Enhanced electric polarizability at the magnetic ordering temperature of La_2CuO_{4+x}

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The low-frequency c-axis dielectric constant of La_2CuO_{4+x} exhibits values ~ 1500 for $T \le 350$ K with an added ~ 2000 enhancement in the vicinity of the magnetic ordering temperature. The possibility of a simultaneous (anti)ferroelectric-antiferromagnetic transition at 270 K is suggested, but experimental confirmation of the ferroelectric state is precluded by the high and field-dependent electrical conductivity.

High-temperature oxide superconductors possess a feature not found in the older metallic materials—the phase proximity of a semi-insulating state, and, thus, the possibility of observing the electric polarizability of the underlying parent phase. Measurements of the near-conducting phases of $YBa_2Cu_3O_{7-x}$,[1-5] $PrBa_2Cu_3O_{7-x}$,[6] and related materials[7-9] have shown the occurrence of low-frequency dielectric values approaching ferroelectric-like values. In this paper we extend these measurements to La_2CuO_{4+x}, show the occurrence, again, of large dielectric constants and, in addition, find a further enhancement of the electric polarizability at the temperature of the magnetic ordering.

The crystals of La_2CuO_{4+x} studied were grown from a CuO flux, and subsequently polished to eliminate all the flux and off-stoichiometric surface layers. The sample had dimensions of $4.1 \times 3.6 \times 0.53$ mm^3, with the smallest dimension being along the crystallographic c axis (direction of longest unit-cell parameter).

Measurements of the impedance of a crystalline slab of La_2CuO_{4+x} with E field parallel to the c axis were made at temperatures between 100 and 400 K in three separate runs with frequencies of 50, 300, and 600 kHz using an HP model 4284A Precision LCR meter. The complex quantity data have been converted to a dielectric constant and electrical conductivity at each frequency using an equivalent circuit of a parallel capacitor and a resistor. To make electrical contacts the two surfaces normal to the field direction were covered with silver paint. We restricted our measurements to an applied voltage of 0.1 V ($E \sim 200$ V/m) in order to obtain a dielectric response that would be field independent.

Figure 1 shows the temperature dependence of the relative dielectric constant in the c-axis direction, K_c, for the three measurement frequencies. Note that values ~ 1500 at room temperature are obtained, again showing the large electric polarizability of the insulating parent oxide phase for the high-T_c superconductors. One notable difference for La_2CuO_{4+x} compared to $YBa_2Cu_3O_{7-x}$ and $PrBa_2Cu_3O_{7-x}$, however, is the substantially smaller frequency dependence of the former's high dielectric constant in the vicinity of 300 K.

The major feature of the dielectric response is the large enhancement in K_c occurring near 270 K. The enhancement shows, qualitatively, relaxation behavior indicating that its underlying mechanism has a characterization time $\sim 10^{-6}$ sec in the vicinity of 270 K. No evidence of a shift in the temperature of the peak K_c (i.e., thermal activation) with frequency can be discerned.

It has been observed that La_2CuO_{4+x}, with the canting of spins out of the CuO_2 planes, orders antiferromagnetically in the temperature range $150 \le T \le 300$ K, and that the Néel temperature T_N is determined more precisely by the oxidation level. The sample studied shows a sharp peak at $T_N \approx 270$ K in the uniform magnetic susceptibility $\chi(T)$ with $H \| c$ (see Fig. 2). A rapid upturn in the isothermal magnetization ($T < T_N$), as expected, is also observed, indicating the weak or hidden ferromagnetic behavior due to the rotation of the CuO_6 octahedra in the orthorhombic phase. We thus infer that the transition state for magnetic ordering is accompanied by a large additional electrical polarizability.

A common feature of the large electric polarizability of the near conducting oxides is the simultaneous presence of a substantial "lossy" component to the polarization response traceable to the electronic conductivity. (The possibility that the near ferroelectric behavior is thus due to "free carriers" rather than bound structural units is

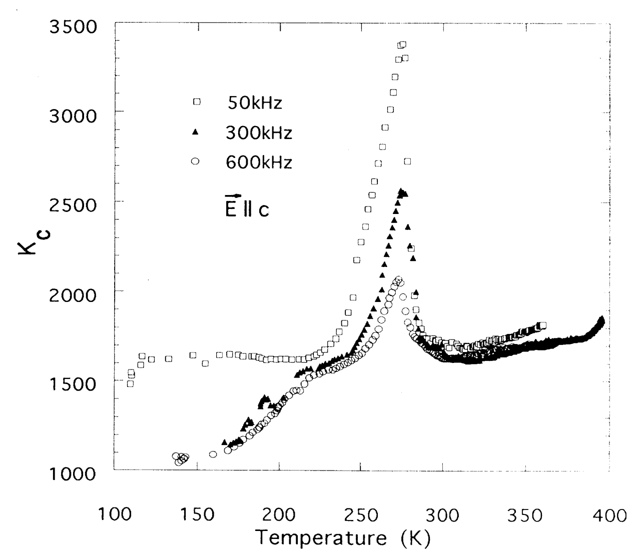

FIG. 1. Dielectric constant in the c-axis direction, K_c, vs temperature for the three measurement frequencies.

