

Changes in the static dielectric constant of $\text{YBa}_2\text{Cu}_3\text{O}_y$ and $\text{PrBa}_2\text{Cu}_3\text{O}_y$ toward the insulator–metal transition

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The changes in the static dielectric constant of the compounds $\text{YBa}_2\text{Cu}_3\text{O}_y$ and $\text{PrBa}_2\text{Cu}_3\text{O}_y$ as the oxygen content is varied near the insulator–metal transition has been studied. The estimate $y_c \approx 7.4$ is found for the critical oxygen concentration for the insulator–metal transition of $\text{PrBa}_2\text{Cu}_3\text{O}_y$. Possible reasons for the pronounced difference between the electronic properties of these Y- and Pr-based 1-2-3 compounds are discussed.

A basic distinguishing feature of the superconducting metal oxides is that their superconducting state prevails in the immediate vicinity of an insulator–metal transition. The predominantly ionic bonding characteristic of oxides with the layered-perovskite structure imparts several distinguishing characteristics to the transition from an insulating state to a metallic one. In addition to the increase in polarizability, resulting from an increase in the concentration of impurity states and an increase in the effective carrier localization radius during doping, which are characteristic of semiconductors and insulators with covalent bonding,¹ these systems exhibit a tendency toward the formation of a ferroelectric state.² The effect of the ferroelectric instability on electron–electron pairing and the formation of (bi-) polaron states are currently regarded as possible mechanisms for the high- T_c superconductivity.^{3–5} There is accordingly interest in the changes in the polarizability toward the insulator–metal transition.

The anomalously large value⁶ of the dielectric constant of $\text{YBa}_2\text{Cu}_3\text{O}_y$ and the structural features in its temperature dependence⁷ have been pointed out previously and have been interpreted as manifestations of ferroelectric properties. Investigators have ignored the circumstance that the overall dielectric constant is the sum $\epsilon = \epsilon_0 + \epsilon_{tr}(\omega, T)$, where ϵ_0 is the static dielectric constant, due to the polarizability of the lattice and localized impurity state, and $\epsilon_{tr}(\omega, T)$ is a contribution from transport electrons, which is related to the hopping nature of the conductivity in the insulating phase. The latter contribution depends on the frequency and the temperature. In this case the conductivity at low frequencies obeys $\sigma \propto \omega^s$, where $s < 1$, and ω is the measurement frequency.⁸ The component $\epsilon_{tr} \propto \omega^{s-1}$ depends strongly on the measurement frequency and increases rapidly with the temperature.^{9,10} In order to study ϵ_0 it is thus necessary to correctly separate the components of ϵ .

In this letter we are reporting a study of two isostructural compounds in the 1-2-3 system, namely, the compounds based on Y and Pr. These compounds differ markedly in electronic properties, for some reason which is not yet clear. We measured the static

