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Magnetic properties, Mössbauer measurements, and specific-heat studies of $La_2MCu_2O_6$ (M = Ca or Sr) compounds

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Magnetic-susceptibility powder-x-ray-diffraction Mössbauer studies on ^{57}Fe-doped samples and specific-heat measurements were used to study the magnetic nature of $La_2MCu_2O_6$ and $La_{1.6}Sr_{0.4}CaCu_2O_6$ materials. The fivefold pyramidal coordination of the double CuO_2 planes is similar to that of the Cu(2) site in $YBa_2Cu_3O_z$ $6<z<7$. All the compounds studied are not superconducting and order antiferromagnetically at $T_N=10$–20 K, which is extremely low as compared with $T_N=420$ K, obtained for nonsuperconducting $YBa_2Cu_3O_6$. The presence of Fe does not affect T_N. The specific-heat curves do not show any anomaly at T_N, and the electronic specific-heat coefficient is around 4 mJ/mol K^2.

I. INTRODUCTION

The delicate interplay between superconductivity (SC) and magnetic order in high-T_c superconductors (HTSC) has been studied by various techniques. Evidence for long-range antiferromagnetic (AFM) order of the Cu(2) layers in nonsuperconducting $YBa_2C_3O_z$ was provided by muon-spin-relaxation (μSR),[1] neutron-diffraction experiments[2] and Mössbauer spectroscopy.[3] In addition to the well-known SC-AFM phase diagram of $YBa_2Cu_3O_z$ with oxygen content,[2] using the Mössbauer technique on ^{57}Fe doped compounds, we found the interrelation between SC and AFM order in a wide family of cationic substitutions in the oxygen-rich $YBa_2Cu_3O_7$ system. It was shown that whenever cations are doped in sites outside the Cu(2) planes sufficiently to make SC disappear [Pr in the Y site and Fe or Co in the Cu(1) site], static long-range AFM ordering is induced in these planes.[4] When these planes become magnetically ordered, they produce an exchange field on the Fe ions located in the Cu(2) planes. The iron nuclei experience a magnetic hyperfine field, leading to a sextet in the observed Mössbauer spectra.

The phase diagram of the $YBa_2(Cu_{1-x}Fe_x)_4O_8$ system which resembles that of $YBa_2Cu_3O_z$ also exhibits structural changes and competition between SC and AFM as a function of Fe concentrations.[5] In the third class of HTSC, Bi-Sr-Ca-Cu-O, substitution of Y^{3+} for Ca^{2+} also changes the electric and magnetic properties, and a quite similar phase diagram involving SC and AFM was obtained.[6] All these examples indicate that antiferromagnetism is commonly found in all these HTSC oxides in a series of compositions which exhibit superconductivity for another series of composition.

The crystal structure of the tetragonal $La_2MCu_2O_6$ (2:1:2:6) M = Ca, Sr, was studied in detail by a number of authors.[7–10] This structure is closely related to other HTSC materials and the space group is $I4/mmm$ with two formula unit in each cell. In contrast to $YBa_2Cu_3O_z$, only one distinct Cu site exists in the structure with a five-fold pyramidal coordination of oxygen in double CuO_2 planes, Fig. 1. The $2b$ site, midway between the Cu atoms of the two pyramids is in principle empty, which means that the local environment of Cu in 2:1:2:6 is similar to the fivefold symmetry of the Cu(2) site in $YBa_2Cu_3O_7$. The distribution of La and Sr or Ca among the $2a$ and $4e$ crystallographic sites depends on the ionic radii of the elements. In $La_2CaCu_2O_6$ ($La^{3+}=1.15$ Å and $Ca^{2+}=0.99$ Å) La and Ca almost exclusively occupy the $4e$ and $2a$ sites, respectively (Fig. 1). On the other hand, La and Sr ($Sr^{2+}=1.13$ Å) in $La_2SrCu_2O_6$ are randomly distributed between the two sites. Moreover x-ray and neutron-diffraction measurements[11] show that the $2b$ site, which is vacant in $La_2CaCu_2O_6$, contains more than 0.48 atom oxygen in $La_2SrCu_2O_6$. That oxygen is intercalated between the CuO_2 planes.

