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Anisotropic electronic and thermal transport properties of lightly oxygen-doped $La_2CuO_{4+\delta}$

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We track the systematic variation in magnetic susceptibility (χ), thermal conductivity (κ), anisotropic resistivity (ρ), an thermoelectric power (S) of crystalline $La_2CuO_{4+\delta}$ as a function of light hole doping. The level of hole doping (δ) was carefull varied by anneals under controlled oxygen-partial-pressure performed in such a way that the antiferromagnetic ordering temper ature T_N ranged from 250 to 310 K. χ data indicate that increased oxygen hole doping acts to reduce T_N below the $\delta=0$ value o 320 K. Anomalies are present in κ at T_n that result from Cu spin fluctuations about the magnetically ordered ground state. Anom alies are also present in ρ and S that occur at T_N for air-annealed samples wherein $T_N=250$ K; when more lightly hole-doped s that $T_N>250$ K, the anomalies in ρ and S do not occur at T_N, but instead occur at $T<250$ K. In analogy with heavily oxygen loaded $La_2CuO_{4+\delta}$, these transport anomalies may result from phase separation involving the diffusion of non-stoichiometric excess oxygen.

1. Introduction

Extensive research carried out during the past three years indicates that $La_2CuO_{4+\delta}$ is remarkable material [1]. In its undoped state ($\delta\approx 0$), $La_2CuO_{4+\delta}$ is a Mott–Hubbard or charge-transfer insulator. In addition, the Cu moments undergo two-dimensional short-range magnetic order at temperatures far above room temperature [2,3], while complete three-dimensional antiferromagnetic order sets in at $T_N\approx 328$ K [2,4]. When the material is hole-doped by replacing 10% of the lanthanum by strontium, it becomes metallic and undergoes a "high-temperature" superconducting transition at $T_c\approx 40$ K [5]. Strontium doping also acts to destroy long range antiferromagnetic Cu order. $La_2CuO_{4+\delta}$ can be hole-doped as well by adding excess oxygen to the system (i.e. $\delta>0$). The presence of the excess oxygen produces frustration in the antiferromagnetic copper-spin sublattice, resulting in the reduction of T_N below 328 K [2,7]. Extreme oxygen loading via high-pressure annealing ($\delta\approx 0.032$) induces bulk superconductivity near 40 K [8].

Temperature-dependent neutron diffraction studies indicate that heavily oxygen loaded $La_2CuO_{4+\delta}$ is susceptible to reversible phase separation involving oxygen diffusion. These studies, which have examined both powder [9] and crystalline samples [10,11], indicate that this material is composed of both oxygen-poor ($\delta\approx 0$) and oxygen-rich ($\delta>0$) phases at temperatures below the phase separation temperature. This phase separation gives rise to dramatic anomalies in both the resistivity and the thermoelectric power which can be understood from the coexistence of a carrier-deficient phase ($\delta\approx 0$) and a carrier-rich phase ($\delta>0$) [12]. Large anomalies have also been reported in the resistivity and thermoelectric power of lightly doped $La_2CuO_{4+\delta}$ [13]. In these 1 bar air-annealed single crystals ($\delta\approx 0.005$ as determined from Hall effect measurements and $T_N=250$ K as determined from χ measurements), the transport anomalies occur precisely at T_N. A large negative magnetoresistance has also been detected in 1 bar air-annealed $La_2CuO_{4+\delta}$ at the onset of a magnetic-field-induced metamagnetic transition [14].

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Hence, there appears to be a strong coupling between transport and magnetism in $La_2CuO_{4+\delta}$. Nonetheless, the transport anomalies present at T_N in air-annealed crystals are thought to be far too large to be attributed solely to the onset of magnetic order [13].

To determine the cause of the anomalous transport in 1 bar oxygen annealed $La_2CuO_{4+\delta}$, as well as to map out the overall evolution of this material's transport properties, we have carried out a systematic doping and transport study of this compound. Anisotropic resistivity (ρ), thermoelectric power (TEP), magnetic susceptibility (χ), and thermal conductivity (κ) measurements were performed on $La_2CuO_{4+\delta}$ single crystals whose excess oxygen content was carefully varied through controlled anneals. The anneals were used to tune the excess oxygen content such that the crystal's Néel temperature could be continuously varied from 250 K (corresponding to a 1 bar air anneal) to 320 K (corresponding to an anneal in pure N_2). For all excess oxygen levels, the thermal conductivity shows a distinctive anomaly near T_N which is attributed to the influence of spin fluctuations about the ordered antiferromagnetic state. For the same weak-doping levels, the TEP and resistivity display high-temperature activated behavior and a low-temperature hopping state. As with the earlier work on samples with $T_N = 250$ K, large anomalies are present in both the resistivity and the TEP at T_N for crystals with $T_N = 250$ K. When the excess oxygen content is reduced, thus increasing T_N, the temperature T_a at which the transport anomaly occurs does not track the Néel temperature, but instead drops in value below 250 K. Hence, in general $T_a \neq T_N$ unless the excess oxygen content is sufficient to lower the Néel temperature to 250 K. Moreover, the anomalies for dopant levels such that $T_a \neq T_N$ are both smaller in magnitude and are spread over a larger temperature range than is the case when $T_a = T_N$. These systematics strongly suggest that the transport anomalies stem from the same type of phase separation that occurs in heavily oxygen-loaded $La_2CuO_{4+\delta}$. In addition, the underlying magnetic order may also have some influence on the separation-induced anomalies when the separation occurs near the onset of antiferromagnetism.