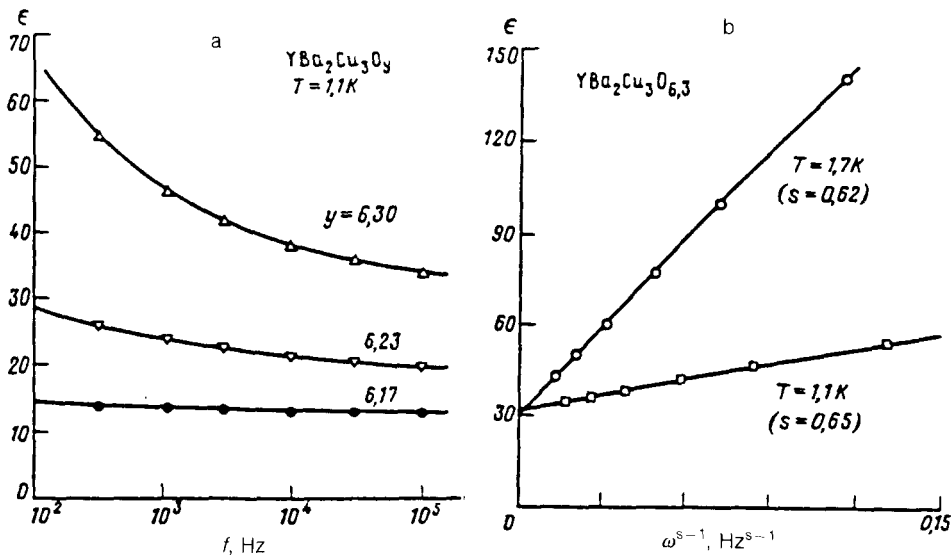


FIG. 1. a: The dielectric constant ϵ versus the measurement frequency for three $\text{YBa}_2\text{Cu}_3\text{O}_y$ samples differing in oxygen content. Filled circles— $y=6.17$; inverted triangles— 6.23 ; upright triangles— 6.3 . b: Frequency dependence of the dielectric constant of a $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$ sample in the coordinates ϵ and ω^{s-1} for two temperatures. Squares— 1.1 K ; circles— 1.7 K .

dielectric constant of polycrystalline samples in the insulating phase: $\text{YBa}_2\text{Cu}_3\text{O}_y$, $y \leq 6.3$ and $\text{PrBa}_2\text{Cu}_3\text{O}_y$, $y \leq 6.9$. We separated the components of ϵ and found ϵ_0 as a function of y . The samples were pellets $\approx 4.5\text{ mm}$ in diameter and $\approx 0.8\text{ mm}$ thick; silver was applied to the two faces. We measured the capacitance and conductivity of the resulting plane capacitors over the frequency range $0.3 \leq f \leq 100\text{ kHz}$ ($\omega = 2\pi f$) at temperatures $T \geq 1.1\text{ K}$ in a circuit which eliminated the effect of the capacitance of the connecting cables. The oxygen content in the samples was varied by varying the conditions of the annealing and of the subsequent quenching in a helium atmosphere.¹¹ The oxygen concentration was uniform within $\Delta y \leq 0.03$ over the volume of the sample according to x-ray diffraction and the width of the Bragg peaks.

Figure 1a shows the frequency dependence of ϵ of a YBCO sample for the three values $y=6.17$, 6.23 , and 6.3 ($\epsilon = Cd/S\epsilon_V$, where C is the capacitance, ϵ_V is the permittivity of free space, and S and d are the area and thickness of the plane capacitor). Similar results were found for PrBCO. The curves are plots of $\epsilon = \epsilon_0 + B\omega^{s-1}$, which describes the frequency dependence of ϵ over the entire frequency range studied. The value $s < 1$ depends on the temperature and the oxygen concentration. An increase in the latter leads to an increase in both ϵ_0 and $\epsilon_{tr}(\omega, T)$. While we have $\epsilon_0 \gg \epsilon_{tr}$ and $\epsilon \approx \epsilon_0$ at $y=6.17$, at $y=6.3$ we have $\epsilon_{tr}(\omega, T) > \epsilon_0$. The effect of the temperature is shown in Fig. 1b, which is a plot of ϵ versus ω^{s-1} for an YBCO sample with $y=6.3$, which is the largest value studied here, so this sample has the largest ϵ_{tr} component. Results are shown for the two temperatures $T=1.1$ and 1.7 K . We see that ϵ_{tr} in-

