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Evidence for antiferromagnetic interactions in the high-temperature superconductor $La_{1.85}Sr_{0.15}CuO_{4-y}$

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Hyperfine specific-heat measurements in superconducting $La_{1.85}Sr_{0.15}CuO_{4-y}$ strongly suggest the existence of a hyperfine field at the copper nuclei. This field is even larger in undoped and semiconducting La_2CuO_4 and is compatible with antiferromagnetic order in that compound. We speculate that mobile Cu^{3+} holes in the Sr-doped samples stabilize a fluctuating antiferromagnetic state which at the same time is superconducting.

A key question today is what kind of interaction causes the high stability of the new ceramic high-temperature superconductors. In the case of $La_{1-x}Sr_xCuO_{4-y}$ ($T_c = 37$ K) it has been argued[1] that its properties are still compatible with the conventional BCS virtual-phonon exchange mechanism. In the case of $Ba_2YCu_3O_7$ ($T_c \cong 92$ K), the virtual-phonon exchange mechanism is less likely, not only because of the excessively high T_c, but also because of the recently reported absence of an oxygen isotope shift in this material.[2,3] Furthermore, reports on traces of superconductivity at temperatures up to 240 K (Ref. 4) in mixtures of $Ba_2YCu_3O_7$ and $Y_2BaCu_3O_7$ reinforce the belief that an alternative mechanism must be causing superconductivity in these cases.

We have recently measured the specific heat of $La_{1.85}Sr_{0.15}CuO_{4-y}$ in the very low-temperature range (from 0.03–5 K) in order to (i) check on the absence of a "metallic" linear specific-heat term in the superconducting state and (ii) to observe the nuclear specific-heat contribution which can be expected from the nuclear quadrupole splittings of both the La and Cu nuclei due to the noncubic crystal-field symmetry. The samples were prepared by mixing the appropriate amounts of the dried oxides and carbonates and reacting them for 2 h successively at temperatures of 850, 950, and 1000 °C with intermediate grindings. They were then pressed into cylinders of 8 mm diameter and ~3 mm long and sintered for another 12 h at 1200 °C. This last step was done under an oxygen pressure of 4 bars in order to minimize the oxygen deficiency. The oxygen concentration was subsequently deliberately reduced by annealing the samples in a vacuum at 950 °C in order to quench their metallic and superconducting states (see below). The samples were characterized by electrical resistance measurements as well as by magnetic susceptibility measurements in a vibrating sample magnetometer. The specific-heat measurements were carried out in a dilution refrigerator using a heat-pulse technique. The thermometer (a thin slice of a carbon resistor), the heater (of metal film type), and the thermal link to a variable temperature platform were connected separately to the sample with small amounts of GE 7031 varnish. At the lowest temperatures, the internal thermal time constant of the sample was long (~2 min) but still shorter than the thermal time constant between sample and platform (30–60 min), so that the specific heat could still be reliably determined.

The data of superconducting $La_{1.85}Sr_{0.15}CuO_{4-y}$ are shown in Fig. 1. At the lowest temperatures, we indeed observe a large nuclear specific-heat contribution varying as T^{-2}, qualitatively as expected, which dominates in the temperature range from 30–200 mK. At our high-temperature end, the specific heat varies as T^3 and is clearly due to phonons. At temperatures in between, the data can best be fitted by assuming a third contribution

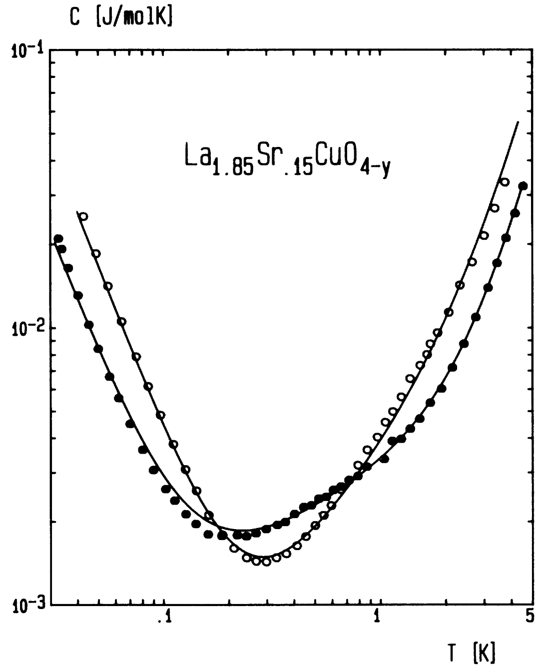

FIG. 1. Molar specific heat of $La_{1.85}Sr_{0.15}CuO_{4-y}$ in the superconducting state (●) and in the oxygen-depleted semiconducting state (○). The solid line fits are the relations $C/R = bT^{1/2} + dT^{-2} + cT^3$ for the former and $C/R = aT + dT^{-2} + cT^3$ for the latter (see Table I for coefficients).

