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PROPERTIES OF La$_2$CuO$_4$ AND RELATED COMPOUNDS

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We review the crystal chemical, electronic, magnetic and superconducting properties of La$_2$CuO$_4$ and related planar-cuprate materials, with emphasis on single-crystal results. Although magnetism due to divalent copper ions clearly is evident in nonsuperconducting crystals, experiments do not reveal any direct relationship between localized copper spins and high temperature superconductivity. We also indicate areas where important information is lacking for our understanding of these materials.

1. Introduction

Cuprate compounds are at present the primary materials in research on high-T_c superconductivity. Although one might claim that rhombohedral La-CuO$_3$ is the simplest such metallic material [1], this phase has only been synthesized at high pressure and appears not to be superconducting. It is La$_2$CuO$_4$ which forms the basis for the simplest layered cuprate superconductors, ones with $T_c \simeq 40$ K.

It is very likely that much of the physics of cuprates with $T_c > 90$ K is already contained in those with $T_c \simeq 40$ K. As we will discuss in the text, there is a very broad composition space in the La$_2$CuO$_4$-based materials. Thus, it is worthwhile to achieve an accurate picture as to what the properties of La$_2$CuO$_4$ and its substitutions are. Our purpose here is to present the current state of experimental knowledge on La$_2$CuO$_4$-based compounds, partially based on our own investigations, and to indicate areas where information is lacking. In comparison with La$_2$CuO$_4$, we also discuss the nonsuperconducting cuprates with CuO$_2$ layers, e.g., Gd$_2$CuO$_4$, Sr$_2$CuO$_2$Cl$_2$, and La$_2$SrCu$_2$O$_6$, and a few other layered metallates, e.g., La$_2$NiO$_4$ and La$_2$CoO$_4$. After reviewing crystal-chemical aspects of these materials in section 2, we describe their electronic and magnetic behaviors in sections 3 and 4, respectively, before coming to a discussion of superconductivity in section 5. Final remarks are given in section 6.

2. Crystal chemistry

La$_2$CuO$_4$ crystallizes in an orthorhombic distortion of the tetragonal K$_2$NiF$_4$ structure [2], a so-called layered perovskite in which the Cu–O–Cu's form infinite two-dimensional (2D) sheets (fig. 1). The structure is one of a series of possible structures of Ruddlesdon–Popper type with formula AO–n(ABO$_3$): an interleaving of perovskite and rocksalt layers–n of the BO$_2$ layers per formula unit. The tetragonal-to-orthorhombic transition [3,4] for

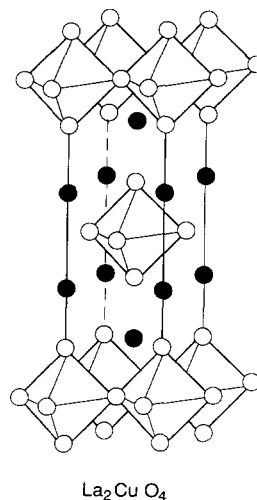La$_2$Cu O$_4$

Fig. 1. Crystal structure of La$_2$CuO$_4$. Closed circles are La ions, open circles are oxygens and Cu ions are hidden in oxygen octahedra.

La$_2$CuO$_4$ occurs at $T_0 \simeq 530$ K and involves a tilting of the elongated CuO$_6$-octahedra. (This distortion is sometimes ascribed to a Jahn–Teller distortion of Cu-d^9; however, the presence of a similar distortion in La$_2$NiO$_4$ [5], La$_2$CoO$_4$ [6], and YCaCrO$_4$ [7] would argue against it being the only cause of the distortion.) The elongation of these octahedra is such that the Cu–O distance in the layers (1.907 Å) is considerably shorter than the Cu–O distance out-of-the layers (2.459 Å). An effect of the orthorhombic distortion is to pucker the CuO$_2$ planes, involving a slight lifting of the degeneracy of the two O–O in-plane distances around the Cu ion (2.685 Å and 2.703 Å) and a tilting of the CuO$_6$-octahedra by $\sim 2.8°$. The orthorhombic b-axis corresponds by convention to the tetragonal c-axis and the ortho-rhombic a- and c-axes are approximately $\sqrt{2}$ times the tetragonal a-axis. (A quasi-tetragonal a-axis can be defined by $[a^2+c^2]^{1/2}/2$ in the orthorhombic structure, which is ~ 3.81 Å in La$_2$CuO$_4$.) The space group of orthorhombic La$_2$CuO$_4$ is Cmca [8], i.e., face-C centered.

Ionic size appears to be an important factor in the formation of various oxide phases. For the simple perovskite structure ABO$_3$, a tolerance factor $(t=r(\text{A–O})/\sqrt{2}\,r(\text{B–O})$, where A is the larger cation) is often used to determine the likelihood of per-ovskite formation, for ions A and B. Generally, t falls in the range $0.9<t<1$ for cubic perovskites; how-ever, there could still be formation of a distorted per-ovskite if t is close to the lower limit of the permis-sible range. The cation pair of La and Cu falls outside this range; however, they are close to the lower limit, and metallic-like rhombohedral LaCuO$_3$ [1] has been formed at high pressure in oxygen. In the case of AO–ABO$_3$, i.e., A$_2$BO$_4$, compounds with the te-tragonal K$_2$NiF$_4$ structure form if the tolerance fac-tor defined similarly is in the range of $0.85<t<1.02$ [9]. The tolerance factor for La$_2$CuO$_4$ is $t\simeq 0.83$, i.e., slightly lower than the lower limit, which is consis-tent with the orthorhombically distorted K$_2$NiF$_4$ structure in La$_2$CuO$_4$. In the RE$_2$CuO$_4$ series of com-pounds (RE = rare earth) [2,10], the rare earths Pr through Gd form in a different, tetragonal structure – t for RE$_2$CuO$_4$ is even lower than that of La$_2$CuO$_4$. However, there are again CuO$_2$ layers in RE$_2$CuO$_4$; the Cu ions are square-planar coordinated by oxy-gens rather than quasi-octahedrally as in the La$_2$CuO$_4$

or K$_2$NiF$_4$-type structures and the REs are coordi-nated by eight oxygens compared with nine oxygens in the cases of La in La$_2$CuO$_4$ or K by F in K$_2$NiF$_4$. We note that nominal EuTbCuO$_4$ [11] and Gd-TbCuO$_4$ [10] form even though Tb$_2$CuO$_4$ does not and that La$_{1.33}$Tb$_{0.67}$CuO$_4$ [10] crystallizes in a phase intermediate to La$_2$CuO$_4$ and RE$_2$CuO$_4$ having quasi-tetragonal lattice constants $a=3.85$ Å and $c=12.25$ Å. The space group of the RE$_2$CuO$_4$ is I4/mmm and its structure is displayed in fig. 2.

Thin, plate-like crystals [11] of RE$_2$CuO$_4$ have been grown from PbO and CuO fluxes with the crys-tallographic c-axis parallel to the thin dimension. Refinement [12] of the X-ray spectra gives lattice constants for Gd$_2$CuO$_4$ of $a=3.892$ Å and $c=11.878$ Å with a site occupancy of 0.99(2) for Gd and 1.01(5) for O, indicating that the crystals grow at or very close to the stoichiometric composition. In the case of PbO flux growth, studies on the possibility of Pb incorporation into the structure, examined by electron-microprobe analysis, show that the Pb con-tent, if any, is less than 1 at% of Cu. The electronic and magnetic properties of RE$_2$CuO$_4$ are insensitive to anneals in various gas atmospheres [11], sug-gesting that the oxygen content is highly stable.

We note that La$_2$NiO$_4$ adopts the K$_2$NiF$_4$ struc-ture at room temperature; however, it undergoes a tetragonal-to-orthorhombic transition [5] at ~ 240 K and an antiferromagnetic transition occurs at ~ 70
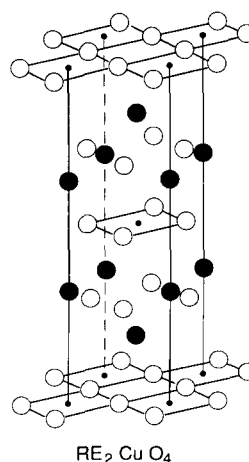

RE$_2$ Cu O$_4$

Fig. 2. Crystal structure of RE$_2$CuO$_4$(RE = Pr, ... , Gd). Closed circles are RE ions, open circles are oxygens and dots represent Cu ions.

K. La$_2$CoO$_4$ [6] and YCaCrO$_4$ [7] have the same structure as that of La$_2$CuO$_4$ at room temperature. La$_2$CoO$_4$ undergoes an antiferromagnetic transition [13] at ~275 K and its structure changes to an unknown tetragonal phase at ~135 K. Some of the compounds with tetragonal or distorted K$_2$NiF$_4$ structure are listed in table I.

