EVIDENCE FOR ELECTRONIC LOCALIZATION IN $YBa_{2-y}La_yCu_3O_x$

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Electrical resistivity, thermoelectric power, magnetic susceptibility and neutron scattering experiments on $YBa_{2-y}La_yCu_3O_x$, with $y=1$, show that this compound is neither superconductive nor magnetically ordered but are consistent with it being an electronically localized system.

In efforts to understand the physics of the $RBa_2Cu_3O_x$ high temperature superconductors, substitutional studies have concentrated on interchanging rare earth R atoms [1] and replacing some of the Cu atoms with various transition elements [2]. Although these studies have proven useful in revealing aspects important for an understanding of high temperature superconductivity, surprisingly little efford [3] has been given to investigating the role that the Ba sites play in these materials. Because trivalent La is nearly the same size as divalent Ba, it is possible to prepare $RBa_{2-y}La_yCu_3O_x$ with y at least equal to 1. With this substitution the nominal valence of Cu is reduced from 2.3 (for $y=0$) to 2.0 (for $y=1$), assuming that the oxygen content $x\approx 7$ in both cases. Here we report characteristics of $YBaLaCu_3O_x$ that are distinctively different than those of $YBa_2Cu_3O_x$ and suggest a substitutionally-induced transition to a localized state.

Polycrystalline samples of $YBaLaCu_3O_x$ were prepared using standard ceramic techniques with starting materials of Y_2O_3, $BaCO_3$, La_2O_3, and CuO. The starting materials were thoroughly ground together, calcined in air, reground, fired at 1080°C in oxygen and slowly cooled to 400°C before being removed from the furnace. X-ray analysis of the resulting pellets showed a dominant ($\lesssim 90\%$) orthorhombic phase, characteristic of $RBa_2Cu_3O_x$ materials, with lattice parameters $a=3.840$ Å, $b=3.856$ Å and $c=11.55$ Å. These values, compared to $a=3.8203$ Å, $b=3.8855$ Å and $c=11.6835$ Å for $YBa_2Cu_3O_{6.9}$ [4], indicate that La addition reduces the orthorhombiticity. The presence of a minority ($\gtrsim 5\%$) phase that could be indexed to $Y_2Cu_2O_5$ and at least one additional unidentified phase ($\lesssim 5\%$) also was detected. The oxygen content of these samples was not determined, although a similar preparation procedure is known to give $x\approx 7$ in $YBa_2Cu_3O_x$. In this regard, however, a crude analysis of the c-lattice parameter change with La substitution in terms of observations by Segre et al. [3] for $LaBa_{2-x}La_xCu_3O_{7+\delta}$ suggests that our sample may be slightly oxygen deficient. Sections from the pellets were used for electrical resistivity, thermoelectric power and magnetic susceptibility measurements. Several large pellets, combined weight ~50 g, were powdered for magnetic neutron scattering experiments at the National Bureau of Standards reactor. The susceptibility of random pieces from the neutron samples all showed the same temperature dependence.

The inverse magnetic susceptibility $1/\chi$ is shown in fig. 1 as a function of temperature. The Curie–Weiss behavior and maximum in χ at 12 K (see inset) suggest the possibility of antiferromagnetic order. Neutron diffraction at low temperatures failed to reveal any evidence for an antiferromagnetic transition in the majority phase $YBaLaCu_3O_x$. However, clear evidence for antiferromagnetic order at 12 K was found in the second phase $Y_2Cu_2O_5$. Recent susceptibility measurements on this compound by Troc et al. [5] show a maximum in χ at 13 K and at higher temperatures $\chi(T)\propto\mu_{eff}^2/(T-38)$ where

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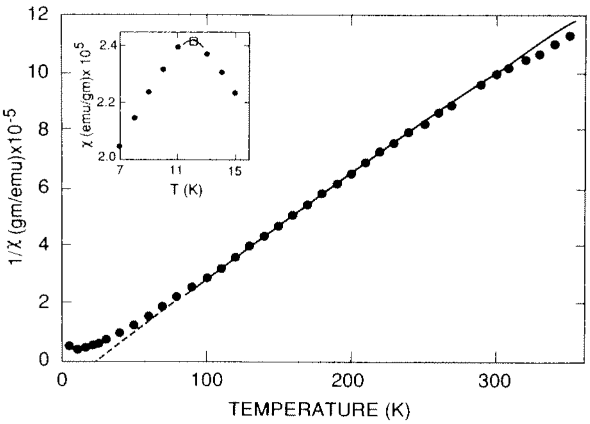

Fig. 1. Inverse magnetic susceptibility $1/\chi$ versus temperature of a sample of nominal composition "$YBaLaCu_3O_x$". The solid line is that expected if 8.5% of the sample weight were $Y_2Cu_2O_5$. The inset shows the presence of a maximum in χ at 12 K that is also consistent with 8.5% $Y_2Cu_2O_5$ (open square symbol).

