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Ground states of a triangular copper oxide system

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The low-temperature specific heat, $C(T)$, of the Delafossite family of triangle-planar cuprates, $R\mathrm{CuO}_{2+\delta}$, has been studied for R = La and Y and $0 < \delta \leq \frac{2}{3}$. Structural transformations between the hexagonal and the orthorhombic phases for R = Y appear as distinct lattice-contribution changes in $C(T)$. Near the oxygen-ordered limit, $\delta = \frac{2}{3}$, $C(T)$ displays a linear-in-T term of 6.5 and 1.3 mJ/mole K^2 for R = La and Y, respectively. The large specific-heat enhancement and a similar enhancement of the magnetic susceptibility for R = La are interpreted in terms of strong correlations near a metal–antiferromagnetic-insulator instability.

The fascinating properties of the copper oxide superconductors result from special microscopic conditions: (1) Cu ions situated in a square-planar arrangement and bridged by oxygen ions, (2) weak coupling to neighboring layers, and (3) doping such that the Fermi level lies near the middle of the Cu-O σ^* band. So far, there is no theoretical consensus regarding the precise role of each of these ingredients in producing superconductivity. Experimentally, it is of course not possible to vary each of these properties at will, though there is by now a large family of cuprate superconductors, each possessing different microscopic properties which can be studied for the purpose of systematic comparison.[1] One shared feature of all of these compounds, however, is the square-planar Cu arrangement. Recently, a class of cuprates has been reported[2] where the Cu ions sit not on a square planar, but on a triangle-planar lattice, allowing a test of geometry-based ideas for superconducting pairing, while retaining some of the unique microscopic features of Cu-O bonds. In the present work, we report on the low-temperature specific heat $C(T)$ of these materials over a wide range of concentrations, in magnetic fields up to 12 T and at temperatures from 0.1 to 15 K. We find that while these compounds are not superconducting, in the most structurally homogeneous members of this family, the low-energy behavior is that of a coexisting Fermi liquid and local moment system, similar in many respects to Si:P. For $\mathrm{LaCuO}_{2.64}$, both the specific heat and magnetic susceptibility of the Fermi liquid components are enhanced above the free electron values, suggesting the possibility of a nearby instability to an antiferromagnetic insulator.

The Delafossite structure is commonly realized for compounds with chemical formula ABX_2, where both A and B cations form two-dimensional arrays.[3] Typically B is monovalent, and variations of ABX_2 involving nonmagnetic Cu^+ and a magnetic trivalent ion have been studied with the focus on the geometrically frustrated magnetism of the trivalent species.[3,4] We recently demonstrated that $R\mathrm{CuO}_2$,[1] where R = La or Y, can be hole doped by oxygen intercalation into the Cu layer with concentrations of up to $R\mathrm{CuO}_{2.7}$, that is, over the same range of Cu valence as found in the square-planar cuprate superconductors. The temperature-dependent susceptibility, $\chi(T)$, and the resistivity, $\rho(T)$, of the triangular systems display two distinct types of behavior which are correlated with two types of oxygen-order-driven space groups. For R = Y and $\delta < 0.56$ in $R\mathrm{CuO}_{2+\delta}[\equiv R\mathrm{CuO}(\delta)]$ the structure is orthorhombic and both χ and $1/\rho$ display an activated temperature dependence. For R = Y and $\delta > 0.56$, the structure is hexagonal and the magnetothermal behavior is more complicated—ρ displays variable-range hopping and χ resembles that of a geometrically frustrated magnet, albeit with a low moment. For R = La, the structure is hexagonal over the range where the material is single phase ($\delta > 0.57$), and the bulk behavior is similar to hexagonal R =Y material. It is believed, on the basis of preliminary neutron scattering work[5] that the hexagonal phase possesses a high degree of oxygen order, corresponding to a $\sqrt{3} \times \sqrt{3}$ oxygen superlattice.

