

Heat capacity of single-crystal La_2CuO_4 and polycrystalline $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0 \leq x \leq 0.20$) from 110 to 600 K

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Heat-capacity $C(T)$ data on the title materials, as well as on CuO for comparison, were obtained with use of a differential scanning calorimeter to a precision of ≈ 0.1 –1%. The measurements were carried out (i) to characterize the thermal anomaly at the tetragonal-orthorhombic transition temperature T_0 of single-crystal La_2CuO_4 and polycrystalline $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0 \leq x \leq 0.20$) and (ii) to search for thermal anomalies at the Néel temperature T_N of La_2CuO_4 (≈ 300 K). We find a cusp-shaped anomaly with a peak at 523 K ($\approx T_0$) for a single crystal of La_2CuO_4 with $T_N = 304$ K and find the transition to be second order, consistent with previous neutron- and x-ray-diffraction measurements. T_N was determined from measurements of the anisotropic magnetic susceptibility on the same crystal, which are also presented. The $C(T)$ anomaly at T_0 is smeared out somewhat in polycrystalline La_2CuO_4 . The size of the anomaly decreases with x in polycrystalline $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ until the anomaly is no longer observable for $x \geq 0.10$. For $0 \leq x \leq 0.08$, T_0 decreases linearly with x at a rate $dT_0/dx = -(2430 \pm 50)$ K. This variation of T_0 with x is consistent with that found previously using x-ray and neutron diffraction. No features in $C(T)$ were observed at the Néel temperature of single-crystal or polycrystalline La_2CuO_4 . This is consistent with the expectation that the magnetic entropy is very small at T_N , since dynamic short-range intraplanar antiferromagnetic ordering, which begins at much higher temperatures, is well developed at T_N . A calculation shows that the expected size of the anomaly at T_N is well below the resolution of the measurements.

I. INTRODUCTION

The occurrence of superconductivity above 10 K in an oxide was first reported for LiTi_2O_4 ($T_c \leq 13.7$ K) with the three-dimensional (3D) cubic spinel structure in 1973.^{1–4} Two years later, superconductivity was found in the $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_3$ system ($T_c \approx 12$ K) with a distorted perovskite structure.⁵ High-temperature superconductors have been the subject of intense study since the discovery of superconductivity above 30 K in the La-Ba-Cu-O system in 1986.⁶ Heat-capacity $C(T)$ measurements have been widely used to study the new materials. The detection of anomalies in $C(T)$ at T_c in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$,^{7,8} $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$,⁹ etc., eliminated the initial possibility^{6,10–12} that the superconductivity was a surface or interface effect. More generally, measurement of $C(T)$ is a tool that allows investigations of the integrated electronic, phononic, and magnetic excitation spectra, together with their interactions. For instance, in the mean-field approximation, a second-order phase transition at T_c is seen in $C(T)$ as a well-defined jump at the transition temperature. When experimental resolution permits, the effects of thermal fluctuations near T_c can modify the observed jump.¹³ However, lattice disorder effects can round the peak and/or make the transition undetectable experimentally. Microscopic parameters can be obtained from $C(T)$ in favorable cases using appropri-

ate models.^{13–15}

In La_2CuO_4 , a tetragonal-orthorhombic phase transition occurs at a temperature $T_0 \approx 530$ K,^{16,17} in which the CuO_6 octahedra rotate in a staggered fashion,¹⁸ as shown in Fig. 1. Substituting an alkaline earth (Sr, Ba) (Refs. 18–21) for La or increasing the oxygen content²² stabilizes the tetragonal structure, lowering T_0 . The 2D–3D antiferromagnetic transition in pure La_2CuO_4 at $T_N \approx 300$ K leads to the magnetic structure shown in Fig. 1.^{23,24} T_N is very sensitive to the oxygen content; changing the oxygen content by ≈ 0.04 changes T_N by ≈ 250 K.^{22,25} Substituting Sr for La in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ increases the hole concentration in the CuO_2 layers and frustrates the long-range antiferromagnetic ordering, resulting in a decrease in T_N to ≈ 0 K by $x = 0.02$.²⁰ For $0.02 < x < 0.05$, the material shows a spin-glass character at low temperature.^{26–29} In this region, the CuO_2 sheets are nearly metallic, exhibiting weak localization,³⁰ which is an effect specific to a 2D disordered electronic system.³¹ $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ has the body-centered-tetragonal ($I4/mmm$) K_2NiF_4 -type structure down to at least 10 K,³² and therefore does not exhibit the orthorhombic distortion found in La_2CuO_4 . In $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, the out-of-plane oxygens in La_2CuO_4 are replaced by Cl and the La by Sr, thereby preserving the +2 oxidation state of Cu. The Néel temperatures of the two compounds are comparable (≈ 300 K).³²

