Magnetic studies of strontium lanthanum copper oxides

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We report measurements of static magnetic susceptibilities for a series of strontium-substituted lanthanum copper oxides prepared under identical conditions. These materials have recently been shown to exhibit bulk superconductivity with high critical temperatures. Measurements of the end member La_2CuO_4 provide evidence for a phase transition of unknown origin at ≈ 260 K. This phase transition is suppressed by the substitution of small amounts of strontium for lanthanum. Understanding the normal-state properties of $Sr_xLa_{2-x}CuO_{4-\delta}$ may provide important clues to the superconducting behavior of these materials.

INTRODUCTION

Recent reports of high-temperature superconductivity in alkaline-earth-substituted lanthanum copper oxides having K_2NiF_4-type structures[1] have led to great interest in these phases. Prior to the discovery of superconductivity, they had been studied for possible applications in electrocatalysis and oxygen sensing and as model systems for magnetism in two-dimensional systems.[2-4] A possible superconducting transition was first reported in the Ba-La-Cu-O system by Bednorz and Müller,[1] with the superconducting phase subsequently identified as having the stoichiometry $La_{2-x}Ba_xCuO_{4-\delta}$ and structure of the K_2NiF_4 type by Takagi, Uchida, Kitazawa, and Tanaka.[5] Superconducting properties of the lanthanum copper oxide system were significantly improved by the substitution of strontium for lanthanum, forming the system[6-9] $La_{2-x}Sr_xCuO_{4-\delta}$ with transition temperatures[10] as high as 40 K.

Few other superconducting oxide systems are known. Those with reasonably high T_c's, A_xWO_3, A = K or Rb,[11] $Li_{1+x}Ti_{2-x}O_4$,[12] and $BaPb_{1-x}Bi_xO_3$,[13] have several features in common.[14] Superconductivity occurs over only a limited composition range with the superconducting region bounded by semiconducting and metallic regions. Also, T_c is highest near the semiconducting phase boundary. Finally, all contain octahedrally coordinated metal atoms. However, $BaPb_{1-x}Bi_xO_3$ is unique among this set of materials in having significant oxygen orbital participation at the Fermi level.[15] Calculations by Mattheiss suggest that in $Sr_xLa_{2-x}CuO_{4-\delta}$, like $BaPb_{1-x}Bi_xO_3$, conduction electrons also have significant O $2p$ character.[16]

To understand superconductivity in $Sr_xLa_{2-x}CuO_{4-\delta}$, it is essential to understand the normal state properties of this material. We report here the magnetic properties of a series of strontium-substituted lanthanum copper oxides $Sr_xLa_{2-x}CuO_{4-\delta}$ prepared under identical conditions to facilitate comparison of their behavior.

EXPERIMENTAL PROCEDURE

Samples of $Sr_xLa_{2-x}CuO_{4-\delta}$ were prepared from high-purity $La(OH)_3$ $SrCO_3$, and CuO powders using standard powder ceramic procedures. Processing steps include reaction at 1000 °C for several days with intermediate grindings, pressing into pellets, sintering at 1100 °C, and a final oxygen anneal, typically at 700 °C. Samples were single phase as determined by powder x-ray diffraction.[6] Properties of samples prepared under identical conditions are reproducible.

Magnetic susceptibility was measured on polycrystalline samples from 4.2 to 400 K using the Faraday technique. While details of this apparatus have been described elsewhere,[17] in brief, low-temperature data are obtained at intervals of about 1 K using a He-flow cryostat cooled at an average rate of 1 K/min. The relative accuracy of χ_g is approximately $\pm 1\times 10^{-1}$ emu/g or less depending on the sample size, although the absolute accuracy of the susceptibility is $\pm 2\%$ as determined by a comparison to several standards. No attempt was made to prove random orientation of the powder which was pressed into pellets prior to the measurement. In all experiments, the applied field was 14 kOe and the measured susceptibility was checked for field dependence at several temperatures.

RESULTS

The temperature dependence of the magnetic susceptibility of La_2CuO_4 had been reported previously.[18,19] In Fig. 1, we show our data for La_2CuO_4. The susceptibility, uncorrected for core diamagnetism, is paramagnetic. A major feature of the data is the steep rise in the magnetic susceptibility below ≈ 380 K. Below 40 K, a diamagnetic downturn, corresponding to the onset of superconductivity in a minor component of the sample, is observed. This superconducting component is estimated to constitute only 0.1–0.01% of the sample based on measurements of the Meissner effect.[20] This concentration is well below the limits of detection of powder x-ray diffraction. Above 400 K, the magnetic susceptibility for this sample shows a slow increase with increasing temperature. The rise in magnetic susceptibility below 380 K is the result of a phase transition occurring at 260 K. This is indicated by the peak in the derivative of the susceptibility with respect to temperature, $d\chi/dT$. A second peak in $d\chi/dT$ at 40 K corresponds to the superconductivity onset. The orthorhombic to tetragonal phase transition reported to occur