As in La$_2$CuO$_4$, there are CuO$_2$ layers in the compounds Sr$_2$(Ca$_2$)CuO$_2$Cl$_2$(Br$_2$) [14] in which Cu ions are coordinated octahedrally by four oxygens and two chlorines (or bromines), i.e. the two out-of-plane oxygens are replaced by two chlorines (or bromines). These compounds crystallize in the tetragonal K$_2$NiF$_4$ structure (e.g. in Sr$_2$CuO$_2$Cl$_2$, a = 3.991 Å and c = 17.136 Å). We point out that, even though there are CuO$_2$ layers in RE$_2$CuO$_4$ and Sr$_2$CuO$_2$Cl$_2$-related compounds, they do not have out-of-plane oxygens coordinating Cu and do not become metallic by hole doping, i.e., oxygenation or replacement of RE or Sr by lower valent ions. We will discuss this is more detail in the next section. Crystalline Sr$_2$(Ca$_2$)CuO$_2$Cl$_2$(Br$_2$) compounds are grown with a Sr(Ca)Cl$_2$(Br$_2$) flux and are very thin and mica-like.

La$_2$SrCu$_2$O$_{6.2}$ [15], which is a kind of AO–2ABO$_3$ compound, is the best known metallic but nonsuperconducting material having CuO$_2$ layers. As shown in fig. 3, Cu ions are coordinated pyramidally by five oxygen in tetragonal La$_2$SrCu$_2$O$_6$. Oxygenation of insulating La$_2$SrCu$_2$O$_6$ increases its oxygen content from 6 to 6.2 and induces metallic behavior; extra oxygens in La$_2$SrCu$_2$O$_{6.2}$ appear to go into the oxygen-missing sites between the CuO$_2$ layers. The ratio of La to Sr can vary from the 2:1 ratio and La and Sr can be replaced by other rare earths and Ca, respectively. In the case of orthorhombic RE$_2$SrCu$_2$O$_6$ (RE = Sm, Eu, Gd) [16], Sr ions tend to go into the structure at a much greater than stoichiometric concentration (RE: Sr ≈ 1.2 : 1.8) and oxygen vacancies distribute differently than in La$_2$SrCu$_2$O$_6$ (some oxygens in the CuO$_2$ layers are missing). RE$_2$SrCu$_2$O$_6$, grown from CuO flux, remains semiconducting even after oxygenation and its morphology is similar to that of RE$_2$CuO$_4$. Studies of the Nd–Sr–Cu–O system [16] reveal two stable phases related to AO–2ABO$_3$ materials, one stoichiometric, tetragonal Nd$_2$SrCu$_2$O$_6$ and the other orthorhombic Nd$_{1.2}$Sr$_{1.8}$Cu$_2$O$_6$. One of the interesting results from these studies [16] is that Nd$_{2-x}$Sr$_x$CuO$_4$ with x ≈ 1.4 forms in the structure of La$_2$CuO$_4$, not that of Nd$_2$CuO$_4$.

The important question in this section concerns the stoichiometry of La$_2$CuO$_4$ prepared by various techniques. Large single crystals have been grown variously from CuO, PbO and Li$_2$O–B$_2$O$_3$ fluxes; the last two fluxes incorporate some Pb and Li, respectively, into the structure. As regards the La and Cu sites, various measurements (X-ray refinement, electron microprobe, classical density and recently neutron diffraction) on samples prepared differently

Table I

Compounds with tetragonal K$_2$NiF$_4$ structure or distorted K$_2$NiF$_4$ structure.

Structure (at 300 K)	Compounds	Ref.	Comments
Tetragonal I [T(I)]	K$_2$NiF$_4$		La$_2$NiO$_4$ undergoes a structural
	La$_2$NiO$_4$	[5]	transition from T(I) to O(I) at
	LaCaCrO$_4$	[7]	~240 K [5]
Tetragonal II	RE$_2$CuO$_4$ (RE = Pr to Gd)	[2,10]	
Orthorhombic I [O(I)]	La$_2$CuO$_4$	[2]	La$_2$CoO$_4$ undergoes a structural
	La$_2$CoO$_4$	[6,13]	transition from O(I) to an un-
	YCaCrO$_4$	[7]	known tetragonal structure at ~135 K [13]
Orthorhombic II	Sm$_2$CoO$_4$	[9]	
Monoclinic	Pr$_2$NiO$_4$	[5]	
	Nd$_2$NiO$_4$	[5]	

La$_2$ Sr Cu$_2$ O$_6$
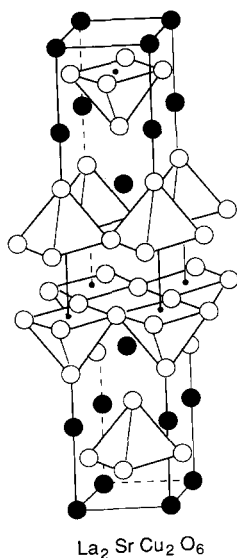
Fig. 3. Crystal structure of La$_2$SrCu$_2$O$_6$. Closed circles are La or Sr ions, open circles are oxygens, and dots represent Cu ions.

have shown that the La:Cu ratio is 2:1 within experimental error ($<1\%$) [17,18].

It is also known that the oxygen stoichiometry corresponds to La$_2$CuO$_4$ within $\sim 1\%$. Extensive transport [19] and magnetic measurements [4] show, however, that the physical properties are extremely sensitive to $\ll 1\%$ changes in the oxygen content. Important clues to understanding the exact oxygen content are the following [4,19]. Firstly, the Hall coefficient is always positive. Secondly, resistivity, the Neel temperature (T_N), the Cu–Cu exchange coupling and the transition temperature (T_0) from the tetragonal-to-orthorhombic structure all increase with decreasing oxygen content. Finally, magnetic defects, as evidenced by a low-temperature Curie tail in the magnetic susceptibility, are reduced upon removing oxygen. A consistent interpretation of these facts is that the oxygen stoichiometry is always richer than that corresponding to a Mott–Hubbard insulator with an exactly half-filled band, implying the chemical formula is more accurately represented by La$_2$CuO$_{4+\delta}$, with small, positive δ if the La to Cu ratio is exactly 2:1.

Several groups also have found that bulk superconductivity above 30 K can be produced in La$_2$CuO$_4$ by annealing powders or single crystals at high oxygen pressure [18,20]. The weight gain in this pro-

cess corresponds to producing La$_2$CuO$_{4.13}$ and these authors believe the excess oxygens go in as O$_2^-$ (superoxide), based on iodometric titration measurements giving the amount of [Cu–O]$^+$ in the sample. X-ray photoelectron spectroscopy [21] studies on oxygen-rich powders have identified the excess oxygens as superoxides. Elastic neutron scattering experiments [18] on oxygen-loaded powder samples show the presence of two nearly identical orthorhombic phases, one being close to a stoichiometry of La$_2$CuO$_4$ and a second with oxygen content much greater than 4. This two-phase behavior is associated with macroscopic phase separation that occurs near 320 K due to long-range oxygen diffusion, with the excess oxygen incorporated in the second, superconducting phase. Although the space group of the oxygen-rich phase could not be identified unambiguously, it is clear that in this phase oxygen atom displacements which lead to a rigid tilt of the CuO$_6$ octahedra have been distorted into random directions. It is not clear whether the transition from an almost-stoichiometric phase to an oxygen-rich phase is continuous and if the extra oxygens in the former phase are superoxides.