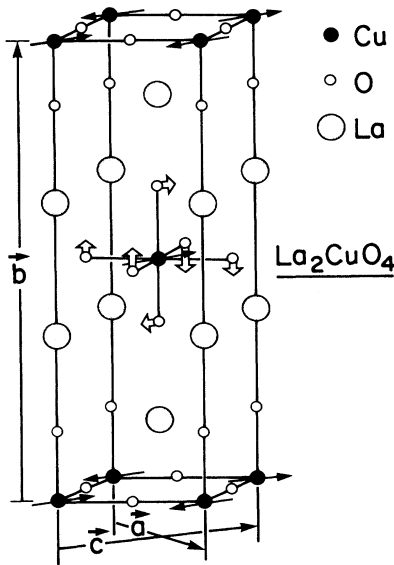


FIG. 1. Structure of La_2CuO_4 , after Ref. 18. The rotation of the CuO_6 octahedra accompanying the tetragonal to orthorhombic transition is shown. Arrows on the Cu atoms give the directions of the ordered moments below the Néel temperature of ≈ 300 K.

Herein, we present heat-capacity studies between 110 K and ≈ 600 K carried out to elucidate the thermal affects at T_0 and T_N in single-crystal La_2CuO_4 and at T_0 in polycrystalline $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0 \leq x \leq 0.20$). For comparison with our $C(T)$ data for La_2CuO_4 , we measured $C(T)$ for polycrystalline CuO, which has square planar coordination of copper by oxygen,³³ unlike the other 3d-transition-metal monoxides which have octahedral coordination of the transition metal by oxygen.

II. EXPERIMENTAL DETAILS

The La_2CuO_4 single crystal of mass 115 mg is the same crystal for which the induced moment form factor above T_N was measured using neutron diffraction.³⁴ Polycrystalline $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples were made by the standard solid-state reaction method. After single-phase powders were achieved according to powder x-ray diffraction, samples of mass 20 to 115 mg were pelletized and sintered or annealed in a tube furnace in flowing O_2 at 950°C for 5 h, then cooled to 600°C in 3 h, held for 24 h, then cooled to 400°C in 5 h, held for 24 h, and finally oven-cooled to room temperature. CuO powder was pressed into a pellet at a pressure of 10 tons/cm², sintered at 900°C and annealed at 600°C and then at 400°C in flowing oxygen in a tube furnace.

Heat-capacity measurements from 110 K to ≈ 600 K were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC). The DSC was calibrated and run in the temperature ranges 110 to 400 K, using liquid N_2 as coolant, and 400 to 600 K, using a water-ice mixture as coolant, respectively. The calibration was checked with pure sapphire. The measured specific heat is compared with standard values³⁵ in Figs. 2(a) and 2(b). This comparison shows that the accuracy of our measure-

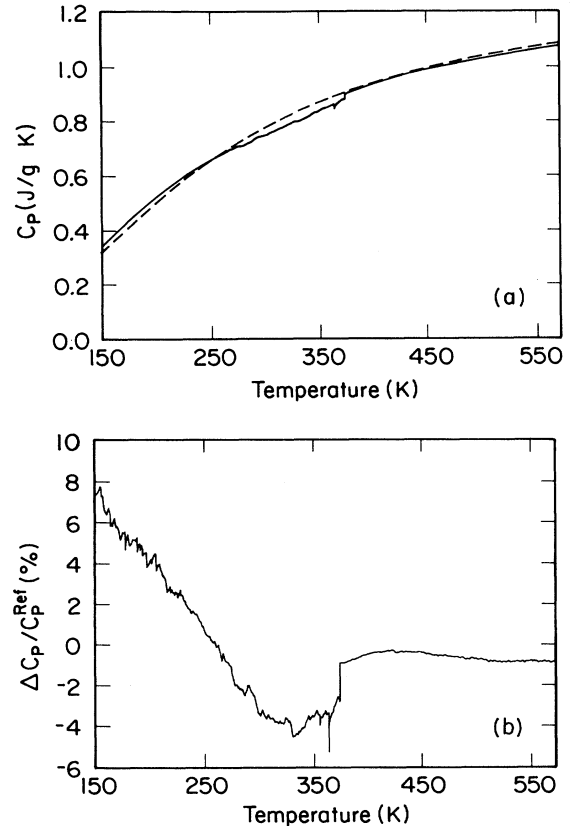


FIG. 2. (a) Comparison of the measured heat-capacity $C_p(T)$ data for a 65.9-mg disc of sapphire (solid curve) with high-accuracy data from Ref. 35 (dashed curve). (b) Percentage deviation $\Delta C_p/C_p^{\text{Ref}}$ of our data in (a) from the data of Ref. 35. The discontinuous changes at ≈ 365 K in (a) and (b) separate the two temperature ranges over which the measurements were separately carried out.