The remainder of this paper is organized as follows. A description of the sample preparation techniques and experimental methods are presented in section 2. The experimental results are presented in section 3, followed by discussion and analysis in section 4. Lastly, a brief summary and concluding remarks appear in section 5.

2. Materials and experimental techniques

The $La_2CuO_{4+\delta}$ single crystals were grown from a CuO-rich La_2O_3–CuO melt in a platinum crucible. Large crystals were obtained, with their ultimate size ($3 \times 3 \times 0.3$ cm^3) limited only by the platinum crucible dimensions. The measurements reported here were performed on three $La_2CuO_{4+\delta}$ single crystals that all came from the same growth batch. The TEP and resistivity measurements were performed on two crystals that were grown from the same batch and post-annealed side-by-side. The first crystal, measuring $1.3 \times 1.1 \times 1.0$ mm^3, was used solely to measure *ab*-plane transport (i.e. in the CuO plane), while the second specimen, measuring $0.8 \times 0.9 \times 1.0$ mm^3, was used to measure the transport properties along the tetragonal *c*-axis (perpendicular to the CuO planes). A third crystal, with dimensions of $1.5 \times 0.8 \times 4.0$ mm^3, was used to measure the in-plane thermal conductivity.

The excess oxygen content δ was tuned in these three crystals by annealing them at 650°C for 12 h in varying relative levels of oxygen and nitrogen gases at 1 bar pressure (throughout this paper we use T_N to specify a crystal's relative oxygen content since the magnetic ordering temperature is a monotonic function [1,2] of δ). By annealing at 1 bar in gas mixtures ranging from pure nitrogen to 21% oxygen (i.e. air), the Néel temperature, and hence δ, could be continuously tuned from 310 down to 250 K; attempts at obtaining $T_N > 250$ K were unsuccessful even with 100% oxygen anneals. Presumably, annealing at a pressure greater than 1 bar is needed to drop T_N below 250 K. Magnetic susceptibility measurements of the magnetic ordering peak were examined to determine the homogeneity of the excess oxygen. An inhomogeneous internal distribution of excess oxygen results in a distribution of Néel temperatures, and hence a broadening of the ordering peak seen in χ rather than a sharp feature as is seen when the excess oxygen level is uniform throughout the sample. The transport properties of the crystals

were only measured after an anneal in which magnetic ordering produced a sharp peak in χ when the field was applied parallel to the tetragonal c-axis. In practice, the crystals would first be annealed in the appropriate relative levels of oxygen and nitrogen, examined for excess oxygen homogeneity by way of magnetic susceptibility measurements, and then mounted for resistivity and TEP measurements. After a particular measurement round, the specimen would then be re-annealed to achieve another excess oxygen level. At the end of the four cycles used in this study, the samples were re-annealed in pure nitrogen and it was found that their physical properties were in no way changed by the many annealing cycles that they had undergone. Hence, excess oxygen can be reversibly added and removed from $La_2CuO_{4+\delta}$ without any hysteretic effects.

The magnetic susceptibility measurements were performed on a Quantum Design SQUID magnetometer. The magnetic field was applied along the tetragonal c-axis to maximize the magnetic ordering signature [13]. The anisotropic resistivity was measured on the ab-plane and c-axis crystals by using a conventional DC four-probe method involving silver paint contacts. These contacts were fired-on in the annealing process and had typical contact resistances of less than 1 Ω. The thermoelectric power was measured by suspending a single crystal between two electrically insulated copper posts across which a variable temperature gradient could be applied [15]. The absolute TEP was measured with respect to copper. The standard configuration employed a maximum relative temperature gradient ($\Delta T/T$) of roughly 0.5%. This gradient was measured with a 25.4 micron diameter chromel-constantan reference thermocouple. Tests with constantan and platinum standards gave TEPs within 5% of their accepted values. The thermal conductivity was measured using a steady-state linear heat-flow method [16]. After the appropriate anneal, the sample was thermally anchored to a copper base with Thermalbond epoxy [17] while the other end was wrapped with a wire-wound manganin heater. κ was determined by measuring the power into the heater and the resulting temperature difference across the sample's length. The apparatus employs a guard heater and numerous control thermocouples, and has an absolute accuracy of roughly 5% [16].