The $La_2MCu_2O_6$ system exhibits a variety of interesting features which depend on the composition. Both parent compounds, $La_2CaCu_2O_6$ and $La_2SrCu_2O_6$, are not superconductors. On the other hand, bulk superconductivity ($T_c=60$ K) has been observed in the Ca based $La_{2-x}Sr_xCaCu_2O_6$ ($x=0.2$–0.4) (Ref. 9) synthesized under high oxygen pressure (20 atm), but SC has not yet been achieved in $La_{2-x}Ba_xCaCu_2O_6$.

The motivation of the present paper is to show that the 2:1:2:6 system behaves in a way which is similar to other HTSC systems, namely, in those compositions which are not superconducting, a static magnetic ordering of CuO_2 double planes is induced. Unfortunately, we could not

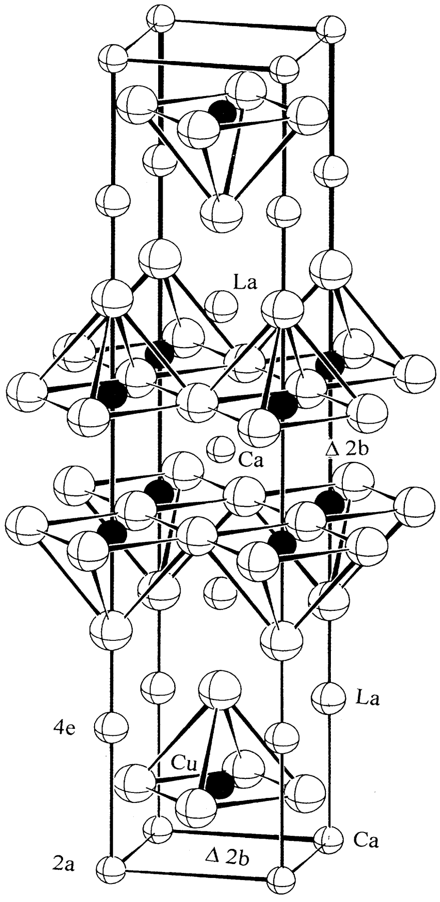

FIG. 1. Crystal structure of $La_2CaCu_2O_6$. For $La_2SrCu_2O_6$ La and Sr are distributed over the 2*a* and 4*e* sites.

obtain the required pressure and thus failed to prepare the SC materials. But all the samples investigated here by magnetic susceptibility measurements and by Mössbauer studies on 1% ^{57}Fe-doped samples show AFM ordering with T_N around 10–20 K. We prove that T_N is not affected by the presence of Fe, and that Fe is thus a reliable probe of the magnetic behavior of the CuO_2 planes. During the course of this work, we found that room temperature Mössbauer studies of $La_2MCu_2O_6$ have been already published by Meyer *et al.*[12] and that our present studies are qualitatively in fair agreement with their results. Specific-heat measurements show no evidence of any magnetic transition, and the γ value obtained the from linear region of C_p/T vs T^2 is 4 and 0.5 mJ/mol K^2, for $M=$Ca and Sr, respectively, typical to nonsuperconducting materials.

II. EXPERIMENTAL DETAILS

The samples with nominal compositions $La_2MCu_2O_6$ and $La_2M(Cu_{0.99}Fe_{0.01})_2O_6$ materials, were prepared by solid-state reaction technique. Prescribed amounts of La_2O_3, and CuO, $^{57}Fe_2O_3$, $SrCO_3$, and $CaCO_3$ were mixed and pressed into pellets and preheated at 950 °C for about 1 day. The products were cooled, reground, and fired again to 1050° and 1100° for $M=$Ca and Sr, respectively, for 48 h and then furnace cooled to ambient temperature. One of the samples was reheated at 900 °C under oxygen pressure of 16 atm in a sealed quartz tube. X-ray-diffraction measurements indicate that all samples are single phase and the lines are indexed on the basis of tetragonal structure with the lattice parameters given in Table I. The dc susceptibility measurements on solid ceramic pieces were carried out in a commercial SHE superconducting quantum interference device magnetome-

TABLE I. Lattice constants, experimental magnetic parameters, and hyperfine parameters deducted from Mössbauer measurements for $La_2MCu_2O_6$ and $La_{1.6}Sr_{0.4}CaCu_2O_6$ samples. The Curie constants are given per mole of Cu ions and Θ_M is the orientation of the magnetic hyperfine field relative to the *c* axis.