ments of C_p is better than 1% for the 400–580-K range, and is better than 8% for the 150–400-K range. The precision of the measurement, on the other hand, is ≈ 0.1 –1%, depending on the temperature [see Fig. 2(b)]. Measurements were made in the two temperature ranges separately. The data presented here were obtained using a heating rate of 10 K/min, except those in Fig. 9 below, which were obtained at 5 K/min.

III. RESULTS

A. La_2CuO_4

Heat-capacity C_p data versus temperature in the ranges 330 to 575 K and 120 to 375 K for single-crystal La_2CuO_4 are shown in Figs. 3(a) and 3(b), respectively. Corresponding data for a polycrystalline sample are shown in Fig. 4. A feature in C_p at $T_0 \approx 530$ K is clearly seen for both samples. The small anomaly in Fig. 3(a) at 429 K is the melting transition of $\approx 2 \mu\text{g}$ of In metal on the surface of the crystal; indium was used prior to the crystal arriving at Ames to attach electrical leads for resistivity measurements. The heat capacities at constant

volume (C_v) are also plotted versus temperature in Figs. 3(a) and 4(a) (in the high-temperature range). C_v was derived using the thermodynamic dilation correction

$$C_p - C_v = T \left[\frac{\partial p}{\partial T} \right]_V \left[\frac{\partial V}{\partial T} \right]_p = Bv\beta^2 T, \quad (1)$$

where B , v , and β are assumed to be independent of temperature, $B = 1/\rho Vc^2 = 1.85 \times 10^7 \text{ N/cm}^2$ is the bulk modulus,³⁶ $v = 1/(7.12 \text{ g/cm}^3)$ is the volume used to normalize C_p , and $\beta = 3.6 \times 10^{-5} \text{ K}^{-1}$ (Refs. 37 and 38) is the volume thermal-expansion coefficient. We find that $C_p - C_v = (3.25 \times 10^{-5} \text{ J/g K})T$, which is about 5% of C_v at 400 K.

Magnetic susceptibility data for the La_2CuO_4 crystal were obtained using a George Associates Faraday magnetometer. The results are shown in Fig. 5. The Néel temperature T_N is taken to be the temperature of the peaks in Fig. 5: $T_N = 304 \text{ K}$.³⁴ From the $C_p(T)$ data for the La_2CuO_4 single crystal from 110 to 380 K in Fig. 3(b), there is no indication of an anomaly at T_N . No anomaly is seen in the $C_p(T)$ data for polycrystalline La_2CuO_4 in Fig. 4(b) either. Thus, the thermal effects associated with the 3D antiferromagnetic transition at T_N are undetectable within our limit of resolution.

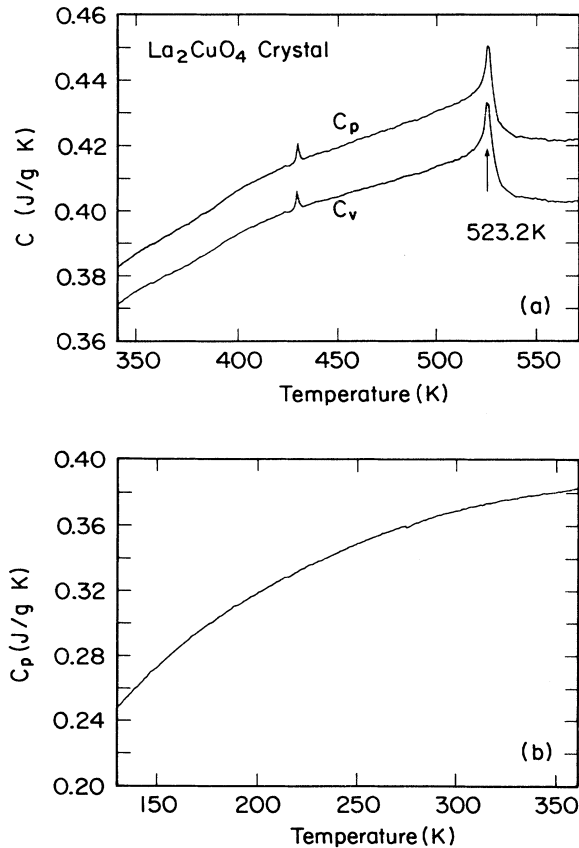


FIG. 3. Heat capacity C_p and C_v vs temperature for a La_2CuO_4 single crystal in the high- (a) and low- (b) temperature ranges. The small anomaly at 429 K in (a) is the melting transition of In metal impurity on the surface of the crystal.