The samples studied here were ceramics, prepared by a method described elsewhere.[2] Specific heat measurements were made using a standard semiadiabatic heat pulse technique. Susceptibility measurements were made using a commercial superconducting quantum interference device magnetometer. Some of the R =Y samples had a 1% admixture of Ca substituting for Y—this was found to stabilize the hexagonal structure while having little effect on the resistivity.[6] In Fig. 1 we show $C(T)$ for all the members of the Delafossite family studied—these span the range of behavior from insulating to conducting. The data can be classified into three groups by virtue of $C(T)$ at high temperatures. The R =Y compounds fall into two groups, $\delta <$ and > 0.56. The different magnitudes of the high temperature $C(T)$ observed for these materials indicate an abrupt structural phase transition at $\delta \approx 0.56$ which correlates with the observed structure change between orthorhombic and hexagonal phases. The inset of Fig. 1 shows the Debye temperature, $\Theta_D(15)$, obtained by fitting the data for $15 > T > 12$ K to the form $C = 7.776 \times 10^3[T/\Theta_D(15)]^3$. These $\Theta_D(15)$ values are similar in magnitude to the copper oxide superconductors.[7] As can be seen by comparing the R = La and R = Y $\Theta_D(15)$ values for the hexagonal phases, about half of the difference can be ascribed to the larger La mass, and the remainder to a modification of the crystal binding energy, related to the difference in

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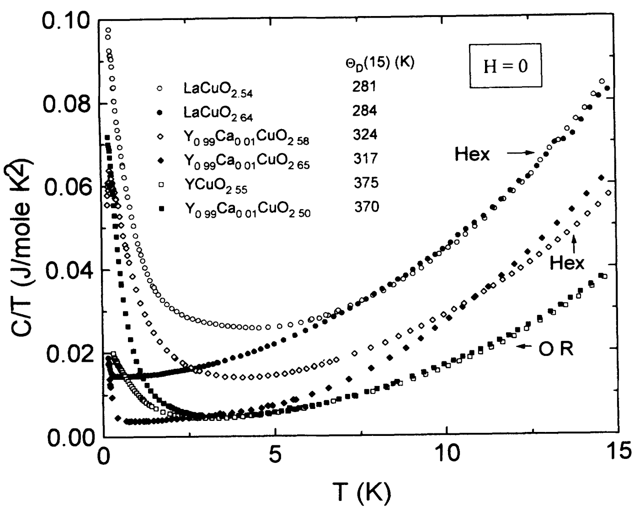

FIG. 1. Specific heat of the copper Delafossites $R\mathrm{CuO}_{2+\delta}$ for R =La and Y, over a range of oxygen concentrations. The difference in $C(T)$ at 15 K between the R = La systems and the hexagonal and orthorhombic R = Y systems is related to different phonons contributions. The table shows the effective Debye temperatures, $\Theta_D(15)$, obtained by fitting the data to a T^3 form between 12 and 15 K.

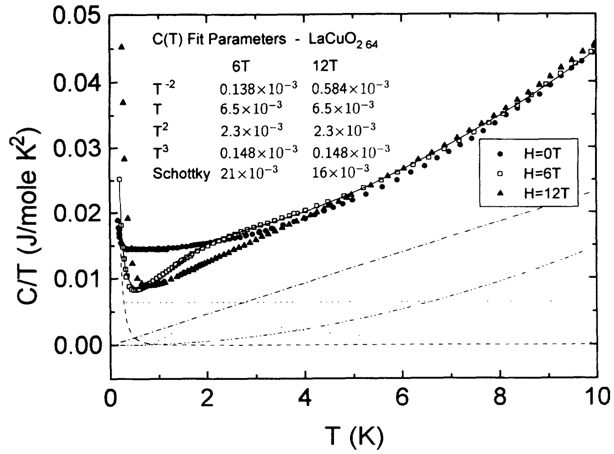

FIG. 2. Specific heat of $\mathrm{LaCuO}_{2.64}$ for various applied magnetic fields. The curves result from a least-squares fit of $C(T)$ with H = 6 T to terms varying as $1/T^2$ (dashed), T (dotted), T^2 (dashed-dot), T^3 (dashed-doubled dotted), and a Schottky anomaly (short dotted). The resulting fit coefficients for both H = 6 and 12 T are shown at the top.

size and electronegativity between the different cations. There is no significant variation in $\Theta_D(15)$ with changing O content, indicating that O affects primarily the high-energy phonon modes. It is interesting, therefore, that the hexagonal R = Y compounds display an effective low-energy phonon frequency 16% higher than their orthorhombic counterparts. Since the orthorhombic and hexagonal materials have a $2H$ stacking sequence, this difference must be related to the effect of O intercalation and, in particular, the greater density of Y-O bonds in the hexagonal material.