3. Experimental results

The magnetic susceptibility of a $La_2CuO_{4+\delta}$ crystal that has been annealed in 1-bar flowing nitrogen is depicted in fig. 1. The sharp peak in χ is due to the onset of antiferromagnetic order at $T_N = 310$ K. This T_N value is somewhat smaller than the maximum typically observed when $La_2CuO_{4+\delta}$ is vacuum annealed ($T_N \approx 328$ K). The second set of data in fig. 1 shows that the ordering peak drops by 60 K after annealing the same sample in air, due to the increase in δ. In both cases, the relatively small width of the ordering peak (15 to 30 K) indicates that the 1 bar anneals result in a uniform excess oxygen distribution.

We next move to the electronic transport displayed by the $\delta \approx 0$ nitrogen-annealed $La_2CuO_{4+\delta}$ single crystals. The resistivity of two side-by-side annealed crystals are shown in fig. 2. Both the ab-plane and the c-axis samples show resistivities that increase with decreasing temperature. The material is extremely anisotropic at high temperatures ($\rho_c/\rho_{ab} \approx 200$ at 300 K) but becomes more isotropic at low temperatures due to the steep increase in the ab-plane resistivity ($\rho_c/\rho_{ab} \approx 10$ at 30 K). With an excess oxygen content such that $T_N = 310$ K, this compound shows activated behavior above 100 K with an ab-plane gap ($E_g \approx 420$ K) that is larger than that along the c-axis ($E_g \approx 226$ K). Below 100 K the effective activation energies appear to gradually decrease with decreasing temperature, a qualitative in-

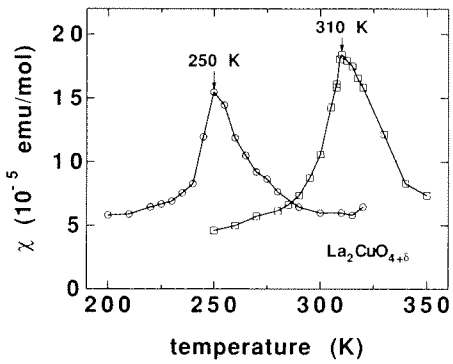

Fig. 1. Magnetic susceptibility vs. temperature measured in a 5 kG field directed along the tetragonal c-axis. The two data sets were obtained from the same single crystal after anneals in air (circles, $T_N = 250$ K) and flowing nitrogen (squares, $T_N = 310$ K).

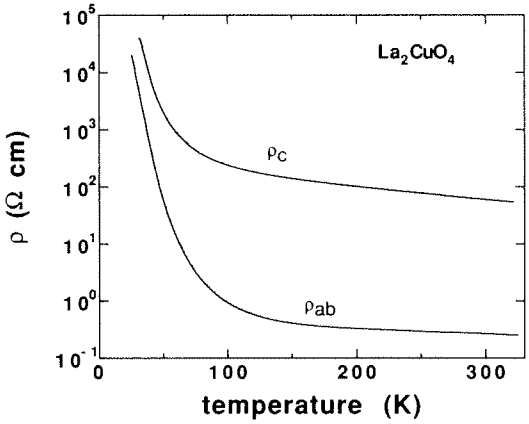

Fig. 2. In-plane (ρ_{ab}) and out-of-plane (ρ_c) resistivity of two La_2CuO_4 single crystals annealed in flowing nitrogen.

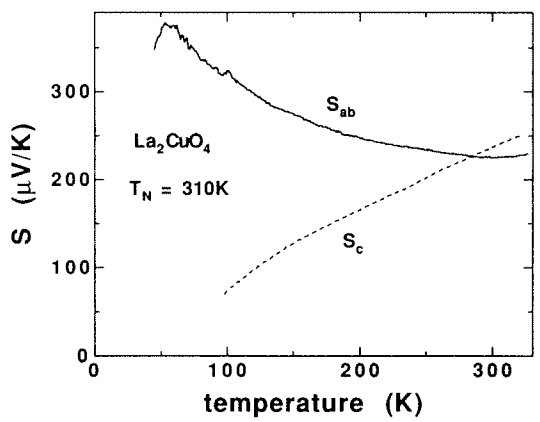

Fig. 3. In plane (S_{ab}) and out-of-plane (S_c) thermoelectric power of the same two nitrogen-annealed La_2CuO_4 single crystals used in fig. 2.

dication of a progressive shift to hopping transport. Attempts to fit the resistivity to a generic low-temperature hopping expression, $R \approx R_0 \exp(T_0/T)^{\alpha}$, did not give satisfactory results; nonetheless, this does not rule out a hopping mechanism as the hopping expression assumes one-phonon processes, an assumption which normally holds only below ~4 K [18]. The resistivity data presented in fig. 2 are in reasonable agreement with previously published works [13,19].

