

NOVEL PHASE TRANSITION IN NON-ANTIFERROMAGNETICALLY ORDERED CRYSTALS OF  $\text{La}_2\text{CuO}_4$

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We report the discovery of a new phase diagram in the magnetic field-temperature plane for single crystals of  $\text{La}_2\text{CuO}_4$  that show no sign of antiferromagnetic order. The phase boundary is defined by magneto-resistance and susceptibility measurements. We discuss several possibilities that may lead to the phase diagram observed.

An antiferromagnetic phase transition, indicated by a maximum in the magnetic susceptibility ( $\chi$ ) and anomalies in the electrical resistivity ( $\rho$ ), has been widely observed in sintered powders and single crystals of  $\text{La}_2\text{CuO}_4$ . Work by Johnston et al. and Freltoft et al.<sup>1</sup> on the variation of the Neel temperature ( $T_N$ ) of  $\text{La}_2\text{CuO}_{4-\delta}$  as a function of  $\delta$  in sintered powders and crystals indicates that  $T_N$  approaches zero as  $\delta$  goes to zero. More recent experiments<sup>2</sup> on single crystals of  $\text{La}_2\text{CuO}_{4-\delta}$  show the presence of strong 2D spin-1/2 antiferromagnetic fluctuations (quantum spin fluid state) in the Cu-O planes above  $T_N$ , with three dimensional ordering setting in at approximately 200 K in the crystal measured. Although the nature of the proposed 2D quantum state is not understood theoretically, its existence is not surprising given the huge anisotropy observed<sup>3</sup> in transport measurements on single crystals of  $\text{La}_2\text{CuO}_4$  that implies a strongly 2D character in this material. To provide further understanding of the highly unusual physical properties of  $\text{La}_2\text{CuO}_4$ , we have investigated the magnetic, transport and thermal properties of single crystals in magnetic fields applied in different directions with respect to the Cu-O plane.

Our samples were  $\text{La}_2\text{CuO}_4$  crystals ( $\sim 1 \times 1 \times 0.1 \text{ cm}^3$ ) grown from a PbO-based flux. Lattice constants were determined by the eight-position Hamilton technique<sup>4</sup> using ten reflections with  $29^\circ < \theta < 37^\circ$ . These x-ray measurements indicated the orthorhombically distorted  $\text{K}_2\text{NiF}_4$  structure at room temperature with lattice constants  $a = 5.358 \pm 0.002 \text{ \AA}$ ,  $b = 13.181 \pm 0.007 \text{ \AA}$  and  $c = 5.403 \pm 0.002 \text{ \AA}$  (volume =  $379.26 \text{ \AA}^3$ ). Wet chemical analyses gave a composition of  $\text{La}_{1.75}\text{CuO}_{4.3}$ , plus  $\sim 2$  at % Pb, for the crystals studied. The presence of Pb and excess oxygen may be associated in part with PbO flux at the

sample surface; however, this cannot account for all the oxygen excess.

Resistance and magnetoresistance were measured with a standard four probe technique using In pressed contacts on the a-c basal plane. As plotted in Fig. 1, the resistance in

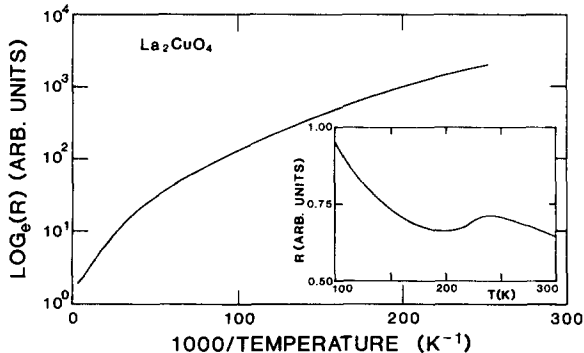


Fig. 1.  $\text{Log}_e R$  vs.  $1/T$  of a single crystal  $\text{La}_2\text{CuO}_4$  sample in zero applied magnetic field which does not show any antiferromagnetic ordering-like resistance anomaly. The inset shows a resistance anomaly characteristic of a single crystal sample which undergoes an antiferromagnetic transition at 240 K.

