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Influence of oxygen defects on the physical properties of La_2CuO_{4-y}

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We present the results of magnetic-susceptibility, heat-capacity, electrical-resistivity, and thermoelectric-power measurements on La_2CuO_{4-y}. The crystallographic, magnetic, and electronic transport properties are found to be extremely sensitive to the oxygen-defect concentration y. Coupled with x-ray and neutron-diffraction data presented in a companion paper, we find that long-range antiferromagnetic order develops with increasing y out of a nonmagnetic ground state at $y \simeq 0$ into a state with a maximum Néel temperature of 290 K at $y \simeq 0.03$.

La_2CuO_{4-y} is the parent compound of the doped high-temperature ($T_c \lesssim 40$ K) superconductors $La_{2-x}(Sr,Ba)_xCuO_{4-y}$ with $x \approx 0.2$.[1,2] It has a room-temperature structure which is an orthorhombic distortion of the tetragonal K_2NiF_4 structure.[3] The latter structure is regained upon heating above a transition temperature T_0 of 506–536 K;[4] the variation in T_0 is thought to arise from differences in y between different samples,[4] but a quantitative correlation has not before been established. The low-temperature structure[5] and the temperature dependence of the orthorhombic distortion parameter[6] have recently been studied using neutron diffraction. The electrical resistivity ρ and thermoelectric power S of sintered samples are nearly independent of temperature from 100–1100 K,[5,7–13] but the carriers appear to localize at lower temperature T.[5,10,13] A large scatter of unknown origin is present in the reported room-temperature S values (100–500 μV/K). Measurements of the magnetic susceptibility $\chi(T)$ have revealed peaks between 220 and 280 K in some samples of La_2CuO_{4-y} [Refs. 7(a), 10, 13–16] but not in others,[9,17] which is another discrepancy of unknown origin. The χ peak has variously been deduced to arise from a smooth vanishing of localized magnetic moments with decreasing T (Ref. 10) or from the occurrence of an antiferromagnetic (AF) or spin-density-wave transition;[13–16] the T at which the anomaly occurs depends on the details of sample preparation and handling.

We have carried out a series of experiments to clarify the physical properties of pure La_2CuO_{4-y} as a starting point to understand and differentiate between various microscopic mechanisms for the occurrence of high-T superconductivity in the Sr- and Ba-doped compounds. Herein, we report the results of $\chi(T)$, heat-capacity, $\rho(T)$, and $S(T)$ measurements which establish that the crystallographic, magnetic, and electronic transport properties are extremely sensitive to the concentration of oxygen defects y in La_2CuO_{4-y}.[15] This sensitivity provides one explanation for the discrepancies noted above. Perhaps our most interesting results are that, in conjunction with companion x-ray and neutron-diffraction results,[6] the χ peak above is indeed due to long-range AF order, and that this order develops with increasing y out of a nonmagnetic ground state for $y = 0$ into a state with a maximum Néel temperature T_N of 290 K at $y = 0.03$. Subsequent polarized[18] and unpolarized[19] neutron-diffraction studies have confirmed the occurrence of AF order in La_2CuO_{4-y}.

La_2CuO_{4-y} was prepared in air at 950 °C and oven cooled. The neutron-diffraction data[6] obtained on this sample revealed no impurity phase peaks. A portion of this sample was heated to 500 °C under 600 psi of O_2, increasing the weight by about 0.06%, corresponding to a decrease in y of about 0.015. From separate gravimetric measurements, the oxygen-treated sample is stoichiometric La_2CuO_4 ($y = 0 \pm 0.02$). Thus, for the oven-cooled sample, $y \simeq 0.015$.

$\chi(T)$ data measured using the Faraday method at a heating rate of 0.6 K/min are plotted in Fig. 1 for the two La_2CuO_{4-y} samples described above, corrected for the contributions of ferromagnetic impurities. Also shown is $\chi(T)$ for the oven-cooled sample after heating to 750 K in the 30 torr of He exchange gas in the magnetometer (labeled "+ VAC/750 K"); these data were obtained immediately following the previous experiment without removing the sample from the magnetometer. The corresponding weight loss, measured *in situ*, was about 0.05%, thereby increasing y from 0.015 to about 0.03.