Figure 3 shows the anisotropic TEP of the same two crystals used to form fig. 2. The TEP is positive in both directions and on the order of a few hundred μV/K at room temperature. S_{ab} shows gapped (i.e. $S = [k_B/e][E_g/k_BT + \text{const.}]$) behavior down to roughly 55 K, below which the large sample resistivity makes a reliable measure of the TEP impossible. The gap determined from S_{ab} ($E_g = 200$ K) is a factor of two smaller than that determined from ρ_{ab}. S_c shows a markedly different overall temperature dependence, varying almost linearly with temperature down to 100 K below which the extremely large sample resistivity again makes a determination of the TEP problematic. Taken together, the resistivity and TEP data on $\delta \approx 0$ $La_2CuO_{4+\delta}$ indicate that electron transport occurs by activation at high temperatures (due either to carriers activated across a gap or to nearest neighbor hopping) and that it switches over to some form of variable-range hopping below 100 K. Moreover, the large anisotropy in the TEP indicates that the specific hopping energetics in the two crystallographic directions are extremely different (see section 4 for a complete discussion of this point).

With increased hole doping, extra carriers are injected into the system, and, as shown in figs. 4 and 5, this has a significant effect on transport in $La_2CuO_{4+\delta}$. As δ is progressively increased by proper oxygen anneals (an increase in δ correspondingly reduces T_N) both ρ_{ab} and ρ_c drop markedly in overall magnitude while still showing activated behavior with a large low-temperature increase. In addition, two anomalies are present in ρ_{ab} when $La_2CuO_{4+\delta}$ is air-annealed ($T_N = 250$ K). The first, a drop in resistivity below 50 K, stems from an oxygen-rich superconducting surface layer (an acid etch removes this feature and ρ_{ab} sharply rises below 50 K). The second, a 70% drop in ρ_{ab} near 250 K, occurs precisely at T_N (this anomaly is associated with the bulk because a surface acid etch leaves it undisturbed). Similar anomalies are present in ρ_c on the $T_N = 250$ K crystal. Hence, resistivity anomalies occur at $T_a = T_N$ for $La_2CuO_{4+\delta}$ crystals which have sufficient excess oxygen such that $T_N = 250$ K. No detectable anomalies appear in ρ_{ab} for $\delta < 0.005$ ($T_N > 250$ K), while distinct anomalies do occur in ρ_c. With $T_N = 264$ K a clear drop in ρ_c occurs at $T_a = 225$K. In addition, a far smaller and broader anomaly occurs in ρ_c at $T_a = 200$ K for the crystal annealed to give $T_N = 280$ K.

The TEP of the *ab*-plane and *c*-axis samples are

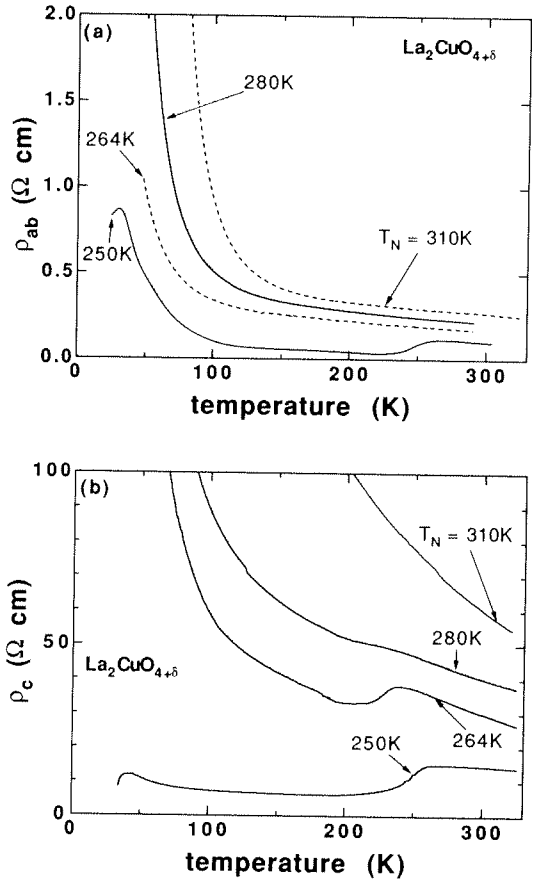

Fig. 4. In-plane (a) and out-of-plane (b) resistivity of two $La_2CuO_{4+\delta}$ single crystals. Each measurement was performed after side-by-side anneals in gas mixtures varying in oxygen content from air (T_N=250 K) to pure N_2 (T_N=310 K). The curves are labeled by T_N (in (b) the arrows also point to T_N).