zero applied field increases strongly with decreasing temperature, with a non-exponential variation characteristic of dirty semiconductors,<sup>5</sup> and does not show any resistance anomaly typical of 3D antiferromagnetic ordering. In contrast, the inset of Fig. 1 shows the typical resistance anomaly of single crystal  $\text{La}_2\text{CuO}_{4-\delta}$

which orders antiferromagnetically near 240 K. All data shown here, except the inset of Fig. 1, are taken from single crystal samples which do not indicate any antiferromagnetic ordering-like resistance anomaly in zero applied magnetic field.

In Fig. 2 resistances at various fixed temperatures are plotted as a function of

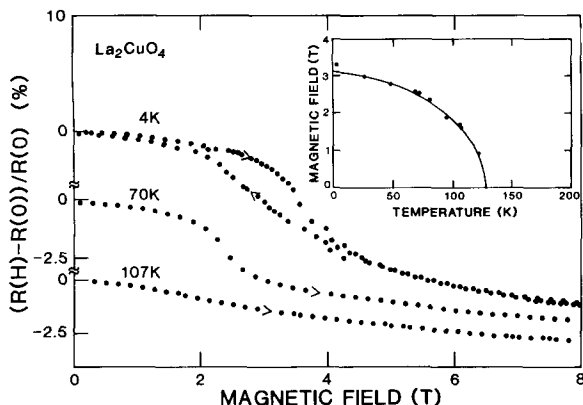


Fig. 2. Representative magnetoresistance curves of  $\text{La}_2\text{CuO}_4$  at various fixed temperatures. The magnetic field is applied perpendicular to the Cu-O plane. The inset displays the phase diagram determined from the mid-point of the magnetoresistance jump.

magnetic field applied perpendicular to the basal plane. The resistance drops rather sharply at some magnetic field, suggesting the presence of a field-induced phase transition. (The notation "phase transition" is used in the sense of characterizing the anomalies observed as the temperature or magnetic field is varied.) The resistance drop is of the order of 10% at 4 K and the effect diminishes as the temperature is raised, becoming undetectable in our measurements above 120 K. This leads to some uncertainty in determining the high temperature portion of the magnetic field-temperature phase diagram shown in the inset of Fig. 2. Hysteresis, seen clearly in the 4 K-curve in Fig. 2, reduces rapidly as the temperature increases and is unnoticeable above 20 K. We note that conduction is highly anisotropic in these crystals. The anisotropy factor was determined by the Montgomery method<sup>6</sup> in several specimens. Although slight variations from sample to sample were found, typical values for the anisotropy are  $>150$  ( $>250$ ) at room temperature (liquid nitrogen temperature), with the lower resistivity in the Cu-O plane. Such a huge anisotropy in the electrical resistivity clearly demonstrates that  $\text{La}_2\text{CuO}_4$  is electronically two-dimensional. Furthermore, the Cu-O plane has a metallic-like temperature dependent resistivity above  $\sim 130$  K but is semiconductor-like at lower temperatures; however, conductivity perpendicular to the Cu-O plane is semiconductor-like for all  $T < 300$  K.

The magnetization  $M$ , with magnetic field  $H$  applied perpendicular to the basal plane, was measured at various temperatures with a Quantum Design SQUID susceptometer and is plotted in Fig. 3. We see no evidence for a "conventional" antiferromagnetic transition, i.e., a sharp cusp in  $\chi(T)$ , in these data. Instead, we find a rounded feature in the vicinity of 120 K in a measuring field of 0.3 T; this bump moves