The great interest in La$_2$CuO$_4$ is based on the change in properties upon substituting some of the La with various lower valent alkaline-earth and alkali metals [22]. The effect of these substitutions is to produce formally some Cu^{3+}, i.e., increasing hole carriers, and eventually metallic behavior. Most of the experimental work has involved the alkaline earths Ba, Sr and Ca. We show in fig. 4 an appro-

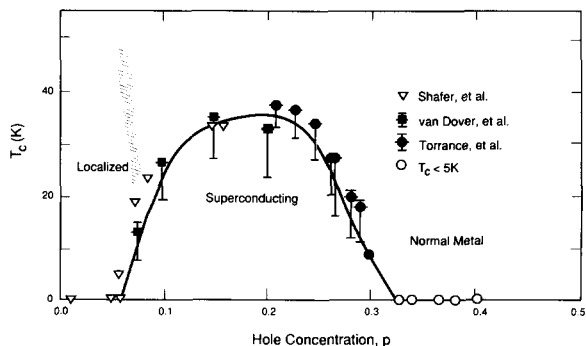Fig. 4. The dependence of T_c on hole concentration in La$_{2-x}$Sr$_x$CuO$_4$ (in the case of the Torrance et al.'s data, T_c and hole concentration are determined from the Meissner effect and an iodometric titration technique, respectively). After ref. [23].
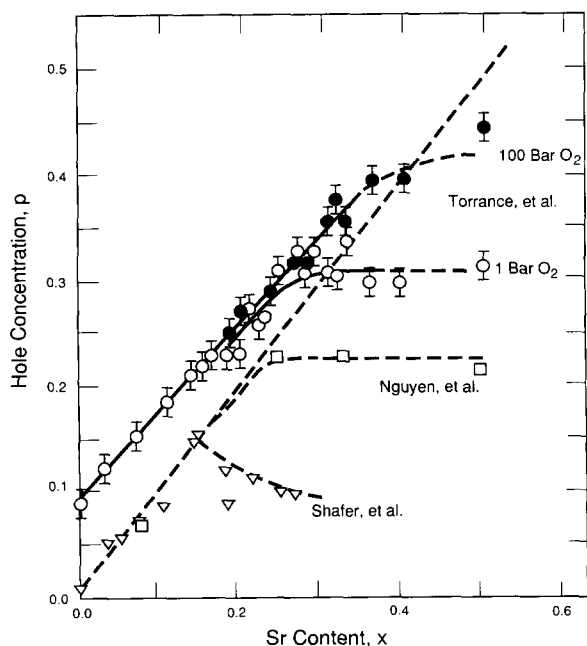
Fig. 5. Hole concentration vs Sr concentration in $La_{2-x}Sr_xCuO_4$. Hole concentration is determined from a titration technique. After ref. [23].

priate phase diagram [23] for Sr-substitution and in fig. 5 the hole concentration, determined by iodometric titration, versus x in $La_{2-x}Sr_xCuO_4$. It is seen from fig. 5 that O-stoichiometry is a serious problem for $x>0.2$ and that for these compositions the O-stoichiometry can fall below 4.0. As a aside, it is interesting that the formally Cu^{3+} material $LaSrCuO_4$ [24], which is know to be a diamagnetic semiconductor, has been formed at high O-pressure. The te-

tragonal-to-orthorhombic transition [3] is strongly depressed by alkaline-earth substitution (see table II). Various aspects of the magnetic behavior also are influenced strongly by the substitutions and they will be discussed in a following section.

We have noted already that Li substitutes into La_2CuO_4 from Li-based flux used in some single crystal growths. This appears to be a substitution of Li for Cu, and powder material independently has been produced corresponding to the trivalent Cu composition $La_2Li_{0.5}Cu_{0.5}O_4$ [1]. (In the case of formally trivalent-Cu compounds like $LaCuO_3$, $LaSrCuO_4$, and $La_2Li_{0.5}Cu_{0.5}O_4$, there may be a substantial number of oxygen vacancies rather than trivalent-Cu ions.) Other substitutions [25] for Cu are also possible, and, in particular, Ni and Zn have been studied in connection with their influence on superconductivity. The substitution [26] of other rare earths into $La_{2-x}RE_xCuO_4$ is possible, typically for $x<0.2$, somewhere beyond which concentration the RE_2CuO_4 phase forms. The light rare earths can be substituted to higher concentrations than the later rare earths, and, for Pr, x as large as 0.6 has been reported [9].

Most substitution work has utilized polycrystalline powder. In the case of Ba, Sr and Ca, the reason for this is that the alkaline-earth oxides are only sparingly soluble in the CuO melts from which the crystals grow. This has prevented obtaining $La_{2-x}M_xCuO_4$ crystals with $x>0.1$, the interesting range of x regarding superconductivity. We also point out that the incongruent melting of La_2CuO_4 (in the 1400-K range) is expected to lead to substitutional

Table II
Substitutional data for $La_{2-x-y}M_xRE_yCu_{1-z}T_zO_4$. T_o is the structural and T_c is the superconducting transition temperature.

M=Ba ($y=z=0$)	$-dT_o/dx=31$ K/at.%	$T_c(x=0.15)=31$ K	[3]
Sr ($y=z=0$)	$-dT_o/dx=23$ K/at.%	$T_c(x=0.15)=38$ K	[3]
Ca ($y=z=0$)	$-dT_o/dx=29$ K/at.%	$T_c(x=0.15)=24$ K	[3]
K ($y=z=0$)		$T_c<4.2$ K	[70]
Na ($y=z=0$)		$T_c(0.2<x<0.5)\sim38$ K	[70,71]
T=Ni (M=Sr, $x=0.15$, $y=0$)		$-dT_c/dz=7$ K/at.%	[25]
Zn (M=Sr, $x=0.15$, $y=0$)		$-dT_c/dz=10$ K/at.%	[25]
Cd, Hg (M=Sr, $x=0.15$, $y=0$)		$-dT_c/dz=1.5$ K/at.%	
RE=Pr (M=Sr, $x=y=0.2$, $z=0$)		$T_c=33$ K	[26]
Eu (M=Sr, $x=y=0.2$, $z=0$)		$T_c=21$ K	[26]
Gd (M=Sr, $x=y=0.2$, $z=0$)		$T_c=18$ K	[26]

atom-concentration variations in crystals grown with excess CuO.

3. Electronic properties

An immediate problem that presents itself in connection with the electronic properties of La_2CuO_4 is the finding of band-structure calculations that this compound should be a metal. The resistivity (ρ) behavior [19] is very different than that of a metal and depends strongly on annealing treatment, that is, oxygen content. As shown in fig. 6 for an air-annealed single crystal grown from CuO flux, the in-plane resistivity ($\rho_\parallel$) is weakly temperature dependent from ~100 K to room temperature, i.e., quasimetallic ($\rho \simeq 0.1 \ \Omega$ cm, larger than the metallic conduction limit), but there is a fairly abrupt up-turn to semiconductor-like behavior below ~100 K. It is not clear what causes the apparent crossover from quasimetallic to semiconductor-like behavior; although, a possible interpretation is a change in the conduction mechanism [27] from diffusion at high temperature, to variable-range hopping at low temperature, through nearest neighbor hopping. The room-temperature Hall coefficient (R_H) of a crystal prepared similarly is $\sim 1.1 \times 10^{-9} \ \Omega$ cm/G, corresponding to ~0.005 holes per formula unit. In this measurement, current flow is in the Cu–O planes and the magnetic field (H) is applied perpendicular to the
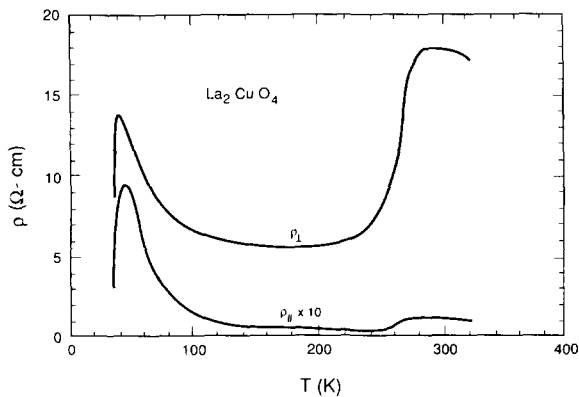
Cu–O planes. Combining the Hall measurements with in-plane resistivity at room temperature allows an estimate of the mean-free-path (l) ~1 Å, using the free-electron approximation. This value of l is less than an interatomic spacing, indicating that the concept of an extended band state is not applicable to La_2CuO_4.

There is a resistivity anomaly associated with surface superconductivity below 40 K in both $\rho_\parallel$ and $\rho_\perp$. Furthermore, in both directions the resistivity exhibits a pronounced change at 255 K that is associated with antiferromagnetic (AF) ordering. A sharp peak in the susceptibility (χ) is observed at the same temperature on a crystal prepared similarly and this will be discussed in more detail in the next section. The change at T_N is more evident for the out-of-plane resistivity $\rho_\perp$ (the drop is on the order of 10 Ω cm). Careful resistivity and magnetic susceptibility measurements show that there is hysteresis (~ 5 K) in the resistivity anomaly even though no hysteresis (< 0.5 K) is observed [28] in susceptibility measurements, which might be explained by the metastability of twins [19,29] present in the orthorhombic structure. We point out that the pronounced effect on resistivity by magnetic order could indicate a strong correlation between ordered spins and itinerant holes. There is also a large anisotropy in ρ that is ~150 at room temperature, indicating that conduction takes place primarily in the Cu–O planes. A pronounced decrease ($\sim 60 \ \mu V/K$) is found [19] upon cooling through T_N in both the in-plane and out-of-plane thermoelectric power S of air-annealed crystals; however, the temperature dependence of S is markedly different in the two directions. There is also a positive anomaly in the in-plane thermal expansion [30] near T_N but no detectable specific-heat anomaly [31,32] at T_N in these crystals, indicating that most of the entropy associated with Cu^{2+} spins has been removed by short range ordering at temperatures above T_N.