In most of the samples studied, the low temperature $C(T)$ is dominated by a rise with decreasing temperature, most likely due to a small fraction of Curie-like impurities. It is expected that this contribution arises from Cu^{2+} ions at crystal defects which fluctuate independently of the majority of the ions. For the sample with the largest such contribution, the total entropy is only a few percent of $R\ln 2$, agreeing with the susceptibility-derived impurity concentration.[2] For the purpose of investigating the behavior of the bulk of the strongly interacting moments, it is clearly desirable to separate out the Curie contribution. This will be easiest done using those samples possessing the lowest such impurity contribution, LaCuO(0.64) and $\mathrm{Y}_{0.99}\mathrm{Ca}_{0.01}\mathrm{CuO}_{2.65}$ [≡ Y(Ca)CuO(0.65)]. In order to perform accurate fits to $C(T)$, we must have an analytical form for the Curie spin behavior. This is difficult to do for $H = 0$ since the precise form of the (small) interaction among these spins is not known. For finite fields, $g\mu_B H \approx k_B T$, however, the low-energy spectrum of paramagnetic impurities is well described by a spin $\frac{1}{2}$ Schottky anomaly, as shown in Fig. 2. The lattice contribution to $C(T)$ can be assumed to have the usual power law form, modified to take into account the two dimensionality. The entropy of the Schottky anomaly at 6 T (0.24% $R\ln 2$) agrees with the entropy at H = 0(0.26% $R\ln 2$) after the linear and lattice terms from the 6 T fit are subtracted. It is interesting to note that the high-temperature data for LaCuO(0.64) can be fitted without an Einstein term, as required for the square-planar cuprates[7]—this suggests a qualitative difference in the phonon spectrum between the two types of compounds. At lower temperatures, an additional term, varying as $(H/T)^2$, is included to account for a nuclear contribution. The constituent fitting components are shown in Fig. 2. A linear term, corresponding to $\gamma_0 = 6.5$ mJ/mole K^2 is clearly visible. A similar-quality fit is obtained at 12 T and yields the same value for γ_0. Below we discuss the implications of the linear term.

In Fig. 3 are shown similar finite-field $C(T)$ data for

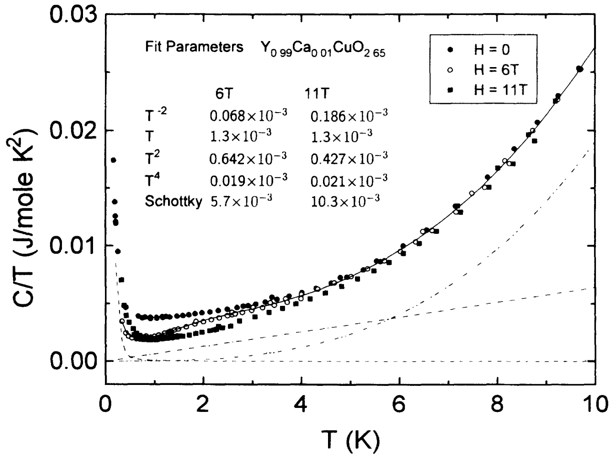

FIG. 3. Specific heat of $\mathrm{Y}_{0.99}\mathrm{Ca}_{0.01}\mathrm{CuO}_{2.65}$ for various applied magnetic fields. The curves result from a least-squares fit of $C(T)$ with H = 6 T to terms varying as $1/T^2$ (dashed), T (dotted), T^2 (dashed-dot), T^3 (dashed-doubled dotted), and a Schottky anomaly (short dotted). The resulting fit coefficients for both H = 6 and 11 T are shown at the top.

Y(Ca)CuO(0.65). Here we see the same qualitative field dependence of the low-temperature Curie-spin contribution as found for LaCuO(0.64), as well as a linear term which is relatively field independent between 6 and 12 T. However, the value of the linear term, as found in an unconstrained fit similar to that shown in Fig 2, is $\gamma_0 = 1.3$ mJ/mole K^2, much lower than for LaCuO(0.64). The Schottky anomaly from the Curie spins is several times smaller than for LaCuO(0.64). In addition, the lattice contribution for $C(T)$ is better fitted over this limited temperature range with a T^4 term—substituting a T^3 term leads to a negative value for the T^2 term. This more rapid temperature dependence suggests either a difference in the photon density of states between Y(Ca)CuO(0.65) and LaCuO(0.64), or a magnetic contribution less sensitive to field than free spins.

Based on existing transport[2] and NMR data,[8] it is reasonable to interpret the finite γ_0 as arising from conduction electrons. The density of these electrons can be estimated from the O density, assuming complete charge transfer between O and Cu. We note that the average Cu valence will correspond to $2^+(d^9)$ for $\delta = 0.5$, and is expected to produce a magnetic insulator. If the conduction electron density per Cu is given by $n = 2(\delta - 0.5)$, then for $\delta = 0.64$, the Fermi energy is $E_F \approx 6060$ K, assuming a two-dimensional Fermi surface. If such a system can be considered weakly interacting, then we can use the free electron relation in 2D, $\gamma_0 = \pi m k_B^2/3\hbar^2 = 1.26$ mJ/mole K^2, similar in magnitude to that found for Y(Ca)CuO(0.65), but a factor of 5 lower than in LaCuO(0.64). The origin of this discrepancy is discussed below.