The $\chi(T)$ data in Fig. 1 for the oven-cooled and vacuum-treated samples are in quantitative agreement

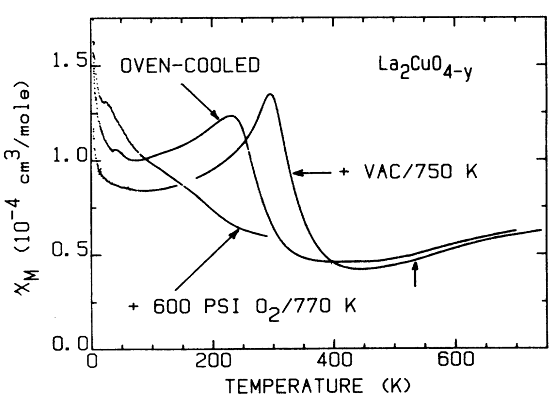

FIG. 1. Magnetic susceptibility χ_M vs temperature for three samples of La_2CuO_{4-y}.

with certain results of the other recent χ studies.[13,14,16] As noted above, the χ peaks above 200 K are due to long-range AF ordering. Several features are important from Fig. 1 and from the gravimetric data above. First, T_N is extremely sensitive to the oxygen-defect concentration y, increasing from $T_N \sim 0$ at $y=0$ to 290 K at $y=0.03$. Second, expanded plots of the data near T_N reveal very smooth maxima, with no distinguishable slope discontinuities as would be expected at the onset of long-range AF order. Third, the temperatures at which χ is maximum, 230 K for $y=0.015$ and 296 K for $y=0.03$, are significantly above those at which $d\chi/dT$ is maximum, 205 and 283 K, respectively; in other cases, the latter temperatures are usually identified as the T_N values. The neutron-diffraction data yielded $T_N=220\pm10$ K for the oven-cooled sample[6] and $T_N=290\pm30$ K for a sample with a nearly identical $\chi(T)$ as our $y=0.03$ sample,[18] consistent with either measure of T_N from the $\chi(T)$ data. Thus, the second and third features above together indicate either that the transition is smeared out due to oxygen-defect inhomogeneity, or that short-range AF order is significant above T_N, or both. Fourth, the magnetism is nearly decoupled from the tetragonal-orthorhombic (t-o) phase transition, as only a small slope discontinuity occurs at $T_0=530$ K for the VAC/750 K sample (marked by an arrow in Fig. 1). Fifth, even though we know from the neutron-diffraction work that the χ anomalies correspond to AF ordering, the Curie-Weiss law $\chi=C/(T-\Theta)$ is not followed above T_N; in fact, $\chi(T>400\text{ K})$ increases with T rather than decreases as expected for a Curie-Weiss law. Further, plotting χ^{-1} vs T for $T\gtrsim T_N$ yields positive values for the Weiss temperature: $\Theta=+203$ and $+270$ K for $y=0.015$ and 0.03, respectively, in contrast to the negative values expected for an antiferromagnet. Finally, the magnitudes of $\chi(T_N)$ are roughly a factor of 2–4 smaller than expected for Cu^{+2} with Landé g factor $g\approx2$ (Ref. 20) and spin $S=\frac{1}{2}$. This reduction does correlate, however, with the reduction of the ordered moment below T_N from the calculated value $\mu=gS\mu_B\approx1$ μ_B/Cu ion to the value of 0.5 μ_B/Cu ion found from neutron diffraction,[6,18] and with the reduced dc χ computed from ESR spectra.[20] Heat-capacity studies from 100 to 300 K (Ref. 21) show no features associated with the T_N values, consistent with oxygen disorder or short-range AF order above T_N.