	Lattice constants		Magnetic parameters				Hyperfine parameters					
Sample	a (Å)	c (Å)	T_N (K)	Θ (K)	c (emu/mol)	χ_0 (emu/mol Oe)	T (K)	I.S. (mm/sec)	$\frac{1}{2}eQq$ (mm/sec)	H_{eff} (kOe)	Ratio (%)	Θ_M
$La_2CaCu_2O_6$	3.827(3)	19.42(1)	13.5(2)	−27.5	0.023	-5×10^{-4}						
$La_2SrCu_2O_6$	3.866(2)	19.92(1)	18.5(2)	−57.0	0.046	-2.7×10^{-4}						
$La_{1.6}Sr_{0.4}CaCu_2O_6$	3.843(2)	19.68(1)	10.0(5)	−3.2	0.021	2.1×10^{-3}						
$Fe\rightarrow La_2SrCu_2O_6$	3.877(3)	19.94(1)					90	0.351(2)	0.407(3)		100	
							4.1	0.396(2)	−0.006(1)	472(1)	100	55°
$Fe\rightarrow La_2CaCu_2O_6$	3.830(2)	19.41(1)	13.5(2)	−16.0	0.057	-1.5×10^{-4}	90	0.356(2)	1.06(1)		70	
								0.342(2)	1.41(2)		30	
							4.1	0.358(2)	−0.518(2)	480(1)	64	90°
								0.388(2)	−0.022(1)	476(1)	36	55°
$Fe\rightarrow La_{1.6}Sr_{0.4}CaCu_2O_6$	3.835(2)	19.64(1)					90	0.336(2)	1.02(1)		83	
								0.353(9)	0.450(3)		17	
							4.1	0.365(2)	−0.22(1)	456(1)	100	64°
$Fe\rightarrow La_{1.6}Sr_{0.4}CaCu_2O_6$ Prepared under high pressure	3.837(2)	19.66(1)					90	0.343(2)	1.04(1)		44	
								0.344(2)	0.34(1)		56	

ter (SQUID) in various fields as a function of temperature in the range of 4.2–100 K. The magnetization was measured by two different procedures: (a) The sample was zero-field cooled (ZFC) to 4.2 K, a field H was applied and the magnetization was measured as a function of temperature. (b) The sample was field cooled (FC) from above T_N in a field to 4.2 K and the magnetization was measured. All ac susceptibility measurements were carried out using a home-built mutual impedance bridge at act amplitude of 80 A/m and frequencies ranging from 80 Hz to 1 kHz. The Mössbauer spectroscopy studies were performed using a conventional constant acceleration spectrometer and a 100 mCi ^{57}Co:Rh source. The spectra at 4.1 and 90 K were least-squares fitted with one or two subspectra. Specific-heat measurements on $La_2MCu_2O_6$ were performed, with a mass of about 2.5 g for M = Ca and 0.75 g for M = Sr over the temperature range 4–60 K in an automated adiabatic calorimeter employing the Nernst step heating method.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Crystal-structure measurements

X-ray-powder-diffraction measurements on $La_2MCu_2O_6$ samples indicate that all the samples are single phase and have the same tetragonal structure with I4/*mmm* space group (Table I). For M = Sr, both a and c lattice parameters are slightly larger than for M = Ca due to the larger ionic radii of Sr^2 (1.13 Å) comparable to Ca^{2+} (0.99 Å). The iron-doped samples have approximately the same size as their parent compounds, whereas the unit cell of $La_{1.6}Sr_{0.4}CaCu_2O_6$ is intermediate between the parent compounds. The lattice parameters a and c decrease for the high-pressure compound in fair agreement with Ref. 10. The Cu-Cu short distance given by $0.172c$ is 3.340 Å and 3.425 Å for M = Ca and Sr, respectively and 3.388 Å for $La_{1.6}Sr_{0.4}CaCu_2O_6$.