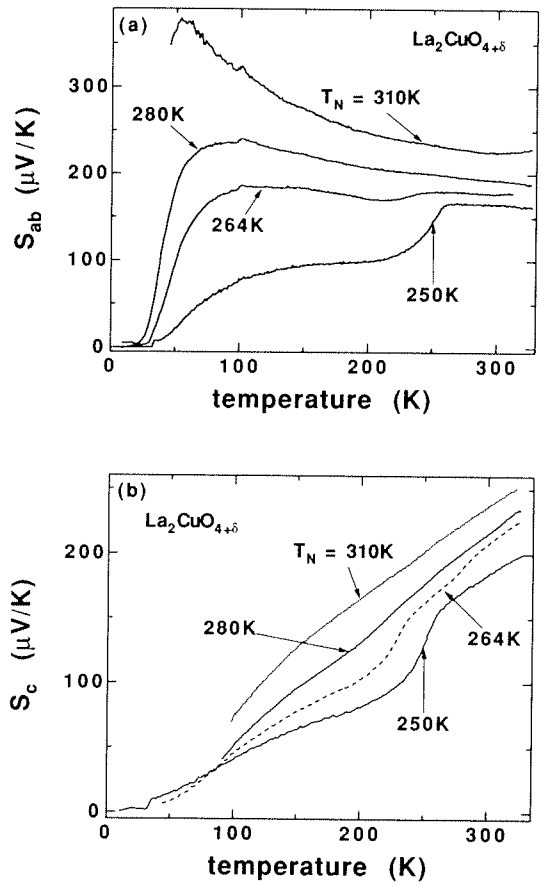

Fig. 5. In-plane (a) and out-of-plane (b) thermoelectric powe of the same $La_2Cu)_{4+\delta}$ single crystals used in fig. 4. The curve are labeled by T_N as determined from susceptibilit measurements.

depicted in fig. 5. With increased hole doping S_{ab} shows a progressive drop both in overall magnitude and in the degree of upward curvature (i.e. activation energy). With increased hole doping, S_{ab} also begins to drop with decreasing temperature below 100 K (part of this drop may stem from an oxygen-rich surface layer that eventually superconducts below 40 K). Disregarding the anomalous drops in S_{ab} in the T_N=250 K and 264 K data, increasing δ appears to convert the overall temperature dependence from $S \propto T^{-1}$ (as with the T_N=310 K and 280 K data) to being essentially temperature-independent (as with the T_N=264 K data), and finally to a regime where S_{ab} decreases with decreasing temperature. In addition to these background systematics clear anomalies in the form of gradual dips are present in the TEP data for T_N=250 K and 264 K anneals at the same temperatures as they appeared in ρ_{ab} and ρ_c. The out-of-plane TEP, S_c, shows the same general linear temperature dependence for all of the excess oxygen levels considered here. The only systematic change is a drop in overall magnitude with increased hole doping (decreased T_N). As with the other transport measurements, distinct anomalies are present in the data for T_N=250 K and 264 K. In addition, a very broad, shallow anomaly is also evident in S_c near 200 K when T_N=280 K.

Figures 6 and 7 show expanded views of the transport anomalies in the TEP and resistivity for

$La_2CuO_{4+\delta}$ crystals annealed such that $T_N=250$ K (fig. 6) and $T_N=264$ K (fig. 7). With $T_N=250$ K the drops in ρ_c and ρ_{ab} amount to a 70% reduction in the overall resistivity upon cooling below $T_a=250$ K. Large drops also occur in S_c and S_{ab} upon cooling through the same temperature. With a slightly reduced excess oxygen content ($T_N=264$ K, fig. 7), the anomalies move to a lower temperature ($T_a=225$ K) and become smaller in magnitude; the anomaly in ρ_{ab} only amounts to a 3% drop. For still smaller hole doping ($T_N=280$ K), no anomaly is evident in the *ab*-plane transport data while very small features are still present in the *c*-axis data with a characteristic temperature $T_a=200$ K. No anomalous features are evident in either ρ or S after a nitrogen anneal ($T_N=310$ K). A quantitative comparison of the parameters which characterize the transport anomalies present in lightly oxygen doped $La_2CuO_{4+\delta}$ is given in table I.

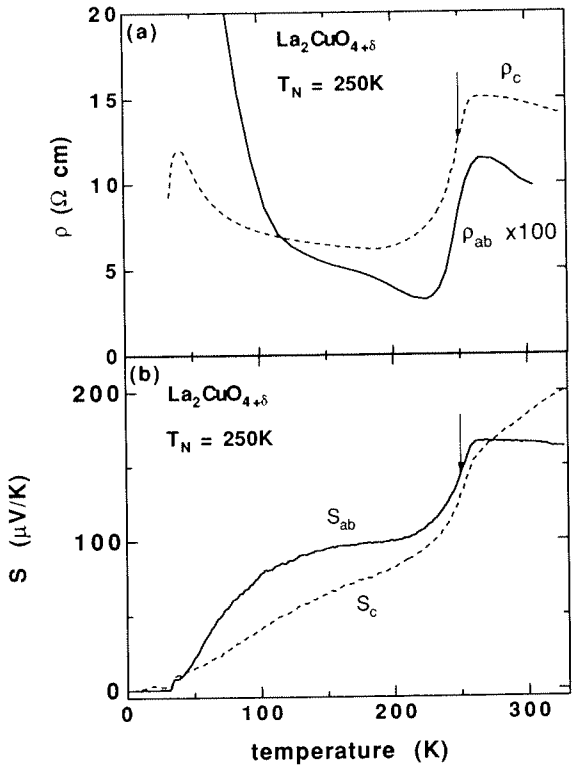

Fig. 6. Expansion of the anomalous resistivity (a) and thermoelectric power (b) of two $La_2CuO_{4+\delta}$ crystals annealed in air. The arrows point to the Néel temperature as determined from χ measurements.