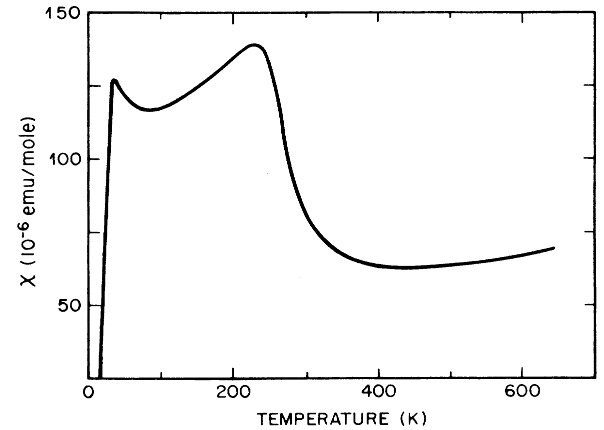

FIG. 1. Susceptibility vs temperature for La_2CuO_4.

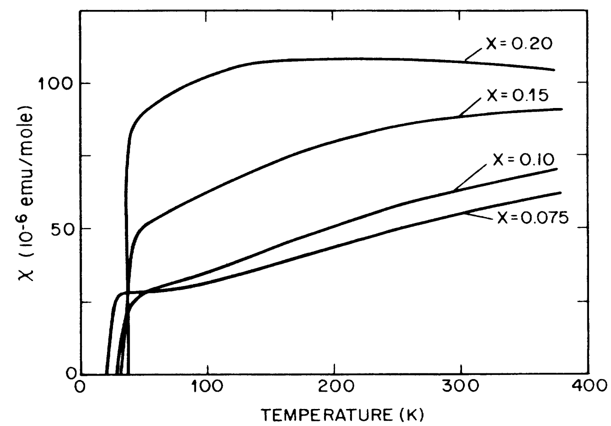

FIG. 3. Susceptibility vs temperature for $Sr_xLa_{2-x}CuO_{4-\delta}$ samples with $x = 0.075$, 0.10, 0.15, and 0.20.

at ≈ 570 K in this material[21] produces no change in the magnetic susceptibility.

Substitution of small amounts of strontium for lanthanum completely suppresses the transition at 260 K. Figure 2 shows data for $Sr_xLa_{2-x}CuO_{4-\delta}$, $x = 0.03$ and 0.05. The net susceptibilities, again uncorrected for the core diamagnetism of the sample, are paramagnetic. The data for the $x = 0.03$ sample can be fit to a Curie-Weiss form $\chi - \chi_0 = C/T - \Theta$ from 0 to 120 K. If higher-temperature data are included, the quality of the fit decreases. The Curie constant C_M is 7690 emu K/mol, corresponding to a moment of 0.15 Bohr magneton (μ_B) per Cu atom. The fit yields a theta value of 2 K. If the Curie-Weiss component is subtracted from the data, a residual remains in which the susceptibility increases slowly with increasing temperature and shows a change in slope at about 120 K. The data contain no sign of the 260-K anomaly seen in La_2CuO_4. For $x = 0.05$, the susceptibility decreases slowly with decreasing temperature, then, below 50 K, rises slightly. The data from 5 to 50 K were fit to a Curie-Weiss form yielding a Curie constant C_M of 490 emu K/mol and theta value of 1 K. Assuming the moment resided on the copper, this Curie constant would correspond to $0.06\mu_B$ per Cu atom, a very small value. Instead, this small Curie constant indicates that the low-temperature tail likely arises from isolated paramagnetic impurities from the starting material or is introduced into the sample during processing. With the low-temperature tail subtracted from the data, the susceptibility is nearly temperature independent. These samples are not superconducting above 4.2 K.

As with the end member La_2CuO_4, samples with $x > 0.06$ in $Sr_xLa_{2-x}CuO_{4-\delta}$ are superconductors.[22] As shown in Fig. 3, in samples with $x = 0.075$, 0.10, and 0.15, the magnetic susceptibility decreases smoothly with decreasing temperature with steep diamagnetic downturns at low temperature corresponding to the onset of superconductivity. This diamagnetic onset increases in temperature, going from $x = 0.75$ to $x = 2.0$. Fleming, Batlogg, Cava, and Rietman have documented[23] the temperature dependence of the tetragonal-orthorhombic transition as a function of x in $Sr_xLa_{2-x}CuO_{4-\delta}$, and there is no correlation between this structural transition and any feature we have seen in the susceptibility. While the rate of