Inert-gas (N_2) or vacuum annealing the air-annealed crystals removes oxygen and increases the overall resistivity and T_N; further, features in both the resistivity [19] and thermoelectric power [33] at T_N become less prominent. The highest $\rho_\parallel \sim 350 \ \Omega$ cm at room temperature and $T_N \sim 328$ K are obtained by vacuum annealing at ~750 K and further

Fig. 6. The temperature dependence of in-plane ($\rho_\parallel$) and out-of-plane ($\rho_\perp$) resistivities in an air-annealed La_2CuO_4 crystal (Montgomery method was employed).

attempts to increase $\rho_{\parallel}$ and T_N induce dissociation of the samples.

On the other hand, oxygenation of the crystals at 1-bar oxygen pressure leads to decreasing ρ, decreasing and broadening the antiferromagnetic transition, and increasing the superconducting fraction, but the susceptibility anomaly associated with magnetic order does not disappear, indicating that superconductivity is still primarily a surface effect. In view of the large changes in ρ due to the annealing treatment, meaningful statements can be made only for carefully characterized samples. We suggest that the value of T_N is a useful marker of the O-stoichiometry; whereas the sharpness of the susceptibility peak at T_N reflects the homogeneity of oxygen content. The full-width at half-maximum of the susceptibility peak near T_N can be as low as 13 K in a crystal annealed in air (see the next section).

As far as superconducting La₂CuO₄-based compounds are concerned, there are no reliable transport data on single crystals. However, by using the room-temperature values of resistivity and Hall constant [34] in sintered compacts of La₁.₈₅Sr₀.₁₅CuO₄, we can estimate the mean-free-path at room temperature within the framework of the free-electron model, giving $l \sim 35$ Å. This value of l is larger than any lattice constant, indicating that a band model could be applicable to La₁.₈₅Sr₀.₁₅CuO₄. That La₂CuO₄ is not a metal suggests strong electron–electron correlations, perhaps described via an appropriate Hubbard Hamiltonian, are opening a gap at the Fermi surface; thus, a localized picture is more applicable than a band model. In the case of metallic, superconducting La₁.₈₅Sr₀.₁₅CuO₄ to which a band model appears applicable, we can estimate the importance of electron–electron correlations by comparing the observed Pauli susceptibility (χ_{Pauli}) with the carrier density inferred from a single-band-model interpretation of the Hall coefficient. The estimated χ_{Pauli} ($\sim 1 \times 10^{-4}$ emu/mole Cu, after core diamagnetism correction and subtraction of a Cu^{2+}-Curie–Weiss contribution [4]) leads to an enhancement factor $\eta \sim 5$ due to electron–electron correlations [35]. Optical reflectivity measurements [36] on La–Sr–Cu–O powder also draw a similar conclusion.

It is particularly illuminating to look at what happens as a function of x to the Hall constant [37] measured on polycrystalline La₂₋ₓSrₓCuO₄ samples

(fig. 7). Fox $x < 0.1$, R_H is inversely proportional to x and corresponds to the addition of one hole per Sr substitution. For $x \gtrsim 0.1$, the linearity between R_H and $1/x$ breaks down abruptly and R_H becomes very small. Something like a metal–insulator transition appears to be taking place. Qualitatively, this is not surprising; as the carrier concentration increases with x, the electron–electron correlations become better screened, and we expect to enter a regime where the electronic structure is quite different. It is fair to say that band-structure calculations for stoichiometric La₂CuO₄ do predict an approximately square Fermi-surface cross-section [38] which is exactly of the sort favoring a nesting instability that could lead to a non-metallic ground state.

Low-temperature specific-heat measurements on La₂CuO₄ generally find a linear specific-heat coefficient $\gamma \sim 1$ mJ/mole K²; however, for samples carefully annealed in an inert gas or vacuum, both polycrystalline [39] and single-crystal [40] samples have $\gamma < 0.2$ mJ/mole K² and $\theta_D \sim 400$ K. These results indicate that the linear specific-heat term likely can be correlated with the carrier concentration. A finite γ, in the range 2–5 mJ/mole K², is also ob-
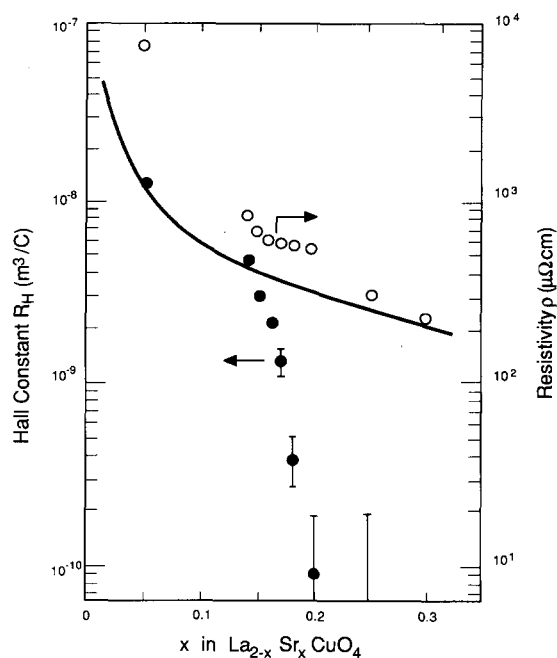

Fig. 7. Hall coefficient and resistivity vs Sr concentration in La₂₋ₓSrₓCuO₄. After ref. [37].

served in $La_{1.85}Sr_{0.15}CuO_4$ (see table III). The specific-heat anomaly [41] at T_c is displayed in fig. 8. From the specific-heat jump (ΔC) at T_c and the BCS relationship, $\Delta C = 1.43 \, \gamma T_c$, γ is estimated to be ~ 7 mJ/mole K². Furthermore, near T_c the upper critical-field slope, in the dirty limit, is $dH_{c2}/dT = -4.48 \times 10^4 \, \gamma\rho(G/K)$. Taking $\rho = 400 \, \mu\Omega$ cm and $dH_{c2}/dT = -1.6$ T/K leads to $\gamma \sim 6$ mJ/mole K², a value in reasonably good agreement with the previous estimate. From the estimated Pauli susceptibility, the free-electron expression ($\gamma = \pi^2 k_B^2 \chi_P/3\mu_B^2$) gives $\gamma \sim 7$ mJ/mole K². Therefore, we

conclude that the Pauli susceptibility and the Sommerfeld coefficient are enhanced similarly by electron–electron correlations and that the Wilson ratio is close to unity, suggesting that the electron–phonon coupling may be small.

Various experiments on $La_{2-x}Sr_xCuO_4$ have been undertaken to reveal the microscopic, electronic properties of La_2CuO_4-based compounds. X-ray absorption spectroscopy measurements [42] on $La_{1.85}Sr_{0.15}CuO_4$ show that the itinerant holes are mainly on the oxygen sites rather than associated with $[Cu-O]^+$ as a whole. Optical reflectivity [36] experiments on La_2CuO_4 find evidence for an optical gap of ~ 1.7 eV. A special feature in Raman experiments [43] has been the observation of two magnon scattering in La_2CuO_4 from which has been deduced a large in-plane Cu–Cu magnetic exchange coupling (~ 1400 K) consistent with neutron scattering experiments.

Electronic properties of nonsuperconducting, layered cuprates have been studied, especially in relation to La_2CuO_4-based compounds. Hall-effect measurements [11] on semiconductor-like RE_2CuO_4 show that the sign of the Hall coefficient is negative when current flows in the Cu–O planes and the magnetic field is applied perpendicular to the Cu–O planes, indicating that carriers are electrons. Analyzing the temperature dependence of the in-plane resistivity in terms of activated behavior gives a gap associated with conduction that is ~ 0.05 to 0.2 eV depending on the sample. This latter result suggests that the gap is associated with an impurity band rather than an intrinsic band ($\rho \sim 1 \, \Omega$ cm at room temperature). The room temperature anisotropy in ρ is also large, greater than 100. Compounds of $Sr(Ca_2)CuO_2Cl_2(Br_2)$ are highly resistive. Figure 9 shows the temperature dependence of the in-plane resistivity of an as-prepared crystal of $Ca_2CuO_2Cl_2$ to be weakly temperature dependent in the interval $\sim 170 < T < 320$ K but it increases rapidly below about 170 K. This behavior is similar to that of $\rho_\parallel$ in La_2CuO_4 only the temperature at which $\rho_\parallel$ begins to increase most rapidly is higher in $Ca_2CuO_2Cl_2$. Further, the in-plane thermoelectric power [44] of this crystal is very large, $\sim -800 \, \mu$V/K at room temperature, and increases with decreasing temperature approximately as $S_\parallel \propto 1/T$, i.e. semiconductor-like, but changes its temperature dependence weakly near