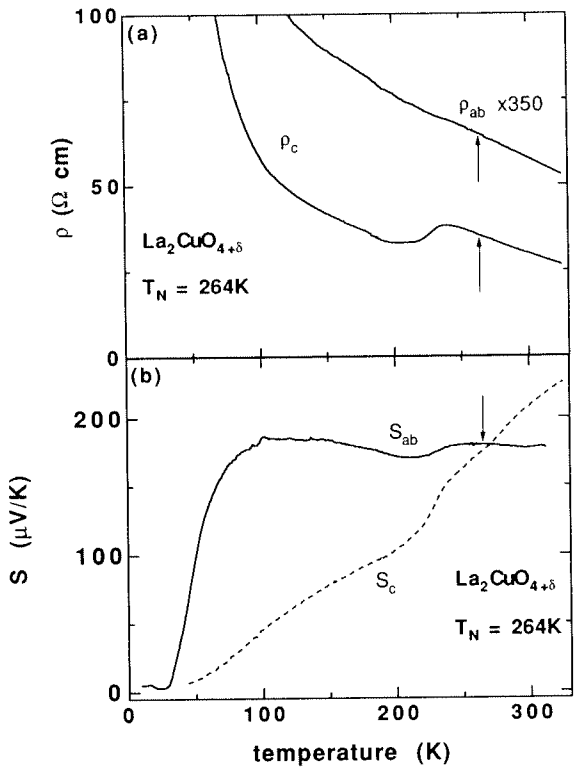

Fig. 7. Expansion of the anomalous resistivity (a) and thermoelectric power (b) of the same two $La_2CuO_{4+\delta}$ crystals used in fig. 6 after annealing in a gas mixture containing 7% O_2. The arrows denote the onset of antiferromagnetic order as determined from χ measurements.

We now consider the in-plane thermal conductivity presented in fig. 8. The air-annealed crystal ($T_N=257$ K) displays a minimum in the thermal conductivity centered roughly 7 K above T_N as well as a gradual reduction in κ below 200 K. The overall temperature dependence is similar to previously reported work [20], although we do not attribute the minimum at 100 K to antiferromagnetic ordering. Rather, we associate the dip slightly above T_N with the onset of magnetic order; the dip occurs because spin fluctuations about T_N significantly increase the scattering rate of heat carriers. Due to the complexity of spin-fluctuation scattering processes, it is common to have the minimum in κ fall just above T_N [21].

As indicated by the $T_N=283$ K and 305 K data in fig. 8, κ decreases in overall magnitude with decreased hole doping, while the dip continues to track

Table I
Summary of the parameters that characterize the anomalies present in the resistivity and TEP of $La_2CuO_{4+\delta}$. The amount of exces oxygen δ is indirectly specified by T_N (a smaller T_N indicates a larger δ).

T_N(K)	T_a(K)	$\Delta\rho_{ab}$(%)	$\Delta\rho_c$(%)	ΔS_{ab}(μV/K)	ΔS_c(μV/K)
310	–	–	–	–	–
280	200	–	−5	–	−14
264	225	−3	−27	−18	−26
250	250	−78	−70	−60	−50

the Néel temperature. Further, no anomalies are seen in the thermal conductivity at the electron transport anomaly temperature T_a. The reduction in κ with decreasing δ cannot be attributed to the accompanying decrease in the electrical conductivity because application of the Wiedemann–Franz law indicates that the electronic contribution to κ is less than 0.1%. Hence, the overall thermal conductivity is due almost entirely to lattice heat conduction, and its change in magnitude with δ indicates that the excess oxygen strongly influences thermal transport. Moreover, the absence of any thermal conductivity anomaly at T_a suggests that the mechanism responsible for the anomalies in ρ and S affects only electronic, and not long-wavelength acoustic-phonon transport.

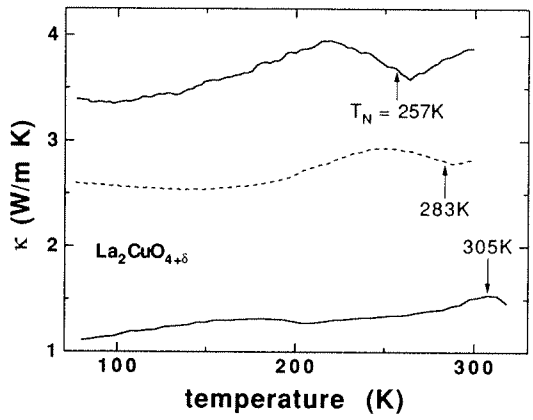

Fig. 8. In-plane thermal conductivity of a $La_2CuO_{4+\delta}$ single crystal measured after three anneals differing only in their relative oxygen contents. The arrows indicate the temperature at which magnetic order occurs as determined from susceptibility measurements.

