Onset of dielectric modes at 110 K and 60 K due to local lattice distortions in nonsuperconducting YBa$_2$Cu$_3$O$_{6.0}$ crystals

Z. Zhai, P. V. Parimi, J. B. Sokoloff, and S. Sridhar

Department of Physics, Northeastern University, 360 Huntington Avenue, Boston, Massachusetts 02115

A. Erb

DPMC, Université de Genève, Genève, Switzerland

(Received 9 May 2000; published 13 February 2001)

We report the observation of two dielectric transitions at 110 and 60 K in the microwave response of nonsuperconducting YBa$_2$Cu$_3$O$_{6.0}$ crystals. The transitions are characterized by a change in polarizability and presence of loss peaks, associated with overdamped dielectric modes. An explanation is presented in terms of changes in polarizability of the apical O atoms in the Ba–O layer, affected by lattice softening at 110 K, due to change in buckling of the Cu–O layer. The onset of another mode at 60 K strongly suggests an additional local lattice change at this temperature. Thus microwave dielectric measurements are sensitive indicators of lattice softening which may be relevant to superconductivity.

DOI: 10.1103/PhysRevB.63.092508

PACS number(s): 74.72.Bk, 74.25.Nf, 77.22.Gm, 74.80.Dm

It was recognized soon after the discovery of the high-temperature superconductors that the cuprates are structurally similar to the ferroelectric perovskites. The basic perovskite ABO$_3$ structure occurs in ferroelectrics like BaTiO$_3$ and incipient ferroelectrics or quantum paraelectrics such as SrTiO$_3$, as well as in subunits of the superconductor YBa$_2$Cu$_3$O$_{6.0}$. Furthermore, theoretical models have been proposed which include the possible competition between ferroelectricity and superconductivity.

In this paper we show some striking dielectric properties of single crystals of insulating YBa$_2$Cu$_3$O$_{6.0}$ which seem to have a strong bearing on the superconductivity of doped YBa$_2$Cu$_3$O$_{6.0}$. Traditionally the information on lattice dynamics has been obtained from inelastic neutron, x-ray absorption fine structure (XAFS), Raman, and infrared spectroscopy measurements. Our microwave measurements probe consequences of lattice modes on the long wavelength (q=0) dielectric properties, and its very high sensitivity leads to the observation of features not detected by other techniques.

In addition to large dielectric strengths $e' \sim 10^2–10^3$, consistent with previous measurements, we report the presence of two dielectric transitions at 110 and 60 K. These transitions are accompanied by the onset of polarization modes indicated by the presence of dielectric loss peaks below the transition temperatures. The transitions arise from structural distortions occurring at these temperatures, such as buckling of the Cu–O plane leading to the 110 K transition, which affect the electrodynamic response. Thus precision microwave measurements are shown to be a sensitive probe of lattice effects, complementing other traditional probes of lattice dynamics. Taken together with numerous reports of lattice effects at or near the superconducting transition temperature $T_c$, the present results demonstrate the importance of charge and lattice dynamics in the high-temperature superconducting oxides.

Ultrapure single crystals of YBa$_2$Cu$_3$O$_{6.0}$ were prepared in contamination-free BaZrO$_3$ crucibles. The high quality of these single crystals has been extensively documented in a wide range of measurements, including structural and transport studies. A brief list of these reports can be found in Ref. 8.

The high sensitivity microwave measurements were carried out in a Nb superconducting cavity resonant at 10 GHz in the $TE_{011}$ mode. The sample is placed at the center of the cavity at a maximum of the microwave magnetic field $H_\omega$. We introduce an electromagnetic susceptibility $\tilde{\chi}_H(T) = \chi'_H(T) + i \chi''_H(T)$ which is related to the measured parameters, the shift in cavity resonant frequency $\Delta f(T)$ and the resonance width $\Delta f(T)$ by $\Delta f(T) = -g [\chi'_H(T) + i \chi''_H(T)]$, where $g$ is a geometric factor. A detailed analysis of the relevant cavity perturbation for general sample conditions including lossy dielectric and metallic or superconducting states, has been recently carried out by us. The analysis shows that for arbitrary conductivity,

$$\tilde{\chi}_H(T) = -\frac{1}{\tilde{\sigma}} \left[ 1 - 3/\tilde{z}^2 + 3 \cot(\tilde{z})/\tilde{z} \right],$$

where $\tilde{z} = k a = k_0 a \sqrt{\epsilon_{tot}}$.