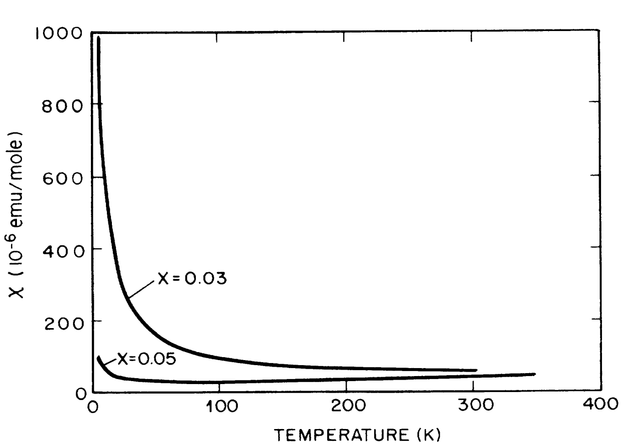

FIG. 2. Susceptibility vs temperature for $Sr_xLa_{2-x}CuO_{4-\delta}$ samples with $x = 0.03$ and 0.05.

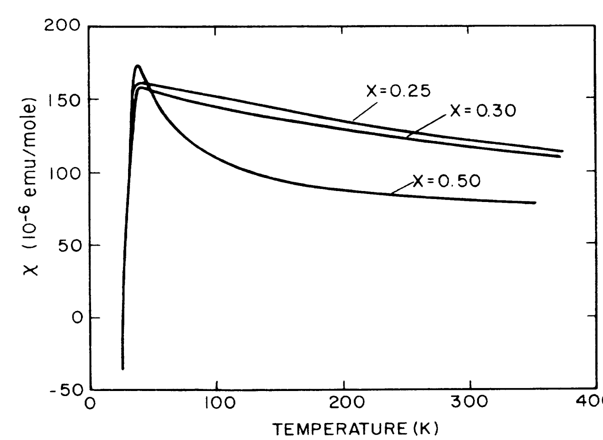

FIG. 4. Susceptibility vs temperature for $Sr_xLa_{2-x}CuO_{4-\delta}$ samples with $x = 0.25$, 0.30, and 0.50.

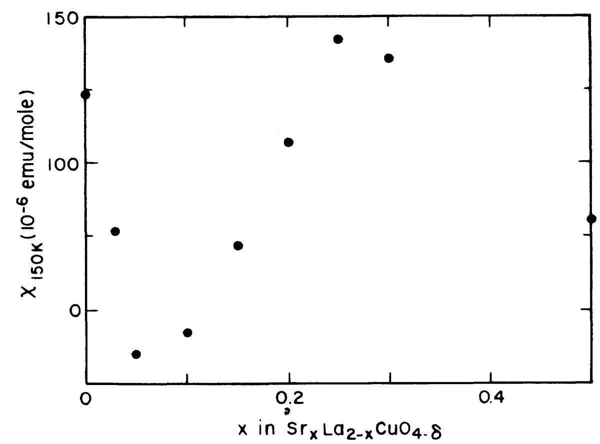

FIG. 5. Molar susceptibility measured at 150 K vs x in $Sr_xLa_{2-x}CuO_{4-\delta}$.

change of the susceptibility with temperature is not constant, no clear signatures of phase transitions other than the onset of superconductivity are observed in the data. For $x=0.20$, the magnetic susceptibility is nearly temperature independent to 120 K, then decreases slowly with decreasing temperature. Again, there is no peak in $d\chi/dT$, indicative of phase transitions, in the temperature dependence of the magnetic susceptibility of any of these samples.

As shown in Fig. 4, the temperature dependence of the magnetic susceptibilities of samples with $x=0.25$ and 0.30 are nearly identical. The susceptibility increases slowly with decreasing temperature. For $x=0.50$, the susceptibility is strongly temperature dependent above the onset of superconductivity. The high-temperature data can be fit to a Curie-Weiss form yielding $C_M=4590$ emu K/mol and $\Theta=2$ K. This would correspond to a moment per copper of $0.192\mu_B$.

Figure 5 shows the variation in molar susceptibility with x for $Sr_xLa_{2-x}CuO_{4-\delta}$ at 150 K. The susceptibility falls sharply from $x=0$ for samples which are semiconducting ($x=0.03$, 0.05), then begins to rise in samples which display superconductivity. Above $x=0.25$, the susceptibility again begins to decrease. The same variation is seen for molar susceptibilities measured at 280 K.

DISCUSSION

In contrast to the other known lanthanide cuprates which are semiconductors, La_2CuO_4 does not exhibit simple semiconducting behavior.[24] Initial measurements[21] found a low, nearly temperature-independent resistivity and weak paramagnetism in the magnetic susceptibility of La_2CuO_4. Resistivity measurements[25] on La_2CuO_4 prepared in our laboratory show a peak in ρ near 200 K and activated behavior at temperatures below this. Ganguly, Kollali, Rao, and Kern,[18] reported that this material shows a slight maximum in χ around 230 K. Similarities were noted between the behavior of this compound and other low-dimensional materials including $KCuF_3$ and Ca_2MnO_4.