4. Discussion

The hole-doping-dependent electronic transport in $La_2CuO_{4+\delta}$ has two general aspects that we will consider in some detail in this discussion section. First, we examine the mechanisms responsible for the overall charge transport in $La_2CuO_{4+\delta}$ as evidenced by the data presented in the previous section. Second, we will briefly discuss the possible physical processes responsible for the anomalous drops seen in the resistivity and TEP in lightly-doped $La_2CuO_{4+\delta}$.

The resistivity in $La_2CuO_{4+\delta}$ displays simple activated behavior at high temperatures which switches over to non-Arrhenius behavior below 100 K. Further, the resistivity is extremely anisotropic at room temperature and becomes less so as the material is cooled into the non-Arrhenius low-temperature regime. Increased hole doping acts only to decrease the resistivity's overall magnitude. These systematics are consistent with carrier activation from localized hole-like states that are associated with the excess oxygen sites. For $T > 100$ K these carriers conduct either via activation to a mobility edge or by way of nearest-neighbor hopping. The large anisotropy indicates that the structural anisotropy found in $La_2CuO_{4+\delta}$ strongly limits transport along the c-axis. As the temperature is lowered below 100 K, insufficient thermal energy exists to continue with nearest-neighbor hopping or mobility-edge activation and the carriers start to conduct through variable-range hopping. In variable-range hopping the characteristic hopping distance R_h grows with decreasing temperature [22]. Hence, the resistivity anisotropy diminishes with decreasing temperature due to the reduction in the structural anisotropy sampled by hopping carriers. Within the confines of the small hole-doping regime considered here, increased carrier doping does not form extended bands, but only serves to add addi-

tional localized states. $La_2CuO_{4+\delta}$ must be heavily hole-doped by high-pressure oxygen anneals to form extended band states [12].

In general, the thermoelectric power of a localized system is the sum of two terms [23]. The first term contributes to the TEP in all electronic systems regardless of whether they contain localized or extended states; this term is proportional to the change in entropy with the addition of a single charge carrier $\Delta\Sigma_n$. (The TEP of a semiconductor is typically two or three orders of magnitude larger than that in a simple metal due to the far fewer number of activated charge carriers and hence the much bigger change in entropy when a single carrier is added to a semiconductor.) This entropy term contributes a temperature-independent term to the TEP in localized systems [24]. The second TEP term, which is often neglected, is proportional to the average energy transported with each carrier hop E_T. This characteristic transfer energy can in general be quite different from the activation energy measured in the resistivity, and is proportional to the square of the difference in energy between the initial and final hopping states $E_T \propto (\Delta E)^2$ [25]. The thermoelectric power in a localized system is thus given by [25]

$$S(T) \propto \Delta\Sigma_n + \frac{\Delta E(T)^2}{T}. \qquad (1)$$

The TEP in a localized system is therefore a sum of a constant term plus a term which can in general be temperature-dependent $S(T) = a + b(T)$.

An examination of the $La_2CuO_{4+\delta}$ TEP shows that it cannot be solely described by a temperature-independent term as was recently suggested by Devaux et al. [26]. Rather, both S_{ab} and S_c are clearly temperature-dependent. Moreover, the temperature-dependence in S_{ab} is also a strong function of excess oxygen content.

The *ab*-plane TEP can be empirically described by the sum of a constant term and a T-dependent term, precisely the prediction of eq. (1). Both terms are strongly influenced by the level of hole doping. The T-independent term is a decreasing function of δ; in a hole-doped localized system this is the expected behavior of the entropy TEP term. The systematic variation in the temperature-dependent term, which we associate with energy transfer during site-to-site hops, indicates that $\Delta E_{ab}(T)$ is extremely dependent on the level of hole doping in $La_2CuO_{4+\delta}$. With few carriers ($T_N = 310$ K) $S_{ab} \propto (1/T)$, indicating that ΔE_{ab} is temperature independent. Based on the evolution of S_{ab} with increased hole doping, ΔE_{ab} becomes increasingly temperature dependent as the number of hopping carriers increases ($\Delta E_{ab}(T_N = 246\ \text{K}) \propto T^{1/2}$, $\Delta E_{ab}(T_N = 250\ \text{K}) \propto T^{\alpha}$ with $\alpha > 1/2$). Hence, the extra carriers added to the system as δ is increased directly influence the way in which the spread in energy of accessible hopping states grows with temperature.

The energy distribution of localized states appears to be quite anisotropic as evidenced by the very different temperature-dependence displayed by S_c. The *c*-axis TEP varies linearly with temperature for all doping levels; a similar $S(T)$ has been reported for boron-carbide systems wherein conduction also involves localized states [25]. Based on eq. (1), ΔE_c must vary linearly with temperature. The energy transfer involved in hopping conduction is therefore also extremely anisotropic. Moreover, the TEP data indicate that the structural anisotropy in $La_2CuO_{4+\delta}$ results in the Cu–O plane hopping energetics being a far stronger function of δ than is the case with transport along the *c*-axis as might be expected if the excess holes are confined primarily to the plane.