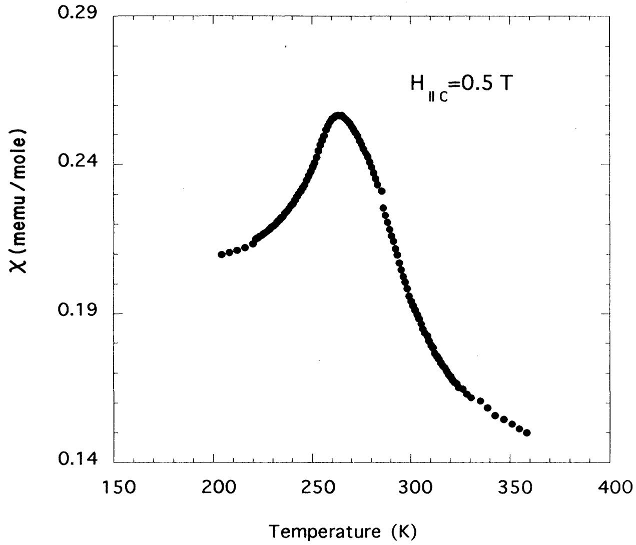

FIG. 2. Uniform magnetic susceptibility $\chi(T)$ with $H \| c$ vs temperature.

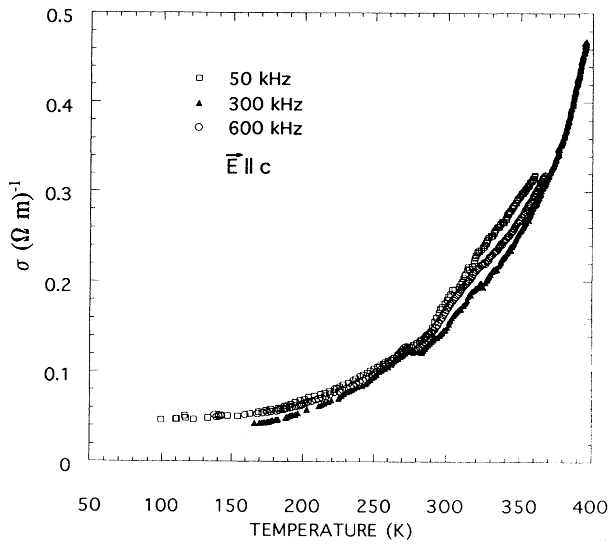

FIG. 3. Electrical conductivity $\sigma(\omega)$ vs temperature for the three frequencies of measurement.

suggestive, but without supporting evidence.) Figure 3 shows the electrical conductivity $\sigma(\omega)$ vs temperature for the three frequencies of measurement. A crude relaxation model analysis of Fig. 1 data yields $T=0.5\times10^{-6}$ s and a conductivity peak of the order of that shown in Fig. 3. We also find $\sigma(\omega)$ to be nearly independent of frequency in our data. Measurements at higher frequencies have been recently reported in greater detail by Lunkenheimer, Resch, and Loidl.[10]

No quantitative model for the strong microscopic magnetoelectric coupling indicated by the data of Figs. 1 and 2 is known to us. Structural instability models of (anti)ferroelectricity driven by O atom displacements or rotations are precedent mechanisms whose similarities in behavior are readily recognized in Fig. 1. Although (anti)ferroelectric antiferromagnets are known to exist, the authors are unaware of a case of simultaneous polarization and magnetization ordering. An experimental test of the ferroelectric possibility for La_2CuO_{4+x}, by the observation of polarization state switching, was attempted using modest electric fields $\sim 10^4$ V/m for temperatures between 100 and 280 K, but a positive identification of polarization changes expected for typical ferroelectrics was precluded by the large electrical conductivity, which makes real currents greatly exceed the expected displacement currents.

It has been tempting to suggest a common origin of ferroelectricity and high-T_c superconductivity in oxides.[11–13] Bussmann-Holder, Simon, and Büttner,[14] in particular, have drawn attention to this point and described a lattice dynamical model for displacive-type (or soft mode) ferroelectrics which might be applied to high-T_c superconductors. The coupling of magnetic ordering and electric polarizability, described in this work, has been previously noted though less clearly in $PrBa_2Cu_3O_{7-x}$.[6]

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