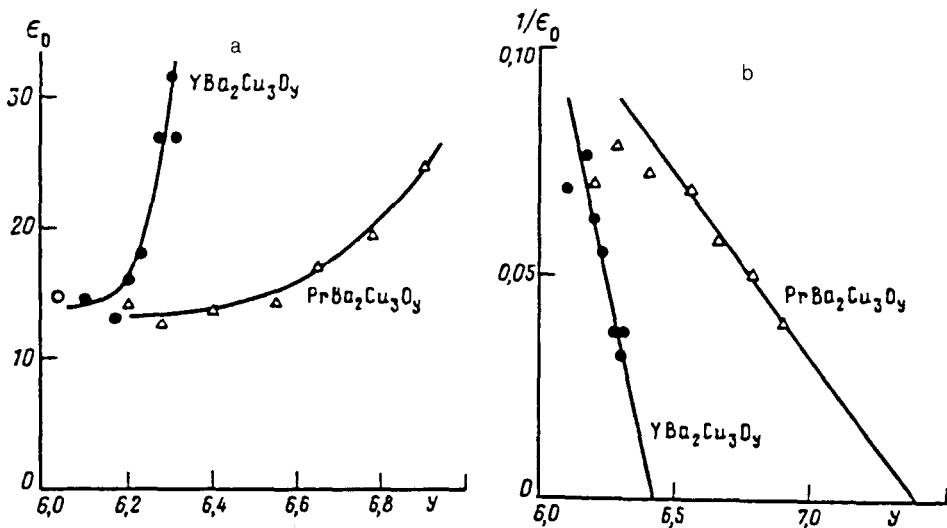


FIG. 2. ϵ_0 (a) and $1/\epsilon_0$ (b) versus the oxygen content in YBa₂Cu₃O_y (filled circles) and PrBa₂Cu₃O_y (triangles). The open circle (o) is a result from Ref. 9.

creases substantially with T and that $\epsilon_0 = \lim \epsilon$ as $\omega^{s-1} \rightarrow 0$ is independent of the temperature.

Figure 2a shows ϵ_0 versus y for YBCO and PrBCO. The open circle shows a value found in Ref. 9 for ϵ_0 for YBCO at 6.04. The quantity ϵ_0 increases with increasing y , because the concentration is approaching the critical value for the insulator-metal transition, y_c . The scatter in the experimental points results from the error in the determination of the oxygen concentration and the variations in this concentration over the volume of the sample. As was shown in Ref. 12, the critical index β for the insulator-metal transition is close to one, and we have $\epsilon_0 \propto |z - z_c|^\beta$, where the parameter z determines the state of the system near the transition. Figure 2b shows the concentration dependence of ϵ_0 for YBCO and PrBCO in the coordinates $1/\epsilon_0$ and y . Within the error, we see a behavior $1/\epsilon_0 \propto |y - y_c|$ near the transition. For YBCO we find a value $y_c \approx 6.45$, in agreement with the data of Refs. 11 and 13, found from measurements of the electrical resistance and the Hall effect. Correspondingly, the value $y_c \approx 7.4$ for PrBCO can be thought of as an estimate of the oxygen concentration required for a transition to the metallic state.

Just why the Pr-based 1-2-3 system is one of the few exceptions to the rule $y_c \approx 6.4-6.6$ for the lanthanides is an open question. Figure 3 shows the value found for y_c in the present study along with data from Refs. 14-16 for Pr_xY_{1-x}Ba₂Cu₃O_y systems, which form a continuous series of substitutional solutions in which Pr atoms replace Y atoms. We see that the dependence is described by $y_c = 6.45 + x$; i.e., an increase in the Pr concentration leads to a linear upward shift in y_c . This behavior is characteristic of compounds containing Pr⁺⁴ ions, which cause a linear (in x) de-

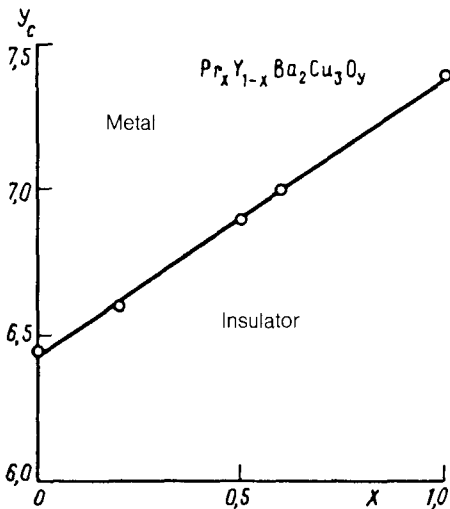


FIG. 3. Critical oxygen concentration for the transition to the metallic state, y_c , of the $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_y$ system versus the Pr content. The values of y_c for $x=0$ and $x=1$ were found in the present study; the other values are from Refs. 14–16.

crease in the number of mobile holes in CuO_2 planes according to measurements of the kinetic properties of $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$ single crystals.¹⁷ At the same time, neutron studies¹⁸ of PrBCO demonstrate convincingly that there are no Pr^{+4} ions, in contradiction of the conclusions reached in Ref. 17. Below we point out a possible reason for this disagreement.