Note that we use time dependences $e^{-i\omega t}$. In the limit $\tilde{z} \ll 1$, $\tilde{\chi}_H(T) \approx (1/10)(k_0 a)^3(\tilde{\epsilon}_{tot} - 1)$ for a lossy dielectric. The dielectric permittivity $\tilde{\epsilon}_{tot}$ was extracted from the data using Eq. (1). $\tilde{\epsilon}_{tot}$ includes both bound polarization ($\tilde{\epsilon}$) and free charge conductivity $\tilde{\sigma}$ contributions, i.e., $\tilde{\epsilon}_{tot} = \tilde{\epsilon} + i \tilde{\sigma}/\omega \epsilon_0$. In the present case the conductivity is negligible and $\tilde{\epsilon}_{tot} = \tilde{\epsilon}$. We have earlier carried out extensive measurements of the surface impedance of a variety of superconductors, metals, and insulators, and demonstrated the validity of these measurements.

0163-1829/2001/63(9)/092508(4)/$15.00 ©2001 The American Physical Society
The dielectric permittivity $\varepsilon'(T)$ and $\varepsilon''(T)$ of YBa$_2$Cu$_3$O$_6.0$ are shown in Fig. 1. Here $H_{ab}||\hat{c}$ axis, so that the displacement currents are in the $ab$ plane, i.e., we are measuring in-plane dielectric permittivity $\varepsilon_{ab}$. The large microwave dielectric permittivity observed in the present composition seems to be a characteristic of some perovskite oxides. Such large dielectric strengths $\varepsilon' \sim 10^2 - 10^3$ in nonmetallic insulating YBa$_2$Cu$_3$O$_{6+x}$ were reported by Rey et al., for ceramic samples which were quenched to retain the oxygen homogeneity. It is worth remarking that the present crystals are also quenched from high temperature and this may be an important requirement for the observation of this effect. We have observed similar response in the microwave dielectric permittivity of another YBa$_2$Cu$_3$O$_6.0$ crystal (Fig. 2, bottom panel) obtained from a different batch, confirming the presence of the dielectric transitions reported here.

The data in Fig. 1 can be analyzed in terms of three dielectric modes, $\tilde{\varepsilon} = \varepsilon_\alpha + \varepsilon_\beta + \varepsilon_\gamma$, each of which is well described by a Debye relaxation form with respect to the temperature dependence:

$$\tilde{\varepsilon} = \varepsilon_\alpha + \varepsilon_\beta + \varepsilon_\gamma = \sum_{i=a,\beta,\gamma} \frac{\varepsilon_i(T)}{1-i\omega \tau_i(T)},$$

(2)

$\varepsilon_\gamma$ appears to represent the low $T$ tail of a high-temperature process, with $\varepsilon_\gamma(0) = 160$, and with a relaxation time $\tau_\gamma(T) = 6.5 \times 10^{-13}$ sec$^{-1}$ exp(1000/T) characterized by an activation energy of 1000 K. The $\varepsilon_\gamma$ process is dominant between 300 K and approximately 180 K, below which it “freezes out” quasistatically as the dipole relaxation rate becomes extremely slow. A residual temperature independent dielectric contribution $\approx 465 + i125$ remains at all temperatures. We believe $\varepsilon_\gamma$ is the contribution which has been measured by several previous investigators for nonmetallic YBa$_2$Cu$_3$O$_{6.0}$ and represents a polarization mode formed at high temperatures $T > 300$ K. $\varepsilon_\alpha$ and $\varepsilon_\beta$ indicate the onset of two dielectric modes which turn on below transition temperatures $T_{c\alpha} = 60$ K and $T_{c\beta} = 110$ K. We describe these modes with the following parameters:

$$\varepsilon_\alpha(T) = 60[1 - (T/T_{c\alpha})], \quad T_{c\alpha} = 60 \text{ K} \quad \text{and} \quad \tau_\alpha(T) = 4 \times 10^{-10} (\text{sec} \cdot \text{K})/(T + 200),$$

for the $\varepsilon_\alpha$ process, and

$$\varepsilon_\beta(T) = 280[1 - (T/T_{c\beta})], \quad T_{c\beta} = 110 \text{ K} \quad \text{and} \quad \tau_\beta(T) = 2.5 \times 10^{-10} (\text{sec} \cdot \text{K})/(T + 5),$$

for the $\varepsilon_\beta$ process.