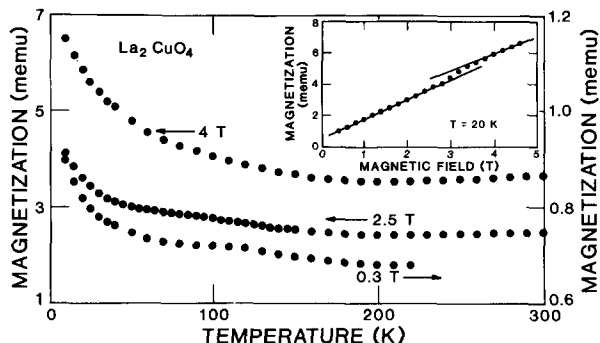


Fig. 3. Magnetization vs. temperature measured with applied field 0.3 T (refer to right vertical scale), 2.5 T, and 4 T (refer to left vertical scale). The temperature at which the rounded peak occurs is approximately 120 K (80 K) at 0.3 T (2.5 T). A magnetization curve at 20 K is plotted in the inset. The total mass of measured crystals was 343.37 mg and the applied field is perpendicular to the basal plane.

rapidly to lower temperatures as the field is increased and disappears in the field of 4 T. [Below  $\sim 170$  K, the susceptibility measured in a 4 T field can be fit to  $\chi_{\text{mole}} = \chi_0 + C/(T + \theta)$ ,

where  $\chi_0 = 8.2 \times 10^{-5}$  emu/mole Cu,  $C = 5.3 \times 10^{-3}$  emu-K/mole Cu, and  $\theta = 37.5$  K, implying an effective moment of  $0.21 \mu_B/\text{Cu}$  if the Curie term is due solely to Cu.] The temperatures at which the peak appears in various fields agree with the phase boundary shown in the inset of Fig. 2, additionally supporting the presence of a phase transition. The magnetization as a function of applied magnetic field perpendicular to the basal plane at 20 K is displayed in the inset of Fig. 3, where a slope change can be seen clearly near 3 T. The jump in magnetization at 3 T and 20 K, defined by the construction shown in the inset, is  $\sim 5.9 \times 10^{-4}$  emu, which implies an increase of  $1.25 \times 10^{-4} \mu_B/\text{formula unit}$ . We

note that the magnetization curve as a function of magnetic field taken at 2 K shows a large hysteresis which by 20 K becomes smaller than the experimental resolution. It is interesting that magnetization vs. magnetic field applied in the basal plane at various fixed temperatures does not show a similar jump within the sensitivity in our measurement. We also note that for  $4 \text{ K} < T < 350 \text{ K}$  the magnetic susceptibility measured with  $H$  in the basal plane is nearly three times smaller than that with the magnetic field perpendicular to the basal plane.

Specific heat ( $C$ ) measurements also were performed on two of these crystals (total mass 39.38 mg) and the results are plotted as  $C/T$  vs.  $T^2$  in Fig. 4. As shown in the inset, an

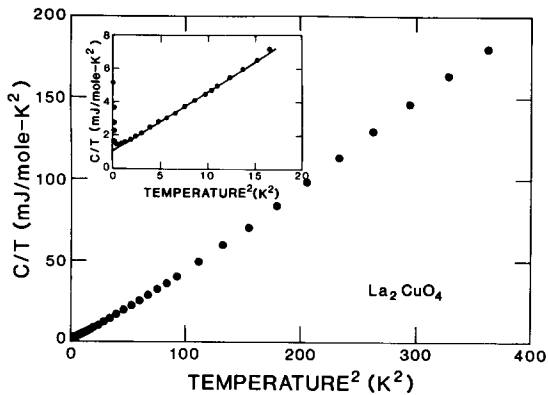


Fig. 4. Specific heat divided by temperature vs. temperature squared ( $C/T$  vs.  $T^2$ ) from 1.8 K to 20 K. As shown in the inset, an extrapolated value for the linear term in the specific heat is 1 mJ/mole  $K^2$  and the Debye  $\theta_D$  is 320 K.