Table III
Superconductivity parameters of $La_{1.85}Sr_{0.15}CuO_4$

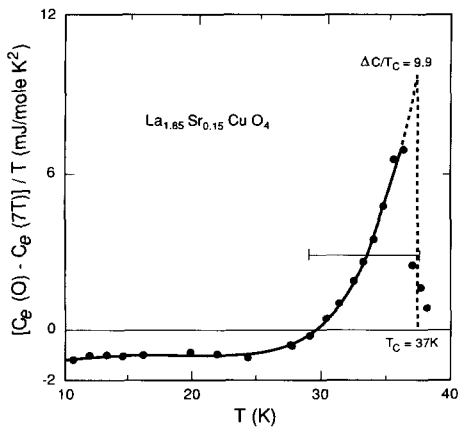| Parameter	Value	Comments
T_c	38 K	typical
$-dH_{c2}/dT$ at T_c	1.6 T/K	typical
$H_{c2}(0)$	50 T	typical of extrapolations from H_{c2} near T_c
$-dH_{c1}/dT$ at T_c	0.5 mT/K	[65]
$H_{c1}(0)$	18 mT	[72]
$\gamma(0)$	2–5 mJ/mole K²	[73,74]
$\Delta C(T_c)/T_c$	10 mJ/mole K²	[74,73]
$\lambda_L(0)$	2250 Å	average of μSR results; [75,76]
ξ_0	26 Å	from $\xi_0^2 = \phi_0/2\pi H_{c2}(0)$
$H_c(0)$	0.9 T	from $H_c = (H_{c1}H_{c2})^{1/2}$
$\kappa(0)$	35	from $\kappa = H_c/\sqrt{2}H_{c1}$

Fig. 8. The temperature dependence of the difference of electronic specific heats with 7 T field and without field in $La_{1.85}Sr_{0.15}CuO_4$. The horizontal bar marks the 10–90% Meissner effect width. The dashed lines represent entropy conserving constructions used to estimate ΔC at T_c. After ref. [41].
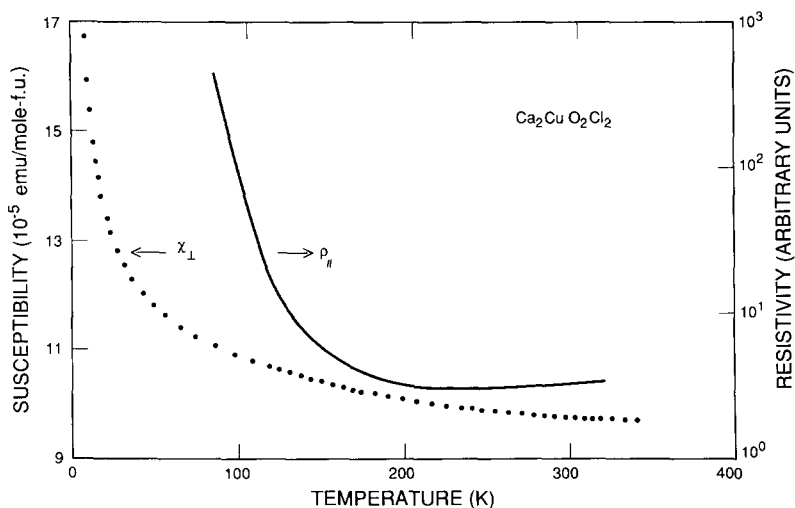
Fig. 9. In-plane resistivity ($\rho_\parallel$) and out-of-plane magnetic susceptibility ($\chi_\perp$) of $Ca_2CuO_2Cl_2$ crystals versus temperature.

170 K. As noted earlier, RE_2CuO_4 and $Sr_2(Ca_2)CuO_2Cl_2(Br_2)$ have CuO_2 layers but are missing out-of-plane oxygens and do not become metallic by hole doping. (In the case of $La_2SrCu_2O_6$, there is one out-of-plane oxygen for every Cu ion.) A possible argument for this behavior is that the d_{z^2} orbitals, rather than the $d_{x^2-y^2}$ orbitals in layered cuprates with out-of-plane oxygens, are half-filled and localized. It that be the case, we would expect a very different intralayer magnetic superexchange coupling since magnetic exchange coupling originates from electronic structure. However, as we will discuss in the next section, the magnetic behavior of Cu ions seems similar in all these compounds with CuO_2 layers. This contradiction needs to be resolved to understand the microscopic origin of electronic and magnetic properties in the cuprates with CuO_2 layers. We finally point out that γ in crystalline Eu_2CuO_4 is 0 ± 0.2 mJ/mole K^2 from specific-heat measurements [44].

4. Magnetic properties

As shown in the left panel of fig. 10, the presence of a sharp peak [4,45] in the susceptibility indicates that La_2CuO_4 undergoes antiferromagnetic ordering at $T_N \sim 257$ K, which has been confirmed by neutron-scattering experiments [46] that find three-di-
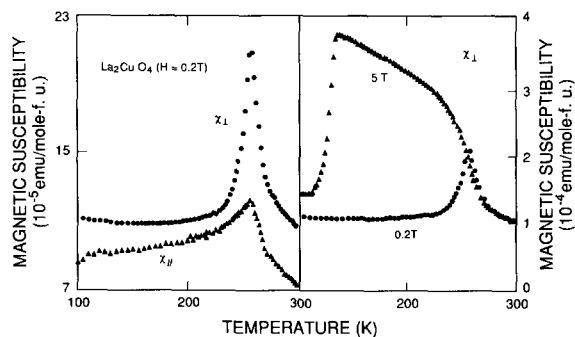

Fig. 10. The left panel displays temperature dependence of the magnetic susceptibility of an air-annealed La_2CuO_4 crystal in the Cu–O plane direction ($\chi_\parallel$) and in the perpendicular direction ($\chi_\perp$) measured with 0.2 T field. The $\chi_\perp$ versus temperature measured with two different fields (0.2 and 5 T) is shown in the right panel (0.2 T data are the same as those shown in the left panel).

mensional Bragg peaks with unit-cell doubling. As noted earlier, T_N is very sensitive to the oxygen content and the highest $T_N \sim 328$ K is achieved by vacuum annealing. It appears that as $\delta \to 0$ in $La_2CuO_{4+\delta}$, T_N approaches its maximum value and as soon as δ becomes negative, the sample starts to dissociate. Susceptibility studies on La_2CuO_4 powders as a function of oxygen content show that T_N vanishes at $\delta \sim 0.03$ [4], which is a hole-doping level comparable to that required to suppress antiferromagnetism by divalent-cation substitution for La. (The correct definition of T_N is not simple [45,47]; however, for

simplicity we defined T_N as the temperature where χ reaches its maximum.) The out-of-plane susceptibility [45] ($\chi_\perp$) exhibits a more sharply defined peak at T_N than does the in-plane susceptibility ($\chi_\parallel$). There is also substantial anisotropy in χ, even though divalent-Cu ions are good Heisenberg ions because of large spin–orbit coupling and the fact that the ground state is a Kramer's doublet. Measurements [48] of the induced-moment magnetic form factor of crystalline La₂CuO₄ indicate that magnetic moments are only on the Cu^{2+} ions.

In the antiferromagnetically ordered state, the Cu spins align along the c-axis in the Cu–O planes. However, a field-induced transition [45,49], which occurs when a magnetic field is applied perpendicular to the Cu–O planes at $T < T_N$, has been observed. The right panel of fig. 10 shows that for temperatures below T_N, $\chi_\perp$ (T) measured with a large field is very different from that measured with a low field. Magnetization ($M(H)$) measurements below T_N also exhibit nonlinear behavior (fig. 11) reflecting the field-induced transition. The origin [45,50] of this field-induced, metamagnetic transition is from the slight canting ($\sim 0.2°$ at 0 K) of Cu spins out of the Cu–O planes due to the rotational distortion ($\sim 2.8°$) of elongated octahedra of oxygen atoms around the Cu ions. The canting of Cu spins, which can described by the Dzyaloshinski–Moriya (D–M) exchange Hamiltonian [51], produces a net magnetic moment perpendicular to the Cu–O planes. At low magnetic fields, however, the spins in alternate layers cant in opposite directions and the net moment in one layer
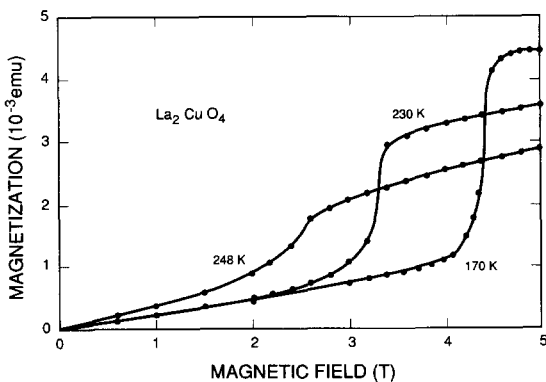
cancels that in the next layer (hidden weak ferromagnetism). However, when a high enough magnetic field perpendicular to the Cu–O planes is applied, the net moment in each layer points in the field direction and produces a weak ferromagnetic (WFM) moment ($\sim 3 \times 10^{-3}$ μ_B/Cu at 0 K). Figure 11 displays the behavior of $M(H)$ as the spin configuration changes from a hidden WFM state to a WFM state at $T < T_N$. The field at which the transition occurs defines the critical field H_c at a given temperature, from which we can construct a phase diagram in H–T space (fig. 12). As shown in fig. 12, the hidden WFM, WFM and paramagnetic states meet at a triple point [45]. Additional studies around the triple point are required to determine if a well-defined phase transition exists between the AFM + WFM and PARA states.