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varying with $T^{1/2}$. Such a fit of the form

$$C/R = bT^{1/2} + dT^{-2} + cT^{3} \tag{1}$$

is shown in Fig. 1 as a solid line, the coefficients b, c, and d being given in Table I. We would like to focus especially on the nuclear specific heat. Expecting it to be due to a quadrupolar splitting of the nuclear sublevels in an electric field gradient, we can calculate this field gradient using the relation

$$(C_Q/R)T^2 = \left[\frac{3eqeQ}{4k_B I(2I-1)}\right]^2 \times \frac{1}{45} I(I+1)(2I+3)(2I-1) \ . \tag{2}$$

Here eQ is the electric quadrupole moment of either the La or Cu nucleus, eq the electric field gradient at the nucleus, and I is the nuclear-spin quantum number. The values of the electric field gradients that we find when assuming that only either the La or Cu nuclei (^{139}La: $I = \frac{7}{2}$, $eQ = 0.21b$; ^{63}Cu and ^{65}Cu: $I = \frac{3}{2}$, $eQ = 0.18b$) contribute to the nuclear specific heat come out to be unusually large, of order 10^{18} V/cm^2 (see also Table I), which is on the upper limit of known values in noncubically symmetric crystals.

In order to check whether the valence-stabilized oxygen deficiency might be causing such enormous electric field gradients, pure undoped and semiconducting La_2CuO_4, which should have no oxygen deficiency, was also measured. This result is shown in Fig. 2. Surprisingly, the nuclear specific-heat contribution is even larger in this compound, by a factor of 10. In the intermediate temperature range, the $T^{1/2}$ term is now absent and is replaced by a term linear in T, as shown by the solid-line fit (see Table I for coefficients). Although the structure of La_2CuO_4 is not identical to the tetragonal K_2NiF_4 structure of the Sr-doped compound, but a slight orthorhombic distortion of it, it is quite impossible to explain this nuclear specific heat by an electric quadrupole splitting. Such large nuclear specific-heat contributions can only be caused by a nuclear magnetic hyperfine field, which clearly can exist only in the Cu^{2+} ions. This hyperfine field is given by

$$(C_{\rm hf}/R)T^2 = \frac{1}{3}\left[\frac{g_N \mu_N H_{\rm hf}}{k_B I}\right]^2 I(I+1) \ , \tag{3}$$

where μ_N is the nuclear magneton and g_N the nuclear g value of Cu, and it amounts to 78 kOe. It constitutes, to our knowledge, the first proof of the existence of an antiferromagnetic state in semiconducting La_2CuO_4 (see, however, Ref. 5). Such a state is, in fact, not unexpected, since the $3d^9$ configurations of Cu^{2+} (with $S = \frac{1}{2}$) are coupled by indirect exchange interactions through the $O-2p$ ligand wave functions (the superexchange interactions), which always favor antiparallel spin alignment on adjacent Cu^{2+} sites. As the Cu^{2+} ions are located inside oxygen octahedra (elongated along the c axis), which themselves are corner sharing and arranged in planes, the strongest superexchange interactions occur in the two-dimensional rectangular lattices of Cu^{2+} ions (we neglect here the slight orthorhombic distortion of this lattice). Thus, no frustration exists (in contrast to a triangular lattice) and a two-dimensional antiferromagnetic structure should be stable. The observed hyperfine field of 78 kOe is quite compatible with the one observed for isolated Cu^{2+} ions [122 kOe (Ref. 6)], as a reduction due to the widening of the sharp $3d^9$ states into $3d^9$-$2p$ bands can be expected.