The variation of T_N with y in La_2CuO_{4-y} from Fig. 1 is plotted in Fig. 2, where we have also included the variation of T_0 with y determined using neutron diffraction[6] and calorimetry (DuPont 1090 Differential Scanning Calorimeter). From these data, the orthorhombic-tetragonal (o-t) transition is second order. T_0 as well as T_N is seen to increase strongly with y. The value of T_0 (450 K) for $y=0$ is much lower than the lowest value (500 K, Ref. 4) previously reported, indicating that this sample is more stoichiometric than obtained until now, consistent with assigning $y=0$ to this sample.

Shown in Fig. 3 are four-probe $\rho(T)$ data for a new sample prepared from La oxalate and CuO with an air quench from 1000 °C. The data were taken with increasing T at 0.6 K/min under 30-torr He gas. The T_N value of 250 K from a separate χ measurement is indicated.

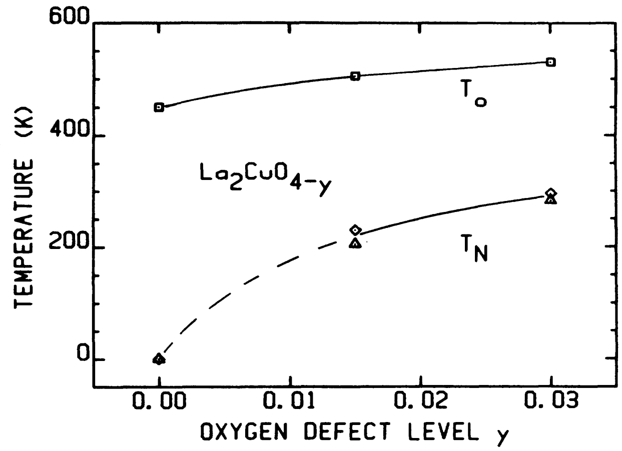

FIG. 2. Orthorhombic-tetragonal T_0 and antiferromagnetic T_N transition temperatures vs oxygen-defect concentration y. For the latter, the diamonds are the temperatures at which χ peaks and the triangles the temperatures where $d\chi/dT$ is maximum.

From Fig. 2 and the values of T_0 (530 K, calorimetric data) and T_N, $y\approx0.02$ initially. A superconducting (SC) transition apparently occurs below 39 K; from Meissner effect data, only about 0.03% of the sample becomes SC, suggesting that a SC impurity phase is present in the grain boundaries. Similar SC transitions have been observed in La_2CuO_{4-y} by others.[16,22] The strong upturn in ρ below 100 K suggests an insulating ground state, but the slope of $\rho(T>300\text{ K})$ is positive, suggesting semimetallic character. A weak inflection point at 250 K is the only manifestation in ρ of AF ordering at that T. Thus, the current carriers are evidently only weakly coupled to the magnetization. This is surprising, since the sources of the carriers and the magnetic moments are presumably the same, namely, the Cu atoms. The strong increase in ρ above 500 K arises from loss of oxygen from the sample, since ρ is nearly independent of T up to 1100 K if the

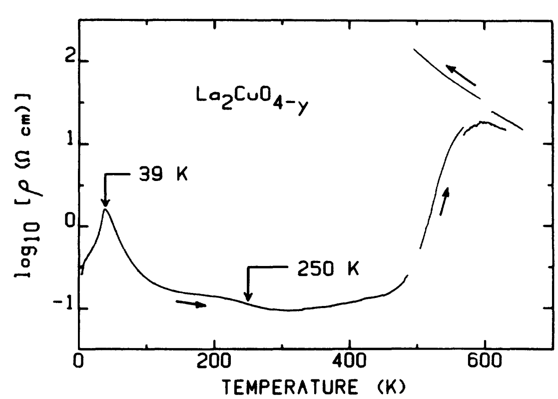

FIG. 3. Electrical resistivity ρ vs temperature for $La_2CuO_{3.98}$. The data have been normalized to $\rho(300\text{ K})=0.1$ Ω cm after Ref. 7.