Insight into the origin of the enhancement of γ_0 is obtained from an analysis of the susceptibility, $\chi(T)$ for LaCuO(0.64) (Ref. 2) and Y(Ca)CuO(0.65), both shown in Fig. 4. Here, a diamagnetic core contribution of -6.27×10^{-5} and -5.48×10^{-5} emu/mole have been subtracted from the data for LaCuO(0.64) and Y(Ca)CuO(0.65), respectively.[9] In order to fit $\chi(T)$ over the entire range of temperatures from 2 to 300 K, it is necessary to include both a temperature-independent (Pauli and Van Vleck) term $\chi_{\rm ti}$, and an inversely temperature-dependent term, $\chi_{\rm td}$. In the simplest of pictures, one assumes that $\chi_{\rm td}$ is given by a Curie-Weiss (CW) expression, $\chi_{\rm CW} = C/(T + \theta_{\rm CW})$, corresponding to interacting local moments. A least-squares fit yields to the data for CaCuO (0.64) $\theta_{\rm CW} = 50$ K and C corresponding to a density of 5.9% of $s = \frac{1}{2}$ moments. Although such an expression fits the data well, [after including a small (0.24%) additional impurity term, consistent with the Schottky term in $C(T)$] it is unlikely to be an accurate description of the ground state since there is no corresponding feature in $C(T)$ [the upturn in $C(T)$ in zero field is an order of magnitude smaller than predicted from the CW fit]. Within the CW analysis, $\chi_{\rm ti} = 2.0 \times 10^{-4}$, roughly four times that expected from Van Vleck processes,[8,10] and therefore attributable mainly to spin susceptibility. Compared to the 2D free electron result, $\chi_0 = \mu_B^2 m/\pi\hbar^2 = 0.17 \times 10^{-4}$, this represents a factor of ~ 9 enhancement.

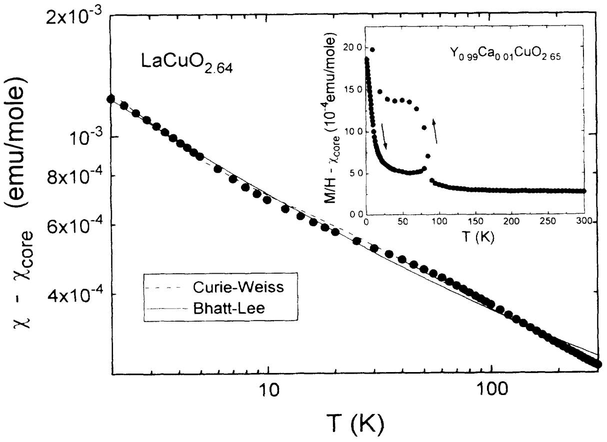

FIG. 4. Magnetic susceptibility of LaCuO$_{2.64}$. The solid and dashed lines are fits using the Bhatt-Lee and Curie-Weiss expressions, respectively. The inset shows the magnetization of Y$_{0.99}$Ca$_{0.01}$CuO$_{2.65}$ on warming after zero-field cooling and cooling in a finite field. In both cases the applied field was 0.1 Tesla.

An alternative picture which incorporates both $C(T)$ and $\chi(T)$, is the cluster-scaling model of Bhatt and Lee (BL).[11] Originally applied to Si:P to explain the absence of ordering in the insulating phase, the model shows that the loss of entropy in a disordered magnet is due to the creation of local singlets as temperature is lowered. An extension of this model was suggested by Paalanen *et al.*[12] to describe the thermodynamic behavior of Si:P in the metallic phase. This involves simply a two-component system, with $C(T)$ and $\chi(T)$ given by