B. Mössbauer studies at 90 K

Figure 2 shows the Mössbauer spectra for ^{57}Fe-doped materials, and the values of the various parameters deduced from their analysis are exhibited in Table I. The experimental spectra obtained at 90 K for the various compounds are in fair agreement with room-temperature spectra obtained in Ref. 12. Figure 2(a) exhibits the Mössbauer spectra of ^{57}Fe doped in $La_2SrCu_2O_6$ at 90 K and the main information obtained from visual and computer analysis is the presence of one quadrupole doublet with a splitting of $\Delta \equiv \frac{1}{2}eQq = 0.41$ mm/sec and an isomer shift of 0.35 mm/sec relative to Fe metal. These parameters can be assigned to Fe^{3+} in a high spin state. [The spectra also contains an additional quadrupole doublet (3%) which is attributed either to $LaSrFeO_4$ as an impurity phase or to Fe in an interstitial site.] We attribute this relatively small doublet to Fe in a sixfold octahedral site which replaces Cu in the 4(e) site. Since Fe has a larger valence than Cu, it attracts oxygen to maintain neutrality[13]. Neutron- and x-ray-diffraction measurements show that in $La_2SrCu_2O_6$ the occupation factor of the 2b site at ambient pressure is around 48%. It means that half of these sites are filled with oxygen. Thus the octahedral site for Fe is obvious.

Figure 2(b) exhibits the Mössbauer spectrum of 1% ^{57}Fe doped in $La_2CaCu_2O_6$ at 90 K. This spectra can be fitted using a superposition of two doublets with the parameters given in Table I. The main doublet which accounts for about 70% with $\Delta = 1.06$ mm/sec, is due to Fe in a fivefold pyramidal site. In this case the Ca^{2+} atoms, being smaller than La, reside completely in the 2a site, and the shorter Cu-2b distance does not permit the occupation of the 2b site by oxygen. It is assumed[12] that Fe in this pyramidal site moves away from the original position toward the apex of the pyramid by ∼0.3 A. In this posi-

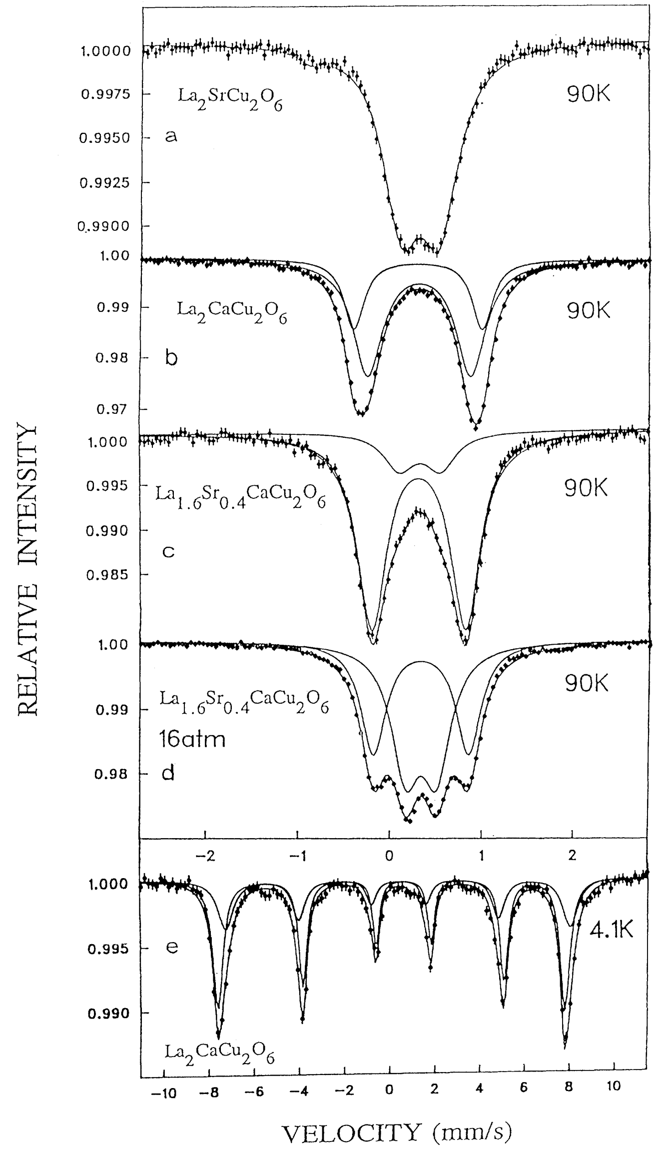

FIG. 2. (a)–(d) Mössbauer spectra of 1% ^{57}Fe doped in $La_2MCu_2O_6$ samples at 90 K. (e) Mössbauer spectra of $La_2CaCu_2O_6$ at 4.1 K. The magnetic splitting disappears at 13 K.

tion the distance of Fe to all its 5 oxygen neighbors is more equal. The configuration of the minor subspectra with $\Delta = 1.41$ mm/sec is not yet clear.

