelectric effects[7] by (a) checking whether the same effect could be produced by a small heater instead of a light pulse and (b) comparing the measured pyroelectric temporal response (which is proportional to dT/dt) with the predicted response: i.e., the derivative of the measured thermopower S, with time, $dV_S/dt = SdT/dt$.

To further test the presence of possible contributions to the signal from photoconductivity and photovoltaic effects, we coated the samples with black absorbing paint. No difference in the signal was found whether the front surface was painted with black absorbing paint or not, leading us to conclude that the contributions to the signal from photovoltaic effects, photoconductivity, and indeed photoeffects of any kind are not present in these experiments.

We still need to rule out the effects of surface space charges which could modify or even dominate the pyroelectric response in $YBa_2Cu_3O_{7-\delta}$, as they do in the paraelectric phase of $BaTiO_3$.[10] The apparent independence of V_p on doping would indeed suggest that we have approximately the same surface charge in all our samples, and our signal is therefore not a bulk, but a surface effect. In the case of surface charges, the total $\mathbf{V}_p \propto \mathbf{V}_1 \pm \mathbf{V}_2 \propto \mathbf{p}_1\delta T_1 \pm \mathbf{p}_2\delta T_2$, i.e., the sum of the pyroelectric contributions from the two contact surfaces. Evidence against the existence of surface space charges is the complete lack of systematic change of $\mathbf{V}_p$ when we move the position of the laser spot from the center to the edge of the sample (i.e., nearer to one of the contacts): If surface space charges were responsible for the pyroelectric effect, moving the laser spot around on the sample would change the relative contributions to $\mathbf{V}_p$ from the two surfaces. This would give either a change of magnitude or change of sign, depending on whether the surface contributions are of the same or opposite sign. We have *consistently* found no evidence for such behavior, and thus conclude that surface space-charge effects cannot explain our observations. The same argument applies for effects due to the Schottky interface barrier: The magnitude of any effect due to contact barriers should be strongly dependent on the position of the laser spot on the sample, and hence the insensitivity of the response to spot position suggests that any transient effects due to diffusion at the Scottky barriers are not present.

A pyroelectric as well as a piezoelectric response can be observed in electrets as well as ferroelectics, but since we observe a pyroelectric signal without any applied field, the present study suggests that YBCO cannot be described as an electret.

To further reject the possibility that trapped charges are responsible for the polarization, we first carefully measured the pyroelectric response of the sample, then heated it to 300 °C, and subsequently measured the pyroelectric response on the sample. A comparison of the signals showed no difference, suggesting that although we have released a great number of trapped carriers (judging by the resulting thermoluminescence), these have no effect on the polarization of the sample. We conclude that trapped charges are not the cause of the polarization in Y-Ba-Cu-O. We therefore need to explore the possibility that the effect is due to symmetry breaking in the bulk, rather than trapped charges.

B. Origin of doping dependence

In order to explain the experimentally found correlation between the c-axis resisitivity and the magnitude of the spontaneous polarization we suggest the following argument: If we assume that the origin of the spontaneous polarization is somehow related to either O defects or more generally a change in symmetry of the unit cell resulting from a change in ionic positions or even electronic structure with O doping, then its magnitude will increase in direct proportion to the oxygen concentration, $1-\delta$. The dc conductivity $\sigma(0)$, on the other hand, is proportional to the density of states involved in carrier hopping along the c axis, and is thus also directly related to the O content. The two quantities are therefore expected to scale in the same way with increasing O concentration, and it is not surprising that $\mathbf{P}/\sigma(0) = \rho\mathbf{P}$ is approximately doping independent, as the experimental results expressed in relation (12) suggest. Possibly, the scaling law is accidental; i.e., the two quantities scale together via two independent mechanisms, both related to O doping, but, for example, Bianconi's measurements of x-ray absorption[17] on YBCO suggest that there is an actual *change in the symmetry of the electronic wave functions* at the Fermi level as we dope with oxygen. Similar evidence for a change in symmetry upon doping comes from resonant Raman experiments.[18] Such a change in electronic symmetry could be accompanied with a change in symmetry of the unit cell and a loss of inversion symmetry.

C. Origin of the polarization

The appearance of ferroelectricity in perovskites is often associated with anharmonicities of O vibrations. These can be surprisingly small, such as in $SrTiO_3$, for example, and may not be immediately obvious. In high-T_c oxides, there have been many different reports of anharmonic O modes, some of which are well understood (for example, the B_{1u} tilt mode in La cuprates), while some are still controversial (in $YBa_2Cu_3O_{7-\delta}$, for example). In $YBa_2Cu_3O_{7-\delta}$, we have recently suggested a possible anharmonic model[19] based on high-temperature Raman data on the apical O(4) atom. While there is still some controversy regarding its anharmonicity,[20,21] it could be related to the appearance of ferroelectric behavior.

A ferroelectric distortion involves small displacements of cations with respect to the anions, leading to a net dipole moment per unit volume. Crucial is the stabilization of long-range order by the Coulomb interaction over the short-range repulsive forces, leading to a net macroscopic polarization. Although it is tempting to attribute the origin of the polarization to the chain O(1) ions in YBCO, especially in view of the doping dependence, the appearance of pyroelectricity and a spontaneous polarization also in La_2CuO_4, which has different structure and no Cu-O chains, suggests that the picture may not be so simple. It would be interesting to find a polarization associated with the apex O(4) ions, as suggested by the anharmonicity data.

Furthermore, recent neutron data performed on YBCO suggest that the motion the O(4) ion is decoupled from the lower part of the unit cell.[22] This would directly imply loss of inversion symmetry and by implication a polar structure compatible with the appearance of ferroelectricity.