We next consider the transport anomalies present in both the resistivity and TEP data. As shown by the data in table I, there is no anomaly evident for $\delta \approx 0$ ($T_N = 310$ K), while for $\delta > 0$ the anomaly temperature and the anomaly's relative effect on the transport coefficients are both increasing functions of hole doping. In addition, $T_a(\delta)$ crosses the decreasing function $T_N(\delta)$ at 250 K. In general, though, the transport anomaly does not occur at T_N. Moreover, Hall effect measurements indicate that no change in carrier density occurs at T_a [13].

The systematic increase in both T_a and in the relative-anomaly-size with increased hole doping suggest that the underlying cause stems from an instability involving the excess oxygen. Evidence for just such an instability has been found in heavily oxygen-loaded $La_2CuO_{4+\delta}$ ($\delta \approx 0.032$) [9–12]. For these 3 kbar oxygen-annealed crystals, the excess oxygen phase separates upon cooling below $T_{ps} = 280$ K into a poorly conducting, oxygen-poor phase ($\delta \approx 0$) and a highly conducting oxygen-rich phase. For $T > T_{ps}$ the oxygen appears to be uniformly distributed

throughout the crystal, albeit with some form of structural stress induced by "forcing in" the extra oxygen; this stress is relieved by the separation into two crystallographically distinct phases at T_{ps}. Further, theoretical evidence also exists that the dilute holes in an antiferromagnet such as $La_2CuO_{4+\delta}$ should be unstable against phase separation [27].

With regard to the lightly-doped $La_2CuO_{4+\delta}$ transport data considered here, the progressive increase both in T_a and in the relative transport-anomaly magnitude with δ can be accounted for by phase separation involving oxygen diffusion. The strain involved with uniform placement of the excess oxygen should be a monotonically increasing function of δ. Hence, the temperature $T_{ps}=T_a$ at which this strain is relieved by phase separation will also grow with δ. Further, a drop in resistance is expected when the material phase separates and forms a small amount of highly conducting oxygen-rich phase because the increase in conductivity in this rich phase will be larger than the small decrease in conductivity of the oxygen-poor phase. The TEP would also be expected to drop below T_a as it will reflect the better-conducting oxygen-rich phase, and the TEP drops with increased carrier concentration in localized systems. With an increase in excess oxygen, the volume of oxygen-rich phase should also increase, and the transport anomalies will correspondingly grow with increased δ. Hence, the progressive systematics involved with the anomalies seen in the TEP and resistivity are consistent with phase separation involving the diffusion of non-stoichiometric oxygen. As with heavily loaded $La_2CuO_{4+\delta}$, a search for two phases via neutron diffraction is needed to confirm this speculation concerning phase separation.

While the magnitude of the changes in ρ and S can be qualitatively accounted for by a simple two-phase conduction model for $T_{ps}\neq T_N$, the anomalies for the case where $T_a=T_N=250$ K seem too large by a factor of 2 or 3. Hence, the absence or presence of a magnetically ordered background may have a strong influence on the change in the resistivity and TEP upon phase separation. This suggests that, as with the negative magnetoresistance seen at the onset of metamagnetism [14], there is a strong interplay between magnetism and transport in $La_2CuO_{4+\delta}$. Clearly, a complete microscopic theory which includes the effects of both copper-spin magnetism and non-stoichiometric oxygen is needed to more fully understand the anomalous features present in the electron transport exhibited by $La_2CuO_{4+\delta}$.

5. Conclusion

Resistivity, thermoelectric power and thermal conductivity measurements indicate that charge transport in lightly-doped $La_2CuO_{4+\delta}$ involves carrier hopping between localized states. This transport is extremely anisotropic owing to the underlying planar structure found in this compound. Further, both the TEP and resistivity change markedly with the level of hole-doping. This indicates that the underlying nature of the hopping transport that occurs in $La_2CuO_{4+\delta}$ is strongly influenced by the amount of excess oxygen present in the system.

Distinct anomalies are evident in both the TEP and resistivity of 1 bar oxygenated $La_2CuO_{4+\delta}$. As with more heavily-doped 3 kbar oxygenated $La_2CuO_{4+\delta}$, we attribute these transport anomalies to macroscopic phase separation involving oxygen diffusion. This indicates that the high-temperature structure of $La_2CuO_{4+\delta}$, which consists of uniformly distributed excess oxygen [28], is actually very unstable The intriguing question remains as to why oxygen-doped $La_2CuO_{4+\delta}$ requires a structurally phase-separated ground state. Theoretical predictions based on a number of models which attempt to describe the copper-oxide planes found in the high-T_c superconductors [27,29] suggest that dilute holes in an antiferromagnet are unstable against phase separation into a hole-rich and a no-hole phase. Hence, the phase separation discussed above may reflect spin-exchange interactions between mobile holes and copper-spin magnetism in $La_2CuO_{4+\delta}$.

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