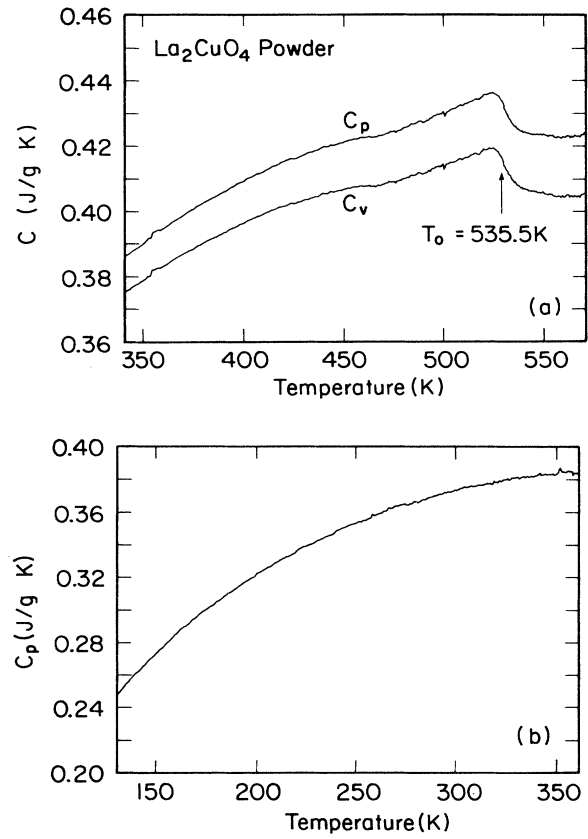


FIG. 4. Heat capacity C_p and C_v vs temperature for polycrystalline La_2CuO_4 in the high- (a) and low- (b) temperature ranges.

B. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

$C_p(T)$ data are presented for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples with $x = 0.02, 0.05, 0.08, 0.10$, and 0.20 . The data for the first three compounds are shown in Fig. 6, and for the latter two in Fig. 7. The structural transition tempera-

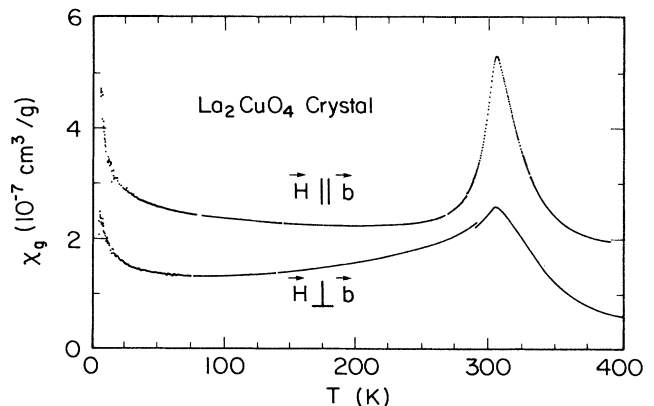


FIG. 5. Magnetic susceptibility χ vs temperature T for the La_2CuO_4 crystal in Fig. 3. The b axis is perpendicular to the CuO_2 planes.

ture T_0 decreases rapidly with increasing x . The transition can be seen clearly in $C_p(T)$ when $x \leq 0.08$, but becomes unobservable within instrument resolution when $x \geq 0.10$. The T_0 values are listed in Table I, and compared with literature data for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (Refs. 18, 19, 21, and 27) and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (Refs. 20 and 26) in Fig. 8(a). We find that T_0 decreases linearly with x for $x \leq 0.08$, at a rate $dT_0/dx = -(2430 \pm 50)$ K. The error quoted is the estimated standard deviation from a least-squares fit, for which $T_0(0) = (532.0 \pm 2.1)$ K, the rms deviation of the data from the fit was 3.4 K, and the abso-