The large room-temperature static dielectric constant $\epsilon(0) \sim 700$ that has been measured[23] in ceramic $YBa_2Cu_3O_7$ suggests a soft transverse optic mode [through the Lyddane Sachs-Teller relation $\epsilon(\infty)/\epsilon(0) = \omega_{\mathrm{TO}}/\omega_{\mathrm{LO}}$]. Although such a mode has so far not been clearly identified, there have been a number of reports in infrared spectroscopy of a high-frequency overdamped optic mode at $\sim$ 560–580 cm^{-1}. Although the assignment of this mode is not unambiguous, we see that in the present context the mode assignment given by Genzel *et al.*[24] is very appropriate: It involves primarily the c-axis motion of the *apex* O(4) atom with admixtures of Cu(1) and O(1). It thus appears as a polar counterpartial to the Raman-active apex O(4) vibration and is a good candidate for causing the ferroelectric properties.

V. CONCLUSIONS

In conclusion, we find that the existence of a spontaneous polarization in YBCO cannot be explained by surface space charges or trapped charges, but instead suggests the material to be noncentrosymmetric with long-range Coulomb ordering giving rise to a net dipole moment per unit cell. Reversal of this polarization can be induced by applying an external field as well as by thermal cycling through domain reorientation. The experimental observation that the product, $\rho\mathbf{P}_s$ is approximately constant with doping suggests that the spontaneous polarization scales with δ. The long-range interactions between O ions in the O(1) basal plane[26] then provides the forces required for the ordering of the O ions into a ferroelectric arrangement. The effects of sample morphology are likely to be important and further careful work on fresh purpose-grown samples on pure as well as impurity-doped samples is required to elucidate the role of domains and domain walls in relation to the spontaneous polarization. In the absence of a crystal growth facility such experiments could not have been presently undertaken.

Finally, we point out that circular birefringence arises naturally upon reflection from crystals with a polar axis. The present temperature dependence experiments clearly demonstrate that there may be structural anomalies in the polar phase preceding T_c as well as thermally activated domain wall motion which will change the birefringence in surface reflection. These effects clearly need to be carefully studied before changes in optical birefringence can be used as conclusive evidence for anyon or flux-phase superconductivity as has been suggested.[25]

ACKNOWLEDGMENTS

We wish to acknowledge valuable comments from M. Čopič, M. Zgonik, S. Barišić, and L. Forro. This work has been supported in part by CEC Grant No. CI1 0568-C.

[1] L.R. Testardi, Rev. Mod. Phys. **47**, 637 (1975).

[2] J. Labbe and J. Friedel, J. Phys. (Paris) **27**, 153 (1966); J. Labbe, Phys. Rev. **172**, 451 (1968), and references therein.

[3] P.W. Anderson and E.I. Blount, Phys. Rev. Lett. **14**, 217 (1965).

[4] S.K. Kurtz *et al.*, Ferroelectrics **87**, 29 (1988).

[5] J.F. Scott, Appl. Phys. Lett. **56**, 1914 (1990).

[6] C.L. Chang, A. Kleinhammes, W.G. Moulton, and L.R. Testardi, Phys. Rev. B **41**, 11 564 (1990).

[7] D. Mihailović and A.J. Heeger, Solid State Commun. **75**, 319 (1990).

[8] R.J. Kennedy, W.G. Jenks, and L.R. Testardi, Phase Transit. **23**, 19 (1990).

[9] D. Mihailović and I. Poberaj, Physica C **185-189**, 781 (1991).

[10] A.G. Chynoweth, Phys. Rev. **102**, 705 (1956); J. Appl. Phys. **27**, 78 (1956).

[11] M. Simhony and A. Shaulov, Appl. Phys. Lett. **21**, 375 (1972).

[12] M.E. Lines and A.M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).

[13] R.P. Vasquez and R.M. Housley, Physica C **175**, 233 (1991).

[14] H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, London, 1959).

[15] C. Thomsen and M. Cardona, in *Physical Propreties of High-Temperature Superconductors I*, edited by D.M. Ginsberg (World Scientific, Singapore, 1989).

[16] A.N. Lavrov, Phys. Lett. A **168**, 71 (1992).

[17] A. Bianconi, in *Proceedings of the International Conference on Superconductivity—ICSC*, edited by S.K. Joshi, C.N.R. Rao, and S.V. Subranyam (World Scientific, Singapore, 1990), p. 448.

[18] E.T. Heyen, R. Liu, C. Thomsen, and M. Cardona, Phys. Rev. B **45**, 3037 (1992).

[19] D. Mihailović and C.M. Foster, Solid State Commun. **74**, 753 (1990); D. Mihailović, K.F. McCarty, and D.S. Ginley, Phys. Rev. B **47**, 8910 (1993).

[20] J. Mustre de Leon *et al.*, Phys. Rev. Lett. **65**, 1675 (1989).

[21] G.H. Kwei *et al.*, Physica C **169**, 217 (1990).

[22] M. Arai *et al.*, Phys. Rev. Lett. **69**, 359 (1992).

[23] L.R. Testardi *et al.*, Phys. Rev. B **37**, 2324 (1990).

[24] L. Genzel *et al.*, Phys. Rev. B **40**, 2170 (1989).

[25] K.B. Lyons *et al.*, Phys. Rev. Lett. **64**, 2949 (1990); H.J. Waber *et al.*, Solid State. Commun. **76**, 511 (1990).

[26] S. Semenovskaya and A.G. Khachaturyan, Phys. Rev. Lett. **67**, 2223 (1991).