Interesting parallels have been noted[16] between the superconducting oxide systems $La_{2-x}Sr_xCuO_{4-\delta}$ and $BaPb_{1-x}Bi_xO_3$. In $BaPb_{1-x}Bi_xO_3$, the magnetic susceptibility is weakly diamagnetic throughout the alloys, consistent with their low density of states $N(0)$. The net susceptibility increases slightly with increasing bismuth concentration, then decreases again as the alloy system approaches the metal-semiconductor transition. The susceptibility rises again in the semiconducting regime,[26] presumably due to a paramagnetic component of unknown origin. Two mechanisms have been proposed to account for the metal-semiconductor instability in the barium lead bismuthate system. The first assumes a strong electron-phonon interaction leading to a charge-density wave (CDW) instability, while the second proposes effects resulting from inhomogeneity, either oxygen vacancies or bismuth segregation.

In contrast to $BaPb_{1-x}Bi_xO_3$, the $Sr_xLa_{2-x}CuO_{4-\delta}$ system is paramagnetic throughout the alloy system. The minimum in the susceptibility occurs at the junction between superconducting and nonsuperconducting samples. The susceptibility reaches its maximum near the doping level yielding the highest T_c and largest Meissner effect.[25] In an earlier study of the high-temperature behavior of the magnetic susceptibility in the series $Sr_xLa_{2-x}CuO_{4-\delta}$,[27] this variation in susceptibility was attributed to the change from localized behavior in La_2CuO_4 to metallic behavior in the doped materials followed by the effects of an increasing Cu III component as a function of strontium incorporation. Superconducting measurements[28] have been interpreted within the context of conventional theories to infer a density of states at the Fermi level for $Sr_xLa_{2-x}CuO_{4-\delta}$ that is four times that of $BaPb_{1-x}Bi_xO_3$. These results are consistent with a higher density of states for this material leading to a larger Pauli paramagnetism and a net paramagnetic susceptibility.

As in the barium lead bismuthate system, charge-density waves have been invoked to account for aspects of the behavior of the $Sr_xLa_{2-x}CuO_{4-\delta}$ alloy system.[16] Mattheiss[16] finds near-perfect nesting of the calculated Fermi surface which would favor a CDW distortion opening up a gap at the Fermi surface and preventing superconductivity. He suggests that the role of the alkaline-earth substituent is to suppress the CDW distortion.

While CDW's may be important in $Sr_xLa_{2-x}CuO_{4-\delta}$ phases, the susceptibility peak observed in La_2CuO_4 is most likely not related to CDW's. The onset of a CDW opens gaps at the Fermi surface thus lowering the density of states at the Fermi surface. Typically, then, the Pauli contribution to the magnetic susceptibility is decreased and the magnetic susceptibility decreases at the CDW onset. In this case, however, the magnetic susceptibility shows a maximum which suggests antiferromagnetic interactions. However, Curie-Weiss behavior is not observed at temperatures above the peak as would be expected in the case of normal antiferromagnetism.

Anderson[29] has proposed an alternative mechanism to account for the peculiar magnetic properties of La_2CuO_4. He suggests that as a consequence of the low dimensionality of the structure formed by La_2CuO_4, with copper in the low spin state $S=\frac{1}{2}$, a "resonanting valence band" state is formed. This state consists of nearest-neighbor singlet pairs stabilized through a Pauling-type resonance among an array of these pairs. In undoped La_2CuO_4, these pairs may lead to the antiferromagnetic-like peak in the magnetic susceptibility at 260 K. Anderson proposes that these preexisting magnetic singlet pairs then convert to charged superconducting pairs upon sufficient doping. Indeed, the peak observed in the magnetic susceptibility of La_2CuO_4 is suppressed with small additions of alkaline-earth dopant. However, superconductivity is not seen until the strontium level reaches $x=0.06$ for $Sr_xLa_{2-x}CuO_{4-\delta}$.

Surprisingly, we do not see a magnetic signature for the othorhombic-tetragonal phase transition at 533 K in La_2CuO_4. Also, we do not see clear evidence for this structural phase transition at lower temperatures in the strontium-substituted lanthanum copper oxides, suggesting that this transition has little effect on the electronic properties of these materials, and casting some doubt on its role in the occurrence of superconductivity.

In summary, then, magnetic susceptibility provides insights into the normal-state behavior of $Sr_xLa_{2-x}CuO_{4-\delta}$. Recent ideas of Anderson concerning a "resonanting valence band" state are consistent with our observation of a peak in the magnetic susceptibility of La_2CuO_4 at 260 K. Incorporation of the alkaline-earth substituent, strontium, causes this feature to vanish and promotes the formation of a superconducting state.

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