measurement is carried out in air or oxygen.[7] From gravimetric data on similarly prepared samples, heating to 650 K in Fig. 3 has increased y from 0.02 to about 0.03. Upon cooling from 650 K, ρ is seen to be much different, increasing with *decreasing* temperature. The data between 500 and 600 K on cooling closely follow the relation $\rho=\rho_0\exp(\Delta/T)$, with $\rho_0=0.03$ Ω cm and a large activation energy $\Delta=4200$ K (0.36 eV). The energy gap is therefore large, $E_g\simeq 2\Delta=0.72$ eV! Thus, $La_2CuO_{3.97}$ is an insulator at low T [ρ(295 K) was too large to measure with the same equipment]. There is no obvious feature at $T_0=530$ K in the data between 500 and 600 K taken on cooling. This indicates that the current carriers couple only weakly to the lattice modes responsible for the orthorhombic distortion, consistent with previous $\rho(T)$ data on more conducting samples.[7]

From the above results, the following important point can be made. The occurrence of neither the o-t phase transition nor the AF transition requires the presence of degenerate current carriers. This limits the range of theories applicable to La_2CuO_{4-y}. For example, the o-t transition is not electronically driven,[23] as often assumed or theorized,[5,24] since a metal-semiconductor transition apparently does not occur there (see also Ref. 7).

We have also investigated the transport properties of the samples in Fig. 1, but only below 350 K. Shown in Fig. 4(a) are $\rho(T)$ data for the three samples and in Fig. 4(b) are S (T) data for two of them. From Figs. 3 and 4, the mobility and/or carrier density first increases with y, then strongly decreases. For $y=0.03$ above 200 K, ρ follows the activated relationship above, with $\rho_0=0.17$ Ω cm and with $\Delta=1340$ K, about a factor of 3 lower than for the $y=0.03$ sample of Fig. 3; however, the present sample was exposed to air following the $\chi(T)$ measurement in Fig. 1, which may have decreased y slightly. From Fig. 4, both $\rho(T)$ and $S(T)$ are strongly dependent on y. The $S(T)$ data near T_N indicate only weak coupling of the carriers to the magnetization, consistent with our conclusion from the $\rho(T)$ data.

In summary, we have quantitatively demonstrated how certain crystallographic, magnetic, and electronic transport properties of La_2CuO_{4-y} vary with the concentration y of oxygen defects present in the samples, and these properties were found to be extremely sensitive to y. The superconducting properties of $La_{2-x}Sr_xCuO_{4-y}$ are also very sensitive to the presence of oxygen defects.[2] It will be important to determine whether the Cu spins survive the doping process in the superconducting $La_{2-x}(Sr,Ba)_xCuO_{4-y}$ systems, since the existence of local magnetic moments and/or strong electron-spin correlations in these compounds might provide one component of a microscopic pairing mechanism for producing the observed high superconducting transition temperatures.[25] A theoretical understanding of why the magnetism of La_2CuO_{4-y} depends so sensitively on y and why $\chi(T>T_N)$ is so uncharacteristic of an antiferromagnet will also be important in the context. Experimental and theoretical investigations of the possible role of La and/or Cu defects[16] would be valuable.

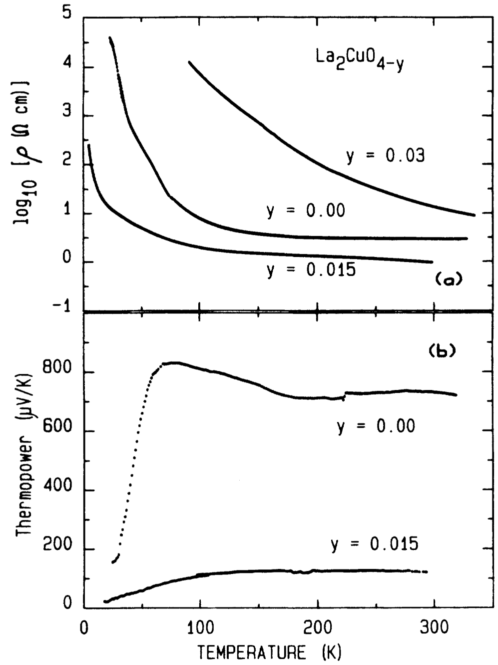

FIG. 4. (a) Resistivity ρ vs temperature for the three samples of Fig. 1. (b) Thermoelectric power vs temperature for two of the samples in Fig. 1.

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