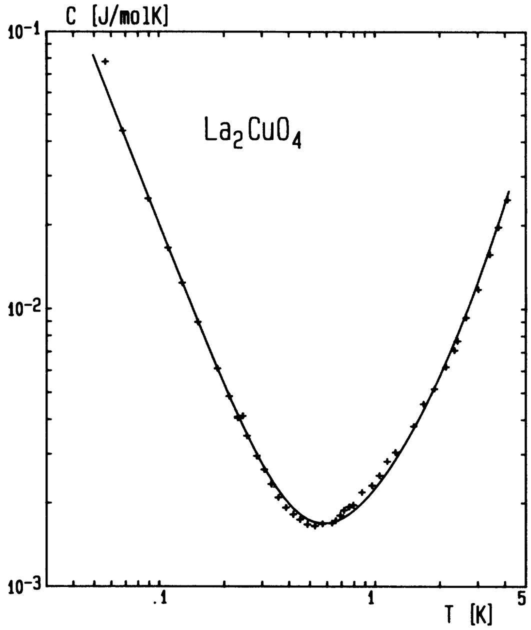

FIG. 2. Molar specific heat of semiconducting La_2CuO_4. The solid line fit is $C/R = aT + dT^{-2} + cT^{3}$, with coefficients given in Table I.

TABLE I. Experimental values for the specific-heat coefficients a, b, c, and d. Deduced values for the electric field gradients eq, the effective magnetic hyperfine fields $H_{\rm hf}$, and the Debye temperatures θ_D are included.

	$a\left[\frac{\rm J}{\rm mol\,K^2}\right]$	$b\left[\frac{\rm J}{\rm mol\,K^{3/2}}\right]$	$c\left[\frac{\rm J}{\rm mol\,K^4}\right]$	$d\left[\frac{\rm J\,K}{\rm mol}\right]$	$eq\left[\frac{\rm V}{\rm cm^2}\right]_{\rm La}$	$eq\left[\frac{\rm V}{\rm cm^2}\right]_{\rm Cu}$	$H_{\rm hf}$ (kOe)	θ_D (K)
$La_{1.85}Sr_{0.15}CuO_{4-y}$								
superconducting	⋯	3×10^{-3}	2.8×10^{-4}	1.9×10^{-5}	3.9×10^{18}	3.4×10^{18}	25	190
semiconducting	3.4×10^{-3}	⋯	3.6×10^{-4}	4.1×10^{-5}	5.4×10^{18}	4.8×10^{18}	35	170
La_2CuO_4	1.8×10^{-3}	⋯	2.8×10^{-4}	2.0×10^{-4}	1.2×10^{19}	1.0×10^{19}	78	190

It is now tempting to assign the smaller but still unusual large nuclear specific heat in superconducting $La_{1.85}Sr_{0.15}CuO_{4-y}$ to a "remnant" (time-averaged) hyperfine field which results from a fluctuating antiferromagnetic state. Such fluctuations would be correlated with the "hopping" motion of the Cu^{3+} states which are introduced by the Sr doping and the ensuing excess concentration of oxygen. This hopping motion consists of a transfer of one $3d$ electron from a Cu^{2+} to an adjacent Cu^{3+} site. As this electron carries the spin orientation of the Cu^{2+} ion with it (because of the Hund's-rule coupling), it mediates an additional exchange interaction to the neighboring (Cu^{3+}) site, which is of the ferromagnetic sign (the double-exchange interaction[7]). Thus, the moving electron has a tendency to "torque" the antiferromagnetic structure, the torque increasing with the size of the transfer integral (or bandwidth) of the moving electron. This effect has been beautifully exemplified by early experiments in the doped perovskite $La_{1-x}Ca_xMnO_3$ by Jonkers and van Santen,[8] where the valence of Mn could be partly changed from Mn^{3+} to Mn^{4+} by the parameter x. For $x=0$ and 1, the material is antiferromagnetic and insulating, for $0.2<x<0.4$ it becomes conducting and ferromagnetic (for a discussion, see, e.g., Ref. 9).