Bulk superconductivity was found in $La_{1.6}Sr_{0.4}CaCu_2O_6$ ($T_c = 60$ K) when the material was synthesized under 20 atm O_2 pressure. The oxygen stoichiometry has a crucial role in the superconductivity of this compound and SC was not observed for samples synthesized in air or in a 1 atm O_2. In those compositions the bilayer intermediate plane $2a$ site is mostly filled by $Ca^{2+} \sim 80\%$ and about 20% of La^{3+}, and most of La^{3+} and all Sr^{2+} ions reside in the $4e$ site.[14,15] All our attempts to produce superconductivity in the Fe-doped $La_{1.6}Sr_{0.4}CaCu_2O_6$ material by heating it under 16 atm at 900 °C failed. The oxygen content was not measured and the absence of SC might be a result of low oxygen concentration. Obviously, it cannot be excluded that the 1% substituted iron has some detrimental effect on suppressing superconductivity, since the pyramidal Cu site is quite similar to the Cu(2) site of Y-Ba-Cu-O which is much affected by substitution. Mössbauer spectra at 90 K of ^{57}Fe doped in $La_{1.6}Sr_{0.4}CaCu_2O_6$ prepared at ambient O_2 pressure and under 16 atm are presented in Figs. 2(c) and 2(d). Generally speaking, the spectrum consists of two doublets with $\Delta = 1.02$ mm/sec and $\Delta = 0.45$ mm/sec (Table I) which may be attributed to pyramidal and octahedral configurations, respectively. In Fig. 2(c) the pyramidal site is the dominant one, $\approx 83\%$, whereas for the high-pressure samples, the intensity of the two sites are comparable. The increase of the second doublet under oxygen treatment could be due to the increase of the occupation factor of oxygen in the $2b$ site, which increases the proportion of sixfold octahedral configuration.

C. Mössbauer studies at 4.1 K

In the Mössbauer spectra measured at 4.1 K for all samples listed in Table I a well-defined sextet is observed, which is clear evidence for long-range magnetic ordering of the Cu sublattice. Figure 2(e) shows a typical spectrum for $La_2CaCu_2O_6$. The spectrum is analyzed as composed of two subspectra with the same H_{eff} (Table I), which differ only in their hyperfine field orientation (Θ) relative to V_{zz} where V_{zz} is the z axis of the electric-field gradient. This orientation can be determined from the effective value of the quadrupole interaction measured at 4.1 K: $eQq_{(\text{eff})} = \frac{1}{2} eQq (3\cos^2\Theta - 1)$ where $eQq = 2\Delta$ are the values obtained at 90 K (Table I). For $La_2CaCu_2O_6$ the hyperfine field of the dominant site is perpendicular to V_{zz} (the same must be true for copper moments which are in the Cu-O planes) as the Cu(2) moments in $YBa_2Cu_3O_6$ and for the minor site $\Theta = 55°$ relative to V_{zz} provided that Δ is positive. Whereas for $La_2SrCu_2O_6$ the orientation of the magnetic moments is 55°. The sharpness of the spectra obtained at 4.1 K indicates a long-range magnetic order and excludes the possibility of a spin-glass state below T_N. Indeed, direct magnetic measurements show that all the samples are antiferromagnetically ordered (Figs. 3 and 4) with T_N listed in Table I.