X-ray diffraction [52] on La₂CuO₄ under quasi-hydrostatic pressure shows that the tetragonal-to-orthorhombic transition temperature is depressed by pressure. Decreasing orthorhombicity with pressure implies a pressure-induced reduction in the interlayer magnetic coupling; whereas the empirical rule [53] that the 2D exchange coupling J_{2D} is proportional to $1/r^{12}$, where r is the distance between magnetic ions, implies an increasing in-plane magnetic coupling with pressure. Resistance measurements at

Fig. 11. Isothermal magnetization versus field at various temperatures below T_N in an air-annealed La₂CuO₄ crystal (sample mass = 105.1 mg).
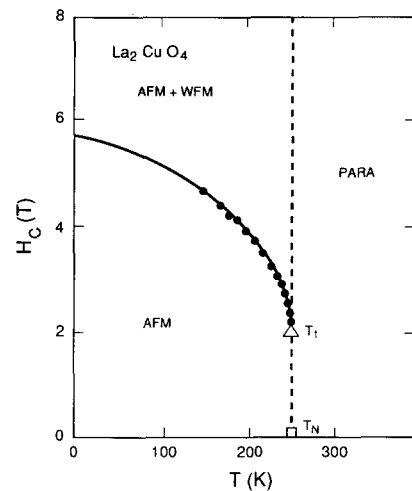

Fig. 12. Field-temperature phase diagram in La₂CuO₄ deduced from magnetization measurements. The dashed line has a slope of ~ -0.8 K/T determined from measurements of $\chi_\perp$ at various applied fields below T_t. The dashed line above T_t is an extrapolation.

75 K find [32,45] dln $H_c/dP \simeq -0.4\%/kbar$, which together with [31] dln $T_N/dP \simeq -0.2\%/kbar$ implies that T_N is determined primarily by the interlayer magnetic coupling rather than the in-plane superexchange. Behaviors depicted in figs. 10–12 can be explained roughly by a mean-field-treatment including the D–M interaction and 2D spin correlations. With this model the estimated [45] interlayer exchange coupling in La₂CuO₄ is $\sim 4 \times 10^{-5}$ of the in-plane superexchange coupling (~ 1400 K); whereas, a typical ratio between them in other 2D magnets [54] is $\sim 10^{-6}$. Magnetization measurements [45] below T_N indicate that the critical exponent β associated with the transition into the WFM state is $\beta \simeq 0.5$, i.e. mean-field-like. The pressure dependences of T_N and orthorhombicity, the reasonably large interlayer exchange and the value of β together imply that critical behavior near T_N is that of a three-dimensional magnetic system rather than a 2D Ising system. Even though three-dimensional antiferromagnetic ordering occurs below T_N, short-range 2D-AF ordering in the CuO₂ layers exists at temperatures even far above T_N, as reflected in a positive $d\chi/dT$ at $T \gg T_N$ [4]. This short-range ordering above T_N is typical of behavior in other two-dimensional magnets [54], e.g. K₂NiF₄, and in fact, neutron scattering experiments [55] on La₂CuO₄ reveal instantaneous spin correlations in the Cu–O planes at $T \gg T_N$. The large in-plane superexchange coupling (~ 1400 K) between Cu ions is expected in view of the relatively short distance between Cu ions and the fact that divalent Cu ions have only one hole [53].

The anomalous temperature dependence [4] of the normal-state susceptibility of La₂₋ₓSrₓCuO₄ (fig. 13) is consistent with short-range 2D antiferromagnetic order in metallic samples (long-range AF ordering no longer occurs for $x > 0.03$), suggesting the coexistence of Cu²⁺ spins and itinerant holes in the normal state of the superconducting material. If the anomalous $\chi(T)$ behavior is due to short-range 2D-AF ordering, then the clear indication of the data in fig. 13 is that the 2D exchange coupling decreases with increasing Sr concentration (up to $x = 0.2$) and increasing oxygen content. In the case of 2D antiferromagnets, the temperature at which χ shows a broad maximum due to short-range ordering is proportional to the 2D exchange coupling. Therefore,
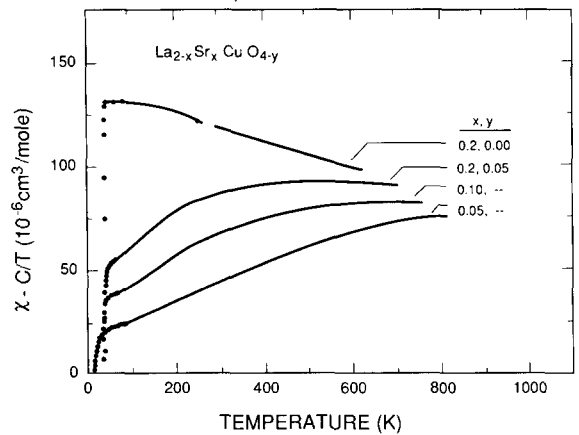

Fig. 13. Corrected magnetic susceptibility χ-C/T vs temperature for several powder samples of La₂₋ₓSrₓCuO₄₋ᵧ. After ref. [4].

we expect $J_{2D} \sim 150$ K in La₁.₈Sr₀.₂CuO₄ (no longer ~ 1400 K), if we use the above analysis. Neutron-scattering experiments [56] on superconducting crystals of La₂₋ₓSrₓCuO₄ ($T_c \sim 10$ K) indicate that Cu ions still have spins associated with them and the itinerant holes limit the spin-correlation length, supporting the implications from $\chi(T)$ measurements. These measurements indicate that the instantaneous spin-correlation length in CuO₂ layers equals the average separation between the holes. In addition, muon-spin relaxation experiments [57] reveal the presence of Cu²⁺ magnetic behavior in the superconducting state of La₂₋ₓSrₓCuO₄ crystals with $T_c \sim 10$ K. The series of experiments discussed here appear to imply the coexistence of bulk superconductivity and short range antiferromagnetic order. However, the question of sample homogeneity must be addressed before definite conclusions can be drawn.

It seems that Cu²⁺ ions in La₂CuO₄ exhibit magnetic behavior typical of a 2D, $S = 1/2$ Heisenberg system; therefore, it is important to establish magnetic behavior of Cu²⁺ ions in other layered cuprates, particularly to determine if the Cu²⁺ behavior in La₂CuO₄ is unique. The temperature dependent susceptibility of crystalline Gd₂CuO₄, measured with a small field (~ 1 G), is displayed in fig. 14. An extremely sharp anomaly in $\chi_\parallel$ occurs at $\simeq 260$ K but no detectable anomaly is observed in $\chi_\perp$ at this temperature. The sharp anomaly [11] is due to the development of an internal field at the gadolinium sites,
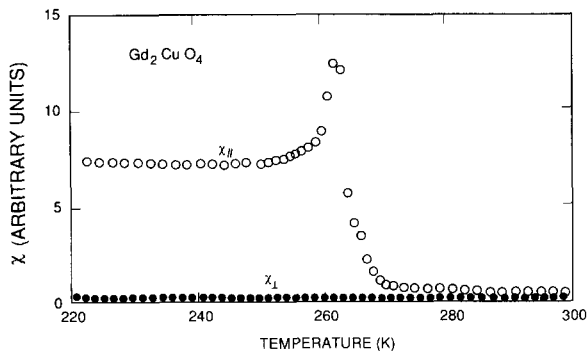
Fig. 14. The temperature dependence of the magnetic suscepti-bility of a Gd₂CuO₄ crystal in the Cu–O plane direction ($\chi_\parallel$) and in the perpendicular direction ($\chi_\perp$) measured with ~1 G field.