$$\gamma/\gamma_0 = m_c^*/m_0^* + (T/T_a)^{-\alpha} \ , \tag{1}$$

$$\chi/\chi_0 = m_\chi^*/m_0^* + \beta(T/T_a)^{-\alpha} \ , \tag{2}$$

where m is the conduction-band mass, the "0" subscript refers to free electron values, and T_a is a constant related to local moment spin density. We have modified the expression used for Si:P to account for spin-fluctuation mass-enhancement of $\chi_{\rm ti}$. In the present case, assuming the validity of this model, we can associate the observed metallic (temperature-independent) components of both $C(T)$ and $\chi(T)$ with quasiparticle mass enhancement, the first terms on the right-hand side of Eqs. (1) and (2). The temperature-dependent contributions are governed by a power law with exponent α and, as shown in Fig 4, this expression works well to describe $\chi(T)$, without the need for an additional free-impurity component used in the CW fit. We find now $\chi_{\rm ti} = 1.16 \times 10^{-4}$, which, after accounting for a Van Vleck component, represents a factor of $m_\chi/m_0^* \sim 4$ enhancement over the free electron value. We also find $\alpha \approx 0.4$, close to the value of 0.62 found for Si:P,[13] though it is three dimensional, unlike RCuO$_2$. For $C(T)$, the linear term in LaCuO(0.64) represents a mass enhancement of $m_c^*/m_0^* = 5$, similar in magnitude to the $\chi(T)$ enhancement, yielding a Wilson ratio of order unity. For the temperature-dependent term, the present $C(T)$ measurements do not extend to low-enough temperatures to accurately determine an exponent to compare with the

$\chi(T)$ value. In the presence of an applied field the BL temperature-dependent $C(T)$ term becomes a Schottky anomaly, corresponding to odd-numbered spin clusters in the inhomogeneous medium. The density of localized moments, n_s, in this model can then be inferred from the height of the Schottky anomaly in finite fields, and we find $n_s \approx 0.25\%$. Comparing this to similar results for Si:P,[14] we infer a density of local moments on the order of 1%.

The BL picture provides a convenient framework with which to parametrize the data presented here. However, the underlying phenomena are quite likely to differ quantitatively from that of Si:P. For instance, in the latter system at the metal-insulator transition, the radius of a donor electron is about an order of magnitude greater than in LaCuO(0.64). The growth of magnetic clusters as T approaches zero will therefore be influenced to a greater degree by longer range forces in Si:P than in LaCuO(0.64). It is intriguing, therefore, that the behavior of the two systems is so similar in such different parameter ranges.

A qualitatively different picture emerges for Y(Ca)CuO(0.65). Here, $\gamma \approx \gamma_0$, whereas the susceptibility enhancement, inferred from the high-temperature data, is ~ 5. [The low-temperature data are obscured by the presence of a second, ferromagnetic, phase ($T_c = 85$ K) incorporating only of order 1% of the spins.] The observation of both a large χ_{ti} enhancement and no γ enhancement suggests that Y(Ca)CuO(0.65) is near a ferromagnetic instability, unlike LaCuO(0.64) which, given its low Wilson ratio, appears near an antiferromagnetic instability of the Brinkman-Rice variety.[15] These different behaviors might be related to the different structures found in structural studies. For both LaCuO(0.64) and Y(Ca)CuO(0.65), a $\sqrt{3} \times \sqrt{3}$ oxygen superlattice structure has been observed in preliminary neutron diffraction studies,[5,16] and the lattice. Constants differ appreciably between the two compounds [Cu-Cu distance is 3.6 Å for Y(Ca)CuO(0.65) and 3.86 Å for LaCuO(0.64)]—given the high sensitivity of exchange interactions to ionic separation, this could significantly alter the exchange Hamiltonian in both magnitude and sign. Furthermore, ^{63,65}Cu NMR studies on both compounds show that, while there is evidence for only one Cu site for the LaCuO(0.64) case, Y(Ca)CuO(0.65) displays a complex spectrum indicative of multiple Cu sites.[8] Clearly the structure needs to be elucidated in detail in order to understand the origin of the different magnetic behaviors observed.

The analogies used in describing LaCuO(0.64) and Y(Ca)CuO(0.65), namely, a semiconductor and a Stoner-enhanced metal, illustrate the marked differences between the present triangular-planar materials and their square-planar counterparts. In particular, the absence of superconductivity in the $R\mathrm{CuO}_{2+\delta}$ materials is possibly related to the triangular geometry of the Cu-O lattice. For example, if spin fluctuations are mediating the superconducting pairing interactions in the square planar systems, then frustration associated with triangular symmetry[17] would inhibit the growth of a correlated quasiparticle state. However, band structure calculations[18] have shown that the density of states at the Fermi level is predominantly composed of Cu-O $d_{3z^2-r^2}$ orbitals which are directed normal to the plane. In contrast, the conduction band in the square-planar cuprates is characterized by highly coplanar $d_{x^2-y^2}$ orbitals. Thus, there are important microscopic differences between the square-planar and triangular systems, apart from the purely geometrical ones. Further theoretical work is needed to ascertain the strengths of these two alternative influences.

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