$\varepsilon_\alpha$ and $\varepsilon_\beta$ are similar to order parameters which grow at temperatures below a transition. As $T$ is lowered, both $\varepsilon_\alpha(T)$ and $\varepsilon_\beta(T)$ increase initially due to the growing polarization. However below a characteristic temperature both $\varepsilon'_\alpha(T)$ and $\varepsilon''_\alpha(T)$ begin to decrease because the dipoles are no longer able to follow the microwave field. The peak temperature $T_{pa} \sim 25$ K is determined by the condition $\omega \tau_\alpha(T_{pa}) = 1$, although the peak for $\varepsilon''_\alpha$ at a higher $T$ than for $\varepsilon''$. The peaks are so-called dielectric loss peaks. Identical arguments hold for $\varepsilon_\beta(T)$ also. Here the peak is much broader and occurs at $T_{p\beta} \sim 75$ K.

For the $\alpha$ and $\beta$ processes, the temperature dependence is too broad to be described by an activated relaxation rate. We have found that a relaxation rate which is linear in $T$, i.e., $\tau_\alpha,\beta(T) = a_\alpha,\beta(T + T_{(a,\beta)0})$, describes the data very well as seen in Fig. 1, with $a_\alpha \approx 0.4 \times 10^{10} (\text{sec} \cdot \text{K})^{-1}, \quad T_{a0} = 5 \text{ K}$.
et al. the oxo-cuprate superconductors implemented by Shenoy, large dielectric permittivities observed. Consequently the O potential is greatly softened leading to the \( \sim \) coupling between Ba–O and Cu–O layers. Since then the contribution should be diamagnetic. We note that the 110 and 60 K onsets cannot arise from any dielectric modes discussed here bear a strong similarity to quantum fluctuations, as was proposed for SrTiO\(_3\), or due to coupling between Ba–O and Cu–O layers (Fig. 3). Consequently the O potential is greatly softened leading to the large dielectric permittivities observed.

We use a modification of the Bilz model specifically for the o xo-cuprate superconductors implemented by Shenoy, et al.\(^6\) The equation-of-motion of the oxygen relative ion-electron coordinate \( \vec{w} \) is given by \( m_{\text{o}}(\vec{w} + \Gamma \vec{w}) + D\vec{w} = Z e \vec{E} e^{-i\omega t} \), where \( D \) is the self-consistent harmonic approximation (SCHA) curvature of the anharmonic Oxygen electronic potential. For a driving electric field \( \vec{E} e^{-i\omega t} \), the susceptibility \( \alpha = Z e w F = Z^2 e^2/m_{\text{o}}(\omega_{\text{o}}^2 - \omega^2 - i\omega\Gamma) \). The dielectric constant \( \varepsilon = n\epsilon/\varepsilon_0 \) then becomes

\[
\varepsilon = \frac{\varepsilon(0)}{(1 - \omega^2/\omega_{\text{o}}^2) - i\omega\tau}.
\]

Here \( \varepsilon(0) = nZ^2 e^2/\varepsilon D \) and \( \tau = \Gamma/\omega_{\text{o}}^2 \).

Rather large dielectric constants are feasible for soft modes. For the case of the O atom in the Ba–O layer in YBa\(_2\)Cu\(_3\)O\(_6.0\), we have \( n = 1.2 \times 10^{28} \text{ m}^{-3} \). With \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m} \), and using the resonance frequency, \( f_0 = 3 \times 10^{13} \text{ Hz} \), \( \omega_{\text{o}} = 2\pi f_0 \), so that \( D(=Z m_{\text{o}} \omega_{\text{o}}^2) = 3.3 \times 10^{-2} \text{ N/m} \), we get \( \varepsilon(0) \sim 10^3 \) comparable to the experimental results. Note that despite the softening, the condition \( \omega < \omega_{\text{o}} \) is well satisfied (\( \Gamma = 10^9 \text{ Hz} \)), and the so-called Drude-Lorentz form of a resonant mode given by Eq. (3) reduces to the Debye-like relaxation forms used in Eq. (2). The above estimate indicates considerable softening of the anharmonic O potential. Indeed this can happen because the curvature is extremely sensitive to interatomic forces in these materials. A mechanism for such softening has been given by Shenoy et al.\(^5\) for the layered HTS.