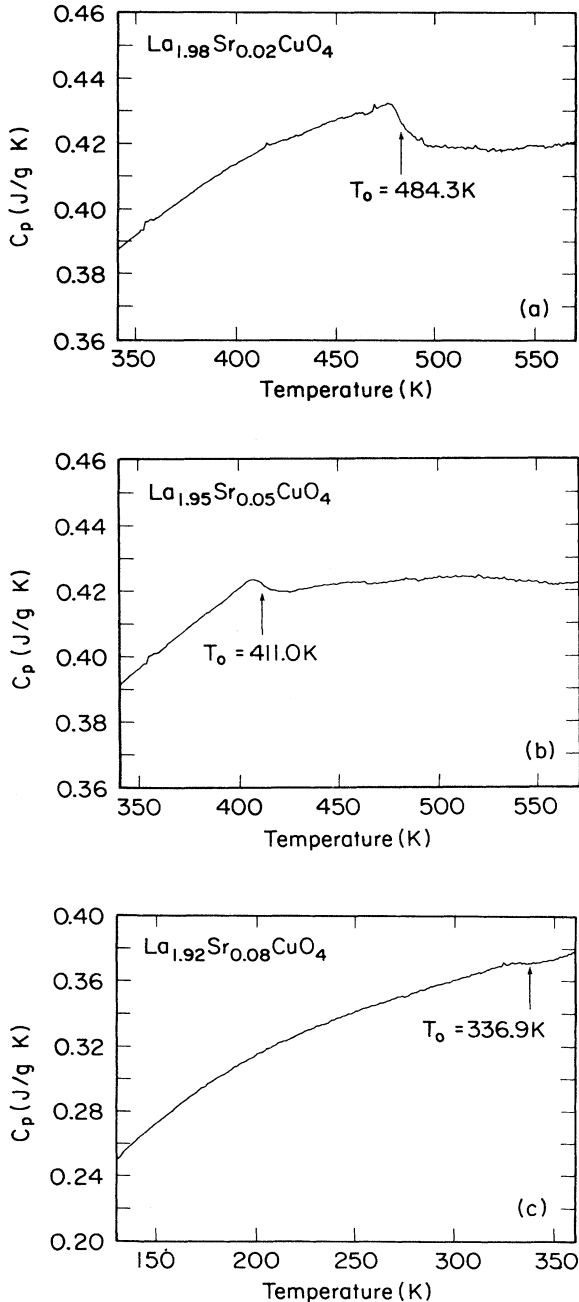


FIG. 6. Heat capacity C_p vs temperature for polycrystalline $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x=0.02$ (a), 0.05 (b), and 0.08 (c).

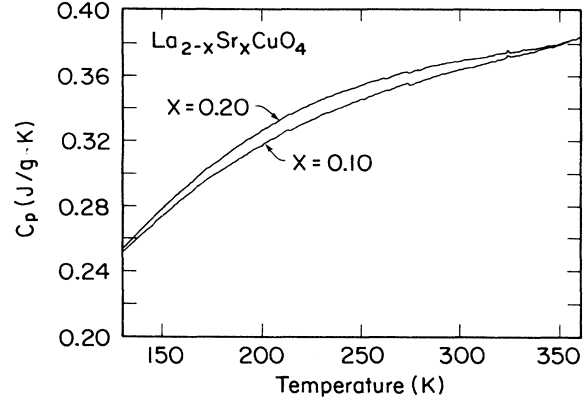


FIG. 7. Heat capacity C_p vs temperature for polycrystalline $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x=0.10$ and 0.20 .

lute percentage deviation was 0.40%. Plotted in Fig. 8(b) is the heat-capacity jump at T_0 (ΔC_p) versus T_0 . The jump increases approximately linearly, but not proportionally, with T_0 .

C. CuO

The heat capacity of a CuO pellet sample of mass 107.568 mg was measured from 130 to 320 K and is plotted versus temperature in Fig. 9. Two peaks are clearly evident. By comparing the data obtained at different heating rates, we conclude that the lower temperature transition at $T_m = 209.5 \pm 0.2$ K is a first-order transition with an enthalpy of transition $H_m = 0.038 \pm 0.004$ J/g. The second one is at the Néel temperature $T_N = 225.0 \pm 0.2$ K; this is a second-order transition with $\Delta C_p = 0.020 \pm 0.002$ J/g K. Furthermore, cooling curves were also obtained (not shown). Comparing the cooling curves with the heating curves, a slight hysteresis at T_m but none at T_N was observed, consistent with our assignments of the thermodynamic orders of transition.