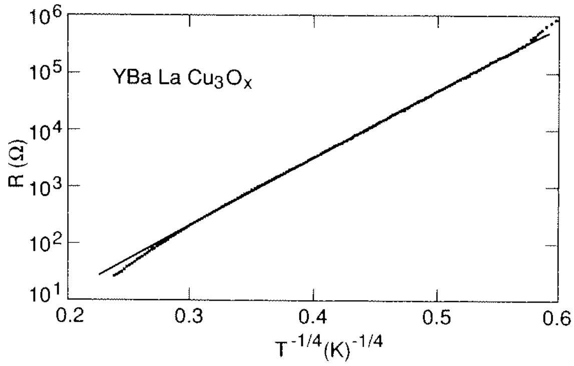

Fig. 2. Resistance of $YBaLaCu_3O_x$ on a logarithmic scale as a function of temperature to the $-1/4$ power.

$\mu_{eff}=2.81\ \mu_B$/formula unit. An analysis of the data in fig. 1 in light of their observations leads to the conclusion that 8.5% of the mass of our sample is $Y_2Cu_2O_5$ and that the remaining fraction has a temperature independent, or at most a weakly temperature dependent, susceptibility of magnitude $\chi_0 \approx 1.6\times10^{-7}$ emu/g. Results of this one-adjustable-parameter analysis are shown by the solid line in fig. 1 and by the square in the inset, which are in good agreement with the data and with the estimate obtained by X-ray analysis of the fractional amount of $Y_2Cu_2O_5$ present. Assuming that χ_0 is due to a Pauli-like contribution from $YBaLaCu_3O_x$ implies that the effective density-of-states at the Fermi energy in $YBaLaCu_3O_x$ is about 1/4 that of the high-T_c superconductor $YBa_2Cu_3O_x$ [6].

The electrical resistance increases monotonically with decreasing temperature and shows no evidence for a superconducting transition above 4 K or for magnetic ordering in $Y_2Cu_2O_5$. In fig. 2 we plot the logarithm of the resistance as a function of $T^{-1/4}$. The linear variation from $9<T<125$ K covers over three orders-of-magnitude increase in resistance and is highly suggestive of transport by three-dimensional (3D) variable-range hopping [7]. Taking $\ln R \propto (T_0/T)^{1/4}$ yields a characteristic temperature $T_0 \approx 5\times10^5$ K, which is comparable in magnitude to values of T_0 found [8] in oxygen-deficient polycrystalline samples of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$. Such behavior is contradistinctive to the linearly temperature dependent resistance observed in polycrystalline $YBa_2Cu_3O_7$ and is indicative of the significant role that Ba atoms play in the conduction process. Although we emphasize that the precise temperature dependence may be influenced by unknown anisotropy effects [9], $YBaLaCu_3O_x$ is not unique in displaying localized-like transport: the resistivity in the Cu–O planes of single crystalline La_2CuO_4 is that expected of correlated 2D or 3D variable-range hopping [9]. For non-superconducting $RBa_2Cu_3O_x$ samples in which $x \lesssim 6.2$ or in which 5 at% Zn has been substituted for Cu, one finds respectively variable-range hopping [10] and weak-3D localization-type conductivities [11].

The thermoelectric power S (fig. 3) of this ma-

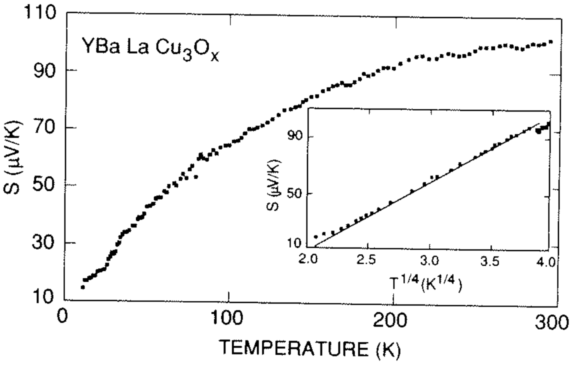

Fig. 3. Thermoelectric power S versus temperature T for $YBaLaCu_3O_x$. The inset shows that S is a linear function of $T^{1/4}$ for the temperature interval $25<T<220$ K.

terial is large and positive, which in a single-band model implies that entropy transport is dominated by a small number of hole-like carriers. The room temperature value of S is nearly 50 times larger than in $RBa_2Cu_3O_7$ [6] and comparable to that found in oxygen-deficient samples of this material [10]. Unlike the nearly temperature independent thermopower of polycrystalline high-T_c compounds [6], we find $S \propto T^{1/4}$ for $25 < T < 220$ K, roughly the same temperature interval over which $\ln R \propto T^{-1/4}$. For 3D variable-range hopping, S should be proportional to $T^{1/2}$ [7,12], clearly not the temperature dependence observed here. However, as in the case of the electrical resistance, anisotropy effects could distort the intrinsic temperature dependence.

Although conductivity in the high-T_c superconductors is generally regarded as being dominated by the Cu–O planes/chains, it is apparant from these results that changes in valence and spatial order of the Ba-site atoms can alter significantly the transport characteristics. In all cases of which we are aware, the approach to a localized-like state (at the expense of superconductivity) is accompanied by a decrease in the state-density at the Fermi level, whether it be produced by oxygen depletion [10], Cu substitution [11] or, in this case, a replacement for Ba, as well as the introduction of disorder on one of these sites. Clearly, these observations should be considered in attempts to raise T_c above 100 K.

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