extrapolation of the data to  $T = 0$  gives a finite intercept of  $1.0 \pm 0.1$  mJ/mole  $\text{Cu } K^2$ ,<sup>7,8</sup> which is unchanged in a 10 T magnetic field, suggesting that the finite value of  $C/T$  at  $T = 0$  may not be related to the phase transition. Normalized per unit volume, the result  $\gamma = 8.8$  J/ $\text{m}^3\text{K}^2$  is smaller than metallic copper by one order of magnitude but several times larger than typical structural glasses, e.g. vitreous silica. The low temperature upturn in  $C/T$  may signal the onset of a nuclear Schottky anomaly; although, an alternative explanation has been proposed<sup>9</sup> that attributes this behavior to the presence of a hyperfine magnetic field at the Cu nucleus produced by itinerant antiferromagnetic order in the Cu-O planes.

We emphasize that our experimental findings are not limited to one crystal but are highly reproducible: the response of the magnetic susceptibility and resistance to temperature and magnetic field reported here has been observed in several crystals from the same preparation batch. Magnetoresistance measurements on  $\text{La}_2\text{CuO}_4$  crystals prepared in a different batch, but using the same growth procedure, also show a phase transition at similar fields and temperatures. Furthermore, the transition was affected only weakly by doping crystals with Zn impurities and by removing small amounts of oxygen via vacuum annealing with a Zr getter. In the latter case, still no evidence for 3D antiferromagnetic order was found but the magnetoresistance anomaly at 4 K was less pronounced. Analysis of resistivity data on these other crystals results in H-T phase diagrams similar to the one in the inset of Fig. 2. Likewise,

the linear term in the specific heat also appears to be intrinsic, being observed in different single crystals as well as in polycrystalline samples of  $\text{La}_2\text{CuO}_4$ .

We believe there is substantial indirect evidence that the phase transition we observe is not of conventional origin and is a bulk property of  $\text{La}_2\text{CuO}_4$  crystals which do not order three-dimensionally. (1) The extreme sensitivity of the transition temperature to applied magnetic fields is to be contrasted with observations<sup>10</sup> on the Neel temperature of oxygen deficient polycrystalline samples in which 4.5 T suppresses  $T_N$  by only ~10%. We find a similar field dependence of  $T_N$  in oxygen deficient single crystals; (2) The temperature dependence of the phase transition field is opposite that expected for a conventional spin-flop transition; (3) The "universality" of results obtained on several different single crystals argues against impurities or defects causing the phase transition; and (4) Rather large changes in the resistivity and magnetization at the transition suggest that it is a bulk effect.

In the absence of detailed microscopic measurements, it is difficult to specify the nature of the phase diagram we have observed. As discussed earlier by others,<sup>2</sup> the small susceptibility for a system such as  $\text{La}_2\text{CuO}_4$  with a large concentration of  $S = 1/2$  spins suggests the presence of strong antiferromagnetic fluctuations at room temperature or below. The absence of a well-defined (i.e., sharp in field and temperature) phase transition may be due to either low dimensionality effects, deviation from perfect stoichiometry, quantum fluctuations, or frustrations arising from nearest and next-nearest neighbor interactions. Low dimensionality has been invoked<sup>11</sup> to account for the relatively low 3D antiferromagnetic ordering temperature in oxygen deficient specimens. Our observations, if related to 3D ordering, are of a distinctly different nature because: (1) a magnetic field suppresses the transition temperature much more rapidly than it does  $T_N$  in oxygen deficient samples and (2) the transition is insensitive to partial removal of oxygen. An attractive alternative is the possibility of an unusual transition not involving 3D order, as could be envisioned for a system with anisotropic magnetic interactions sufficiently weak that it could not be described within the framework of either 2D Ising or Heisenberg models. Frustration effects, common to the resonating valence bond model of Anderson,<sup>12</sup> also are distinctly possible explanations for the observed phase transition. Some of these questions may be resolved by additional experiments on single crystals in which both metal atoms and oxygen content are varied systematically.

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