which is induced by antiferromagnetic order of cop-per ions. From the general rule $J_{2D} \simeq 1/r^{12}$, we es-timate the 2D-exchange coupling in Gd₂CuO₄ to be ~1100 K by scaling from $J_{2D} \sim 1400$ K in La₂CuO₄. It is interesting to note that the ratio between T_N in Gd₂CuO₄ and the highest T_N (328 K) in La₂CuO₄ is very close to the ratio of the estimated 2D-ex-change couplings in the two materials. Specific heat and susceptibility measurements show that Gd in Gd₂CuO₄ orders antiferromagnetically at 6.5 K in the a–b plane [11]. In the case of Eu₂CuO₄ [11,58], a weak anomaly in the susceptibility, indicating an-tiferromagnetic order of Cu ions, is found near 245 K. There is no evidence from susceptibility mea-surements on other RE₂CuO₄ indicating Cu order-ing. The presence of an internal field in Gd₂CuO₄ from ordered Cu ions could be allowed by a crys-tallographic distortion of the tetragonal RE₂CuO₄ structure. As progressively smaller rare-earth atoms are substituted into RE₂CuO₄, the tolerance factor (t) also becomes progressively smaller, and, there-fore, a crystallographic distortion may become fa-vorable. This trend in t versus rare-earth ionic radius may explain why Cu order induces a large χ anomaly in Gd₂CuO₄, a small susceptibility feature in Eu₂CuO₄ and no detectable anomaly in the other RE₂CuO₄. The presence of a large susceptibility anomaly in nominally EuTbCuO₄, in which the av-erage of ionic radii of Eu³⁺ and Tb³⁺ is very close to that of Gd³⁺, also supports the above suggestion. We note that complex susceptibility behavior ob-served [11] at low temperatures in Gd₂CuO₄ and EuTbCuO₄ is indicative of a strong interrelationship

among RE–RE, RE–Cu and Cu–Cu interactions. The magnetic susceptibility of other RE₂CuO₄'s appears to be understandable straightforwardly from crystal-field effects. Unfortunately, no neutron-scattering experiments on RE₂CuO₄ have been reported. Clearly, the possibility of instantaneous spin corre-lations in RE₂CuO₄ materials needs to be investigated.

The insulating Sr₂(Ca₂)CuO₂Cl₂(Br₂) com-pounds do not show any indication of Cu order in susceptibility measurements (fig. 9). However, a re-cent neutron-scattering experiment [59] indicates that Cu ions order at ~320 K in Sr₂CuO₂Cl₂. As dis-cussed earlier, La₂NiO₄ below 240 K and La₂CoO₄ at room temperature have structures isomorphic with La₂CuO₄. Usually, the effective spin of Ni²⁺ ions is 1 at $T \gg 10$ K and divalent Co ions, in an octahedral environment, at $T \gg 10$ K show classic $S = 3/2$ Ising behavior. Neutron-scattering experiments [13], in fact, show 2D Ising critical behavior in La₂NiO₄ and La₂CoO₄.

5. Superconductivity

We have given arguments above contending that pure La₂CuO₄ is not superconducting and that the superconductivity observed [60] in various prepa-rations of it is a surface, not a bulk effect. Bulk su-perconductivity [20], however, is implied from sus-ceptibility measurements on powder samples of La₂CuO₄.₁₃ that have been loaded with oxygen at 3 kbar pressure and 500°C. Specific heat measure-ments [61] on these samples do not show an anom-aly at $T_c \simeq 28$ K, even though Meissner-effect exper-iments at low temperature indicate at least 30% of the sample is superconducting. Both resistive and magnetic measurements [61] find the supercon-ducting transition to be rather broad, which is prob-ably why a specific heat jump at T_c is not found. These observations also suggest that the oxygen con-tent is not homogeneous even in powder samples and that the hole concentration in the superconducting phase may be greater than 0.065 estimated [20] from iodometric titration. Interestingly, La₂CuO₄.₁₃ has a finite electronic specific-heat coefficient $\gamma \sim 2.5$ mJ/mole K²; whereas, a sample prepared under similar conditions but not oxygen-loaded has $\gamma \sim 0$. Accom-

panying the change in γ is a decrease in the Debye temperature of $La_2CuO_{4.13}$ by $\sim 22\%$ relative to that of La_2CuO_4 [61].

Single crystals of La_2CuO_4 can also be oxygen-loaded to produce $La_2CuO_{4.13}$ with T_c near 35 K. Magnetic susceptibility measurements in a field of 10 G show perfect diamagnetic shielding, independent of whether the field is applied parallel or perpendicular to the Cu–O plane direction; however, the Meissner signal is only $\sim 1\%$ of $-1/4 \pi$. The difference between shielding and Meissner results could be due to very strong flux pinning or to a gradient in the oxygen concentration such that superconductivity is present only on a surface layer that is several penetration-depths thick. Results of magnetization measurements at 7 K on an oxygen-loaded single crystal are shown in fig. 15 for fields applied parallel and perpendicular to the Cu–O planes. Analysis of these measurements in terms of Bean's critical state model [62] gives critical current densities at low fields that are approximately 4×10^4 A/cm² for the field perpendicular to the Cu–O planes and about half this value for H in the plane direction. This anisotropy ratio maintains approximately to the highest field at which point the critical current density has decreased by a factor of ~ 5. Although the anisotropy is not as large as found in $YBa_2Cu_3O_7$ crystals [63], the magnitude of the critical current density is comparable to that determined [64] by magnetization measurements on annealed single crystals of $YBa_2Cu_3O_7$. The relatively low critical current density calculated assuming bulk superconductivity, however, appears to be inconsistent with

a small Meissner fraction arising from strong flux pinning. Further, high-temperature susceptibility measurements on these crystals are consistent with a distribution of Neel temperatures, again supporting the possibility that not all of the sample contains extra oxygen. Inspection of the initial, linearly increasing portion of the M vs H curves suggests that H_{c1} (7 K) is rather small, at most 300 Oe, for both crystallographic directions. Comparable values of H_{c1} (0 K) have been estimated [65] for powder samples of Sr-doped La_2CuO_4.

The most extensively studied superconductors based on La_2CuO_4 are the alkaline-earth substituted ones $La_{2-x}M_xCuO_4$, where M is Ba, Sr or Ca. The general trend of T_c with x is very similar for all these elements [23,66,67] (fig. 4), showing that the important variable is x which corresponds in some way to hole concentration. The maximum $T_c \simeq 38$ K is achieved [23] with M=Sr for $0.15 \le x \le 0.20$. T_c's are substantially less for the smaller Ca-ion substitutions [67], but the qualitative trends are the same for all three ions. We reiterate that the tetragonal-orthorhombic transition temperature [3] is strongly depressed by these substitutions, but there appears to be no clean correlation between this transition and T_c. The point to make about the alkaline-earth substitutions and superconductivity is that properties of La_2CuO_4 change qualitatively with increasing x: first, the 3D magnetic ordering [66] is completely suppressed for $x \ge 0.03$ and second, an incoherent magnetic state [68] (possibly a spin glass state) occurs in the region between $x=0.03$ and 0.05. Finally, some kind of transition to metallic behavior occurs near $x=0.1$ [69]. This transition is most clearly evident in Hall-constant measurements [37], and superconductivity is first observed very close to this transition. It is not clear from experiment whether the abrupt change seen in the Hall constant is identical with an abrupt onset of superconductivity. Experiments do not indicate this in any clean way, but it must be appreciated that sample inhomogeneities and aspects of O-stoichiometry may make the observation of an abrupt onset of superconductivity with x difficult to defect. It is not clear, in addition, whether T_c near $x=0.15$ starts at a finite value or rises from 0 K with increasing x; low T_c can be confused experimentally with very broad T_c, and this could very well happen in a regime of x where the underlying
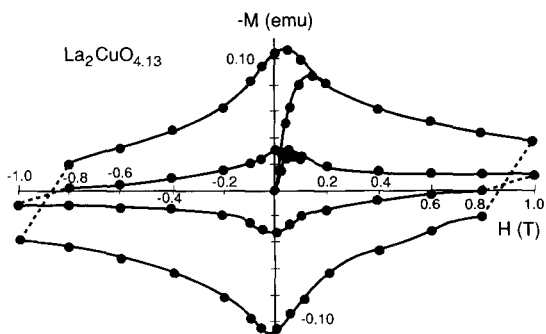

Fig. 15. Isothermal magnetization curves in a $La_2CuO_{4.13}$ crystal measured with field parallel (inner loop) and perpendicular (outer loop) to the Cu–O planes at 7 K.

electronic structure is undergoing a qualitative change.

In the region $x > 0.20$ [23], the O-stoichiometry at 1-bar O_2 pressure falls below 4.0. It is possible to maintain a stoichiometry close to 4.0 using higher O_2-annealing pressures [23] (fig. 5). The behavior of T_c with increasing x for these samples (fig. 4) is interesting: T_c falls off and disappears above $x \sim 0.30$. The indications are that T_c goes smoothly to 0 K in this regime of x. This interesting observation prompts the obvious speculation that the increased carrier density may go hand in hand with increased screening of, for instance, excitons responsible for the superconducting pairing interaction.