IV. ANALYSIS AND DISCUSSION

A. Crystallographic transition in La_2CuO_4 at $T_0 \approx 530$ K

The La_2CuO_4 single crystal and powder samples show almost the same Debye temperature, as can be seen from

TABLE I. Néel temperatures T_N and tetragonal to orthorhombic transition temperatures T_0 for the samples studied. An asterisk indicates a single crystal; the other samples are polycrystalline pellets.

Material	T_N (K)	T_0 (K)
$\text{La}_2\text{CuO}_4^*$	304	527.5
La_2CuO_4		535.5
$\text{La}_{1.98}\text{Sr}_{0.02}\text{CuO}_4$		484.3
$\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$		411.0
$\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$		336.9
$\text{Sr}_2\text{CuO}_2\text{Cl}_2^*$	$\approx 250^a$	$< 10^a$
CuO	225.0	

^aReference 32.

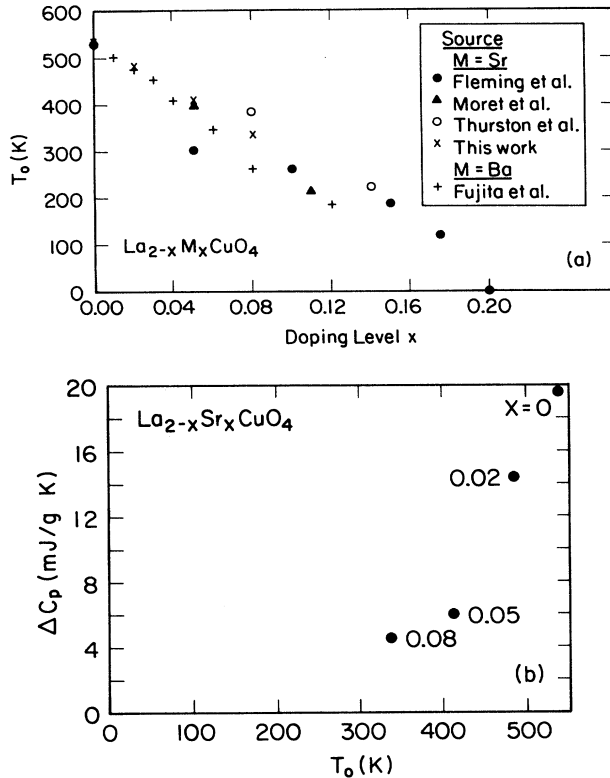


FIG. 8. (a) Tetragonal to orthorhombic transition temperature T_0 vs doping level x in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. A selection of literature data for $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Sr}, \text{Ba}$) are included for comparison: Fleming *et al.* (Ref. 19) Moret *et al.* (Ref. 21), Thurston *et al.* (Ref. 18), and Fujita *et al.* (Ref. 20). (b) Specific-heat jump $\Delta C_p(T_0)$ vs T_0 for the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system.

the same magnitude and slope of the C_p curves. They also have about the same tetragonal to orthorhombic transition temperature T_0 . However, the single-crystal sample has a sharper peak at T_0 and a cusplike shape indicative of fluctuation effects. The C_p jumps at T_0 are roughly the same for the single crystal and powder. A

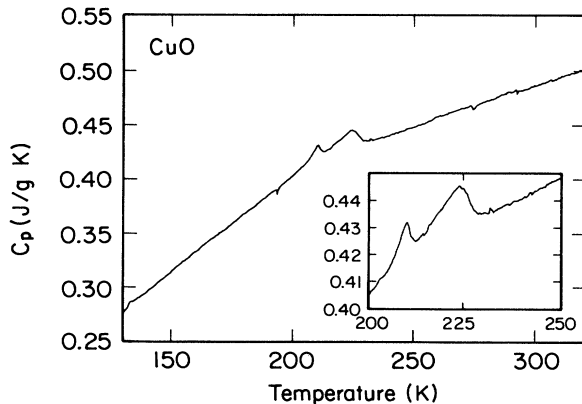


FIG. 9. Heat-capacity C_p vs temperature for polycrystalline CuO .

slightly nonuniform oxygen distribution in the powder may contribute to broadening the peak. The granular nature of the powder may also contribute in some way.