At $y < 6.35$, the $\epsilon_0(y)$ dependence for YBCO (Fig. 2a) is similar to the dependence of the hole density on the oxygen content (Fig. 10 in Ref. 19). The implication is that the observed increase in ϵ_0 with increasing y stems from an increase in the number of impurity states. If we estimate the effective first Bohr radius of the impurity state, a_B , from $\epsilon_0 - \epsilon_{0h} = 4\pi N\alpha_B$, where ϵ_{0h} is the dielectric constant of the lattice in the insulating phase at $y=6.0$, N is the hole density, and $\alpha_B = 9/2\epsilon_{0h}a_B^3$ is the polarizability, then with $y=6.3$ for YBCO and $NV \simeq 0.1$ (Ref. 19), where V is the volume of the unit cell, we find $a_B \simeq 3.1 \text{ \AA}$, i.e., a value on the order of the lattice constants. This result means that describing the localized states in the cuprates by the simple Bohr model for an isolated impurity casts some doubt on its validity. On the other hand, the substantial value of the polar coupling constant, $\alpha_p = (\epsilon_\infty^{-1} - \epsilon_{0h}^{-1})[\text{Ry}/\hbar\omega_{LO}]^{1/2} \simeq 4$, where $\epsilon_\infty \simeq 3.5$ is the optical dielectric constant,²⁰ and $\hbar\omega_{LO} \simeq 35 \text{ meV}$ is the energy corresponding to the midpoint of the phonon spectrum due to vibrations of oxygen atoms,²¹ shows that polaron effects must be taken into account. The pronounced localization of carriers and the large lattice polarizability are apparently governing factors in the shaping of the metallic state in the cuprates.

For PrBCO, in contrast with YBCO, we have no data on the number of impurity states. Nevertheless, the increase in ϵ_0 of PrBCO as it becomes saturated with oxygen correlates with the number of mobile holes,¹¹ and we can estimate an upper limit on the orbital radius of the localized state. With $y=6.9$ and $NV \simeq 0.15$ (Ref. 11) we find $a_B < 2.4 \text{ \AA}$, which implies a localization of the hole within a unit cell. The Pr^{+3} ions in the 1-2-3 system are thus centers of a pronounced localization of holes. At low

temperatures, this circumstance should be manifested in the kinetic properties in the way that the presence of Pr^{+4} ions is manifested.

The relation $\epsilon_{\text{tr}} \gg \epsilon_0$ at elevated temperatures seriously complicates efforts to find a possible contribution to $\epsilon_0(T)$ from ferroelectric transitions. No structural features standing out from the experimental errors have been found in $\epsilon_0(T)$ at low temperatures, where it is possible to correctly separate ϵ_0 and ϵ_{tr} . Measurements of the dielectric constant (Fig. 2) again reveal no manifestations of a structural phase transition involving an ordering of oxygen at $y=6.6$ (Ref. 11).

Finally, we should mention that the linear extrapolation of $1/\epsilon_0$ as a function of y used here (Fig. 2b) is merely the particular way in which the experimental results on polycrystalline samples are represented. It does not have any clear theoretical foundation, since (first) there is a large anisotropy in ϵ_0 along and across the CuO planes as the impurity concentration is raised.²² Second, the strong lattice polarizability near an impurity center and the small localization radius mean that the representation $\epsilon_0 = \epsilon_{0h} + \epsilon_{0i}$, where ϵ_{0h} is the lattice dielectric constant, and ϵ_{0i} is the component due to the impurity polarizability (for which, strictly speaking, the expression $\epsilon_{0i} \propto |z - z_c|^\beta$, holds), requires further justification for the cuprates, which are systems with a predominantly ionic bonding.

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