Substitutions analogous to those with Ba, Sr and Ca have been made with K [70] and Na [70,71]. Superconductivity does not occur for K substitutions but does for the Na ones: T_c rises to ~ 40 K for $La_{1.6}Na_{0.4}CuO_4$. It is to be expected that the physics here parallel that connected with alkaline-earth substitutions. It is interesting to note that Na-doped La_2CuO_4 annealed in inert gas exhibits an unknown magnetic state at ~ 10 K (possibly ferromagnetic order or spin glass state) [70]. The substitution [26] of other rare earths for La depressed T_c slowly and in a way that correlates with the rare earth size, and not at all with its 4f-moment (table II).

It is generally believed on both theoretical and experimental grounds that the conductivity in La_2CuO_4-based materials arises from Cu–O hybridized orbitals in the Cu–O planes. Substitutions [25] for Cu, therefore, should lead to drastic effects on T_c. Magnetic Ni ions, surprisingly, have a very modest effect on T_c, whereas the effect produced by strictly divalent Zn ions is striking. The Zn additions have the effect of moving the materials closer to the metal–insulator boundary. A systematic investigation of this involving Hall-constant measurements would be useful in the interpretation of the large effects produced by Zn substitutions. Data related to the effects of various substitutions on T_c have been placed in table II.

Most of the questions one has about the superconductivity in high-T_c oxides, such as what is the mechanism and what kind of pairing is involved, can only be answered indirectly. We will now attempt to address some of these issues. The first order of business is to parameterize the superconductivity; these

data are presented in table III. It is important to note that the extremely short coherence length inferred from critical-field measurements places the physics in an unusual regime where the pair size is only a few interatomic spacings. This obviously has important implications for a Ginzburg–Landau description of these superconductors. The lack of high quality single crystals of the superconducting materials has prevented the obtaining of much data concerning anisotropic superconducting properties.

An immediate question about the superconductivity concerns the critical-coupling strength. An analysis of the specific-heat anomaly at T_c [73,74] indicates that the superconductivity is in the weak-coupling limit of the BCS theory if one assumes that the samples are 100% superconducting. There have also been questions concerning the possibility of anisotropic pairing that could be visible in the specific-heat behaviors as $T \to 0$ K. In particular, a power law in T, rather than an exponential dependence of the electronic part of the specific heat, would be expected for a superconducting state which had zeros of the gap on parts of the Fermi surface [77]. One problem with much of the specific-heat data on high-T_c oxides, in fact, is that a large linear-in-T term [40] is seen, of the kind expected for gapless superconductivity. This term has turned out to be very sample dependent, which could be due to impurities [73,74] that also could smear gap-zeros. We are not aware of any data analysis drawing conclusions concerning anisotropic superconductivity from the $T \to 0$ K specific-heat data. There are experiments, however, which address this same question via the temperature dependence of the London penetration depth. The results are in conflict: a muon measurement on powder finds [78] a BCS temperature dependence; whereas, microwave absorption measurements [79], also on powder, find a power law. The resolution of these two results has not been made.

In principle, an estimate of the coupling strength also could be obtained by direct measurement of the superconducting energy gap by optical or tunneling methods. Virtually all of these experiments have been performed on powder samples, with results that range from $2\Delta/k_B T_c \lesssim 2$ for La–Ba–Cu–O [80] to $2\Delta/k_B T_c \sim 7$ for La–Sr–Cu–O [8]. Certainly, tunneling or optical reflectance measurements would be expected to be extremely surface sensitive and, there-

fore, possibly not reflect bulk behavior. On the other hand, infrared transmission [82] should be more characteristic of the bulk. Even in this case, there is a rather broad distribution of values for $2\Delta/k_BT_c$ but they tend to cluster [83] more closely about the BCS weak-coupling limit of 3.5. Sample inhomogeneity is a serious problem that must be addressed before reliable gap measurements can be made.

The question of perhaps more interest to the material physicists concerns the mechanism. Isotope experiments [84,85] using ^{16}O and ^{18}O find $T_c \propto M^{-0.16}$, where the exponent is reduced from the maximum value (-0.5) expected for a phonon mechanism. However, what one really expects is that the sum of the partial isotope effects over all the atoms will be -0.5. Although it has not been studied in La$_{2-x}$Sr$_x$CuO$_4$ superconductors, the copper-isotope effect [86] in YBa$_2$Cu$_3$O$_7$ is vanishingly small. It is also possible that more than one mechanism is active, phonons plus something else, in which case a reduced isotope effect would occur. Finally, it is possible that some other mechanism, excitonic for example, may have an isotope effect associated with it. We point out that the isotope effect arises through the ion-mass dependence of the phonon frequency in the phonon-mediated mechanism; even for a non-phonon mechanism, decreasing T_c by increasing oxygen mass could be expected, e.g., by reducing the Cu–Cu transfer integral which, in turn, reduces the superexchange interaction [87].

In addition to the remarkably high superconducting transition temperature in these materials, there is very strong dependence of T_c on pressure. Although early measurements on poorly characterized La–Ba–Cu–O showed [88] $dT_c/dP \sim 0.6$ K/kbar, this value now appears to be settling in at the still large value of $\sim 0.28 \pm 0.02$ K/kbar for La$_{1.85}$Sr$_{0.15}$CuO$_4$ [89] and approximately the same value [90] for La$_{1.85}$Ba$_{0.15}$CuO$_4$. To place these in perspective, dT_c/dP for the A15 compounds V$_3$Si with $T_c = 16.8$ K is ~ 0.035 K/kbar [91]. Further, high-T_c cuprates show a strong, positive change in T_c with pressure [89,90–93]; whereas the elements [94] and A15 compounds [95] have dT_c/dP both positive and negative. In these latter cases, in which superconductivity is well established to arise from electron–phonon coupling, the sign of dT_c/dP can be understood as arising generally from changes in the phonon spectrum with pressure that compete with a pressure derivative of the electron-density of states at the Fermi level $\mathscr{D}(E_F)$ which can be either positive or negative. It seems unlikely that all high-T_c materials would have a comparable energy dependence of $\mathscr{D}(E)$ around E_F, or that pressure would favor stronger electron–phonon coupling in each system. Another feature common to all the high-T_c materials is the increased conductivity above T_c with decreasing volume [90,92]. Unfortunately, no measurements have been made on the effect of pressure on the anisotropic conductivity in single crystals, but taking the results on sintered compacts leads to the problem of understanding the interrelationship between enhanced superconductivity and increased conductivity.

6. Final remarks

While not much is understood in detail about La$_2$CuO$_4$-based materials, we do have some clues as to how to think about them. In particular, it appears that the CuO$_2$-layers behave qualitatively like a 2D Hubbard model with half-filling. These properties of the CuO$_2$ layers appear, in fact, to be rather insensitive to external environment – witness the RE$_2$CuO$_4$ compounds. Introducing holes at the 0.15 per Cu level into La$_2$CuO$_4$ renders the material metallic, with superconductivity and possibly a remnant of magnetism. The effect of pressure on the Neel temperature and the superconducting transition temperature is opposite. The simplest, but strongly contested, conclusion is that magnetism and superconductivity are hostile to one another in these materials. The estimated small in-plane magnetic exchange coupling in superconducting La$_{2-x}$Sr$_x$CuO$_4$ and weak (relative to Zn) reduction in T_c with Ni substitution seem to indicate that magnetism is not the primary mechanism responsible for high temperature superconductivity.

The heterogeneous nature of these and higher T_c materials at the atomic level seems tailored for the Allender, Bray and Bardeen [96] exciton mechanism: metal–dielectric–metal...... . This raises the question as to whether a similar mechanism is disguised in the BaBiO$_3$-bases superconductors. Then we will have to think how the quasi-2D aspects of

cuprates are important for the occurrence of super-conductivity. It is also important not to forget that the electron–phonon interaction has not yet been ruled out as a possible mechanism for oxide superconductivity.

The central point about La$_2$CuO$_4$ is that it is under good control from the materials stand-point. We know how to make good, reproducible single crystals, and we are rapidly getting an accurate picture of the physics in the pure, undoped materials. The stage is set for the investigation of the properties of isolated holes in La$_2$CuO$_4$ and these investigations hold great promise for our understanding of oxide magnetism and superconductivity.

Acknowledgements

Note added: Very recently Tokura et al. [97] have discovered *electron* superconductivity in RE$_{2-x}$Ce$_x$CuO$_4$, with RE = Pr, Nd and Sm, having a maximum superconducting transition near 20 K for $x = 0.15$. Their results show superconductivity existing over a very limited range of x and metallic but not superconducting behavior for $x \geq 0.18$.

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