Measurements using different heating rates indicate that the transition is second order, consistent with previous measurements of the variation of the lattice parameters with temperature,^{18,21,23} as well as with theoretical considerations. As La_2CuO_4 transforms from the tetragonal to the orthorhombic structure, its unit-cell volume doubles, with a symmetry change from space group $I4/mmm$ (D_{4h}^{17}) to $Cmca$ ($D_{2h}^{18} = V_h^{18}$). Since the latter has exactly half the group elements (8) as the former (16) space group, a second-order phase transition is expected. Various models have been put forward to explain the T-O transition, including a nonmagnetic Peierls mechanism,³⁹ a magnetic Jahn-Teller deformation caused by the d^9 configuration of Cu^{2+} ,⁴⁰ or ionic interactions involving La^{3+} cations.⁴¹

The free energy of the system is given by¹⁸

$$F(T) = F_n(T) + (a/2)(T - T_0)(Q_\alpha^2 + Q_\beta^2) + u(Q_\alpha^2 + Q_\beta^2)^2 + v(Q_\alpha^4 + Q_\beta^4), \quad (2)$$

where $F_n(T)$ is the free energy in the absence of the orthorhombic distortion, a , u , and v are constants, and where the order parameter Q has two components Q_α and Q_β corresponding to the two equivalent orthorhombic domains. Thus, $F(T)$ is minimized below T_0 for either Q_α or $Q_\beta = 0$, and Q_β or $Q_\alpha = a(T_0 - T)/4(u + v)$, respectively, with $u + v > 0$ and $v < 0$.¹⁸ The heat capacity above T_0 in this model is $C_n(T)$ and below T_0 is

$$C(T) = C_n(T) + [a^2/8(u + v)]T, \quad (3)$$

and the predicted heat-capacity jump $\Delta C(T_0)$ at T_0 is proportional to T_0 ,

$$\Delta C(T_0) = [a^2/8(u + v)]T_0. \quad (4)$$

To our knowledge, there are no microscopic calculations of the Landau parameters a , v , and u , although a weak temperature dependence of v has been extracted from neutron-scattering data.¹⁸ From the observed values $\Delta C(T_0)$ and $T_0 = 528$ K, we have $\Delta C(T_0)/T_0 = 15$ mJ/mole $\text{K}^2 = a^2/8(u + v)$.

B. Antiferromagnetic transition in La_2CuO_4

The maximum C_p we measured for La_2CuO_4 is $C_p = 25.1$ J/g-atom K, larger than the Dulong-Petit limit $3R = 24.9$ J/g-atom K, where R is the molar gas constant; after the dilation subtraction, the maximum $C_v = 24.0$ J/g-atom K, now smaller than $3R$. We infer that the magnetic contribution to $C(T)$ is not large in our measurement temperature range. The magnetic properties of undoped La_2CuO_4 can be modeled rather well by a nearest-neighbor spin- $\frac{1}{2}$ antiferromagnetic (AF) Heisenberg Hamiltonian on a square lattice, with a large intraplanar exchange constant $J/k_B \approx 1400$ K.⁴²⁻⁴⁴ Above T_N , there are strong 2D fluctuations, with correlation lengths ranging from 40 Å at 500 K to above 1000 Å just above T_N .⁴⁵ Below T_N , the planes order three dimen-

sionally, driven by weak interplanar coupling; the ordered moments do not lie exactly in the CuO_2 planes, but are canted out of the plane by a small angle (0.17°). This canting is driven by the rotation of the CuO_6 octahedra in the orthorhombic phase which allows an antisymmetric superexchange term in the spin Hamiltonian. The net ferromagnetic moment for $H=0$ is zero because anti-ferromagnetic interlayer coupling causes alternate layers to cant in opposite directions. The anomalous²² large peak in the susceptibility $\chi(T)$ at T_N for $\mathbf{H} \parallel \mathbf{b}$ (Fig. 5) arises from the antisymmetric exchange.⁴² The $\chi(T)$ of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (Ref. 32) does not exhibit a peak at T_N , consistent with its tetragonal crystal symmetry and 2D character.

Although the interplanar coupling J' is very small, it is evidently responsible for the long-range 3D order when the in-plane correlation length ξ becomes sufficiently large. The transition should occur when $J'(S_0/S)^2(\xi/a)^2 \sim k_B T_N$, where S_0/S is the reduction in the zero-temperature staggered magnetization relative to the Néel value induced by 2D quantum fluctuations, and a is the Cu-Cu intraplanar distance.⁴⁶ Using $\xi(T_N) = 200a$ and $S_0/S = 0.6$, one finds $J'/k_B = 0.015$ K; i.e., the ratio of the two couplings $J'/J \sim 10^{-5}$.⁴²⁻⁴⁴ The weak interplanar coupling has a negligible effect on the 2D fluctuations and $\chi(T)$ above T_N .⁴⁶ The critical region about T_N in which J' is expected to have a major effect is extremely narrow.