There have been extensive studies of lattice dynamics in superconducting oxides, especially in YBa\(_2\)Cu\(_3\)O\(_6.0\).\(^1\) One of the key features that has emerged is that there are small structural distortions which occur although there is no change in the overall structure. Particularly well-established are the structural distortions reported at \( T_c \) in YBa\(_2\)Cu\(_3\)O\(_6.0\), \( \text{Hg}_2\text{Ba}_2\text{Cu}_2\text{O}_8 \), and \( \text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8 \).\(^2\) Also, lattice instabilities have been reported, in the dialanometry measurements on doped and undoped La\(_{2/3}\)Sr\(_{1/3}\)NiO\(_4\).\(^3\) In YBa\(_2\)Cu\(_3\)O\(_6.0\), the coupling between apical O(1) and planar O(2) oxygen changes at the superconducting transition due to the displacements of O(2) in the directions perpendicular to the CuO\(_2\) plane (Fig. 3) changing the buckling in the plane.\(^4\) The nearness of the \( \beta \) dielectric mode around 110 K to the \( T_c \) = 93 K (YBa\(_2\)Cu\(_3\)O\(_6.95\)) is striking and suggests a possible change in the O(1) dynamics in YBa\(_2\)Cu\(_3\)O\(_6.0\) (YBCO) as well, and hence we attribute this \( \beta \) mode to the change in the dynamics of O(2).

In Ref. 6 the possibility of dielectric modes in coupled Ba–O and Cu–O layers is described. Including the various interatomic forces, it can be shown that the curvature \( D \) becomes a function of the buckling angle \( \theta \). The change in buckling at 110 K would lead to a change in the mixing of the \( ab \) plane acoustic and \( c \)-axis optic mode, resulting in a new set of mixed modes which would move to lower frequency due to softening. The resulting decrease in \( D \) would then explain the \( \beta \) mode at 110 K. The calculation of Shenoy et al.\(^5\) based on the mean-field approach support our description of the dynamics of O(1).

The presence of the 60 K mode suggests another local structural change at this temperature scale, possibly in the chain layer. It is very interesting to note that this temperature scale is present in the doped YBCO as well.\(^2\) In addition to
the proximity of the 110 K transition to the optimum superconducting $T_c$ of 93 K noted above, equally important is the presence of a secondary temperature scale around 60 K in certain measurements of YBa$_2$Cu$_3$O$_{6+x}$.

This temperature scale has manifested itself in various experiments whose connections are becoming apparent only recently. Thus the present results may have important implications for superconductivity in these materials.

In optimally doped single crystals of YBa$_2$Cu$_3$O$_{6.95}$ an additional onset of pair conductivity at 65 K was noted in Ref. 10, well below the main $T_c = 93$ K. The consequences of this on the thermal conductivity and vortex transport have been observed. The present temperature scales also have striking resemblance to transitions around 110 and 65 K in over doped YBCO observed in nuclear quadrupole resonance (NQR) measurements by Grevin et al., which have been interpreted in terms of charge-density wave (CDW) correlations. In their results a short-range CDW sets in the Cu–O chains at 110 K which becomes long range around 65 K. The formation of CDW in the chains modulate the charge in the planes leading to a transition between an inhomogeneous charge state to a low-temperature ordered charge state in the planes. Keeping in view the fact that NQR probes the electric field gradient around the Cu nucleus the NQR transitions could as well be due to changes in local structure which leads to CDW formation in the doped metallic YBCO. Together, the NQR, thermal conductivity and the present results stress the importance of the 110 and 60 K temperature scales. These results indicate that local distortions in the structure at 110 and 60 K would lead to changes in polarization as we have observed in YBa$_2$Cu$_3$O$_{6.6}$ and charge ordering in doped YBCO. Microwave conductivity measurements on doped crystals from $x = 0$ to 1, when taken together with these other observations, strongly suggest that doping moves this onset temperature from 60 K at $x = 0$ to ~70 K at $x = 1$. Also the superconducting $T_c$ increases with $x$, but never exceeds 93 K. An interesting implication is that the implied structural distortion transition at 110 K may represent an upper limit on the superconducting transition, $T_c$.

In conclusion we have observed three paraelectric modes with temperature onsets at 60, 110, and >300 K in the nonmetallic YBa$_2$Cu$_3$O$_{6.0}$. These modes are well described by the change in polarizability of apical O(1) oxygens due to change in lattice dynamics with temperature. A striking observation is that the two low-temperature modes have direct connections with the transitions observed by traditional lattice probes as well as NQR and thermal conductivity measurements on doped superconducting YBa$_2$Cu$_3$O$_{6.0+x}$, strongly suggesting that oxygen and lattice dynamics play an important role in both the superconducting and nonsuperconducting materials.

We thank C. Kusko, R. S. Markiewicz, C. Perry, and S. R. Shenoy for useful discussions. This work was supported by ONR and NSF-ECS-9711910.