To check on this point of view, we have introduced additional oxygen vacancies in our superconducting samples by annealing them in vacuum at 950 °C for 6 h. This has the effect of reducing the Cu^{3+} content by the valence count. Indeed, samples so treated become semiconducting and lose their superconductivity (Fig. 3). At the same time, their nuclear specific-heat contribution increases substantially and is now intermediate between that for superconducting and that for pure undoped and antiferromagnetic samples (Fig. 1). This observation strongly reinforces our belief that the stable antiferromagnetic state in insulating samples is destabilized by the introduction of carriers which mediate the ferromagnetic double-exchange interaction. If a moving electron rotates the antiferromagnetic structure, it is clear that it is of advantage to correlate the motion of many such electrons. One of the current theories to explain the strong pairing interaction in these materials is the bipolaron theory.[10] It supposes that the moving electron carries with it a local lattice distortion (the Jahn-Teller distortion of Cu^{2+}), and that two such electrons can profit from each other's distortion, provided they stay spacially close to each other. This type of pairing, which, in k-space, would be equivalent to a $+\mathbf{k}/+\mathbf{k}$ pairing with opposite spins (as opposed to the classical $+\mathbf{k}/-\mathbf{k}$ pairing in the BCS theory) would also be of advantage when including the double-exchange mechanism discussed above. $3d$ electrons (or Cu^{3+} holes) moving, say, on adjacent Cu-O-Cu-O chains, could best profit from each other's torque on the antiferromagnetic structure by moving together (with opposite spins). The gain in condensation energy would be of the order of the double-exchange energy between neighboring Cu sites. It should be pointed out that Anderson[11] comes, in part, to similar conclusions. In his superexchange theory, however, the insulating ground state is described in terms of the so-called resonating valence bound (RVB) state. It can be understood as a (quantum spin) liquid of magnetic singlet pairs located on neighboring sites, and resonating between various possible combinations, which become charged superconducting (Cooper) pairs in the doped metallic state. Interestingly, the excitation spectrum of the insulating state is that of a Fermi liquid of magnetic excitations and implies a linear term in the specific heat, not expected for ordinary semiconductors. The superconducting specific heat, on the other hand, will behave exponentially in temperature, because the (anisotropic) gap vanishes nowhere on the Fermi surface.

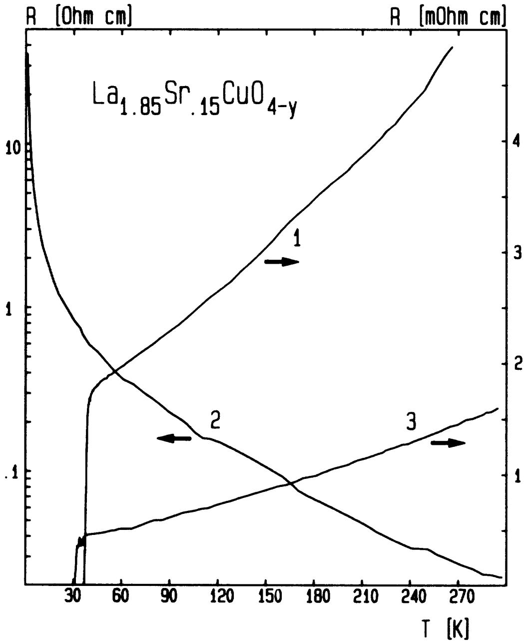

FIG. 3. Specific resistance R of $La_{1.85}Sr_{0.15}CuO_{4-y}$. The sequence 1-2-3 denotes different states of the same sample. Superconductivity (1) is lost by vacuum annealing at 950 °C and semiconducting behavior (2) is observed. Subsequent reannealing at 950 °C in an oxygen pressure of 20 bars brings back the superconducting state (3).

Note also that, in general, low-lying collective Bose excitations with a dispersion $\omega \simeq k^{\nu}$ in a system with dimension d lead to a power-law dependence of the specific heat $C \propto T^{d/\nu}$. For the two-dimensional structure believed to characterize La_2CuO_4, antiferromagnetic (ferromagnetic) magnons, for example, would cause a $T^2(T)$ behavior of the specific heat at not too low temperatures, whereas in one-dimensional systems one expects a T ($T^{1/2}$) law, respectively.

In conclusion, we have shown experimentally that semiconducting La_2CuO_4 is antiferromagnetic and that this antiferromagnetic state becomes unstable when doping this material with Sr and introducing mobile Cu^{3+} holes. These carriers presumably cause the antiferromagnetic state to fluctuate due to the double-exchange interaction mediated by them. These fluctuations could correlate the motion of the $3d$ holes in pairs and explain a high superconducting condensation energy. On the basis of this we would predict an absence of the oxygen isotope shift in $La_{1.85}Sr_{0.15}CuO_{4-y}$. We have also found novel terms in the specific heat of these samples: A $T^{1/2}$ term in superconducting ones and a T term in the semiconducting ones. Further studies will have to show whether these contributions can be explained with magnetic excitations in the more and less fluctuating antiferromagnetic states. Presently, similar specific-heat investigations are underway in superconducting and nonsuperconducting $Ba_2YCu_3O_{7-\delta}$ samples in order to see whether a similar mechanism operates in this compound.

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