Since $J' \sim 10^{-5}J$, we expect the change in $C_p(T)$ caused by the 3D ordering at T_N to be small. The heat-capacity contribution $C_m(T)$ due to the short-range ordering is easily calculated to first order using simple spin-wave theory. Assuming a dispersion relation $\omega = \omega_{\text{ex}} |\sin(ka)|$, where $\omega_{\text{ex}} = 8|J|S/\hbar$ and $S = \frac{1}{2}$, one finds the heat capacity per mole of Cu ions to be

$$C_m = 7.21 \frac{R}{8\pi} \left[\frac{k_B}{J} \right]^2 T^2. \quad (5)$$

Taking $J/k_B = 1400$ K yields $C_m = (1.22 \times 10^{-6} \text{ J/mole K}^3) T^2$. At 300 K, $C_m = 0.11$ J/mole K, which is about 0.06% of the phonon contribution at that temperature. The magnetic entropy at 300 K from Eq. (5) is $S_m(300 \text{ K}) = 0.055$ J/mole K, which is only 0.95% of the maximum entropy of the spin system at high temperatures $S(\infty) = R \ln 2$. The heat-capacity jump at T_N , $\Delta C_m(T_N)$, is expected to be of order $[S_m(T_N)/S_m(\infty)](S_0/S)^2 \Delta C_m^{\text{MF}}$, where ΔC_m^{MF} is the mean-field value ($1.5R$), which yields $\Delta C_m(T_N = 300 \text{ K}) = 0.04$ J/mole K, well below the resolution [~ 0.2 to 0.5 J/mole K at 300 K, see Fig. 3(b)] of the measurement. This explains the absence of anomalies at T_N in single crystal and polycrystalline La_2CuO_4 in our heat-capacity experiments. Large ($\lesssim 11\%$) anomalies in $C_p(T)$, obtained with a precision of $\approx 0.1\%$, were reported at 201, 205, and 214 K, respectively, for three polycrystalline samples of La_2CuO_4 in Ref. 47 and were attributed to 3D antiferromagnetic ordering transitions. We infer that these anomalies are not due to that cause; the anomaly for each sample is also apparently not due to magnetic ordering of the possible CuO impurity phase, since the

temperatures of the anomalies are too low (see below). Our $C_p(T)$ data are consistent with the $C_p(T)$ data of Ref. 48 for single-crystal La_2CuO_4 , which also showed no evidence for an anomaly at $T_N = 250$ K to within a precision which we estimate to be $\sim 5-10\%$.

C. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

Our $C_p(T)$ data indicate a linear decrease of T_0 with doping level x up to at least $x=0.08$, with $dT_0/dx = -(2430 \pm 50)$ K, in general agreement with existing data [see Fig. 8(a)]. Because T_0 varies strongly with oxygen content,²² the discrepancies between the $T_0(x)$ data from various studies are probably due to differences in the oxygen content of the respective samples. We find an approximately linear, but not proportional, variation of the heat-capacity jump $\Delta C_p(T_0)$ with T_0 . Indeed, from Fig. 8(b), $\Delta C_p(T_0)$ increases much faster with T_0 than proportionately, perhaps exponentially. This is in disagreement with Eq. (4) derived from Landau theory; the reason for this discrepancy is not clear. Additional terms in the free energy [Eq. (2)] and/or a strong dependence of the Landau parameters a , u , and/or v on composition x are evidently required to account for the effects of doping. It is perhaps significant that ΔC_p goes to zero as the system becomes metallic.

D. CuO

Between 200 and 230 K, there are two transitions for CuO, as reported by others.⁴⁹⁻⁵³ The $C_p(T)$ data indicate a second-order transition at T_N , in agreement with the previous work. However, our $T_N = 225.0 \pm 0.2$ K is about 5 K lower than found in the previous studies, possibly due to differences in the oxygen contents of the samples. The discontinuity at T_N , $\Delta C_p = 0.02$ J/g K $(= 2.4 \times 10^{-3})R$, is much smaller than the value of $1.5R$ expected in a mean-field model, due to the existence of strong short-range dynamic antiferromagnetic order at T_N ,⁴⁹⁻⁵³ as in La_2CuO_4 and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. The second, but first-order, transition occurs at $T_m = 209.5 \pm 0.2$ K. At T_m , there is a discontinuous change in the propagation vector and spin orientation, with the propagation vector becoming commensurate with the lattice.^{52,53} Our measured enthalpy change at T_m , $\Delta H = 3.1 \pm 0.3$ J/mole, is somewhat smaller than the literature data [4.8 (Ref. 49) and 4.5 J/mole (Ref. 51)].

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