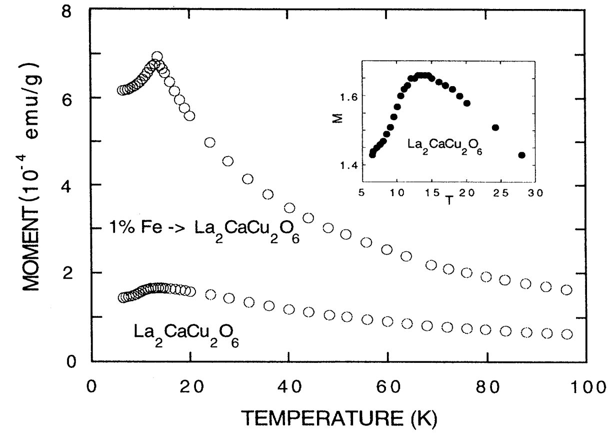

FIG. 3. Temperature dependence of the magnetic moment for $La_2CaCu_2O_6$ and for 1% Fe-doped material measured at 100 Oe. The inset shows magnetization for $La_2CaCu_2O_6$ on an extended scale. Note that T_N is identical for both samples.

Above T_N all the magnetic six line patterns collapse, and the spectra are quite similar to those obtained at 90 K.

D. Magnetic measurements

The results of the magnetic measurements uncorrected for demagnetization factors are shown in Figs. 3 and 4 and summarized in Table I. One definitely sees that at low temperatures all the compounds become magnetically ordered, and the maxima in the curves are typical of antiferromagnetic transition. Figure 3 exhibits the magnetic behavior of pure $La_2CaCu_2O_6$ and the 1% Fe-doped material measured at 100 Oe. The transition at $T_N = 13.5$ K obtained for both samples is undoubtedly associated with the Cu-O sublattice in the 2:1:2:6 structure. The fact that doping of Fe does not affect T_N is clear evidence that Fe serves only as a probe. Its contribution to the large magnetic moment will be discussed later. At

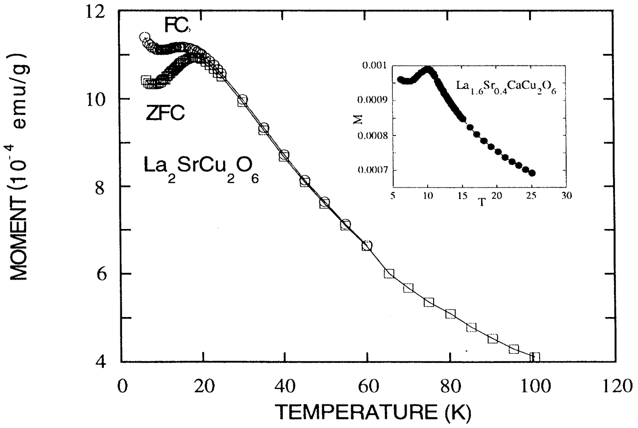

FIG. 4. The variation of the magnetic moment with temperature measured at 750 Oe for $La_2SrCu_2O_6$. The inset shows the temperature dependence of M for $La_{1.6}Sr_{0.4}CaCu_2O_6$ measured at 100 Oe.

4.1 K the magnetization as a function of the applied magnetic field H is essentially linear up to $H=16$ kOe, and no hysteresis loop is observed. For $La_2CaCu_2O_6$ the same magnetization curves are obtained whether the procedure was ZFC or FC. Ac susceptibility measurements also show a small peak around 13 K, and no frequency dependence of this peak is observed between 80 and 1000 Hz. In the case of $La_{1.6}Sr_{0.4}CaCu_2O_6$ the same $T_N=10$ K is obtained for the sample prepared under ambient pressure and for the sample prepared under 16 atm (inset, Fig. 4). In this Ca-based material T_N decreases due to the elongation of the c lattice parameter whch increases the Cu-Cu short distance from 3.340 to 3.388 Å.

On the other hand $La_2SrCu_2O_6$ exhibits very interesting magnetic nature as shown in Fig. 4. The transition temperature is higher ($T_N=18$ K) although the Cu-Cu distance is longer—3.425 Å. Another interesting observation in Fig. 4 is that the ZFC curve differs significantly from the FC one. The difference in the behavior between the two systems presumably arises primarily from the difference in the orientation of the magnetic moments mentioned above. Since the direction of the moments for $La_2SrCu_2O_6$ is not in the CuO_2 planes, in the FC process the external field causes the spins to cant slightly out of their original directions. This canting abruptly aligns a component of the moments with the direction of the field and the FC curve is obtained. It is likely that the presence of partially filled $2b$ vacancies with oxygen (see above), which establish direct exchange coupling between CuO_2 planes, leads to a higher T_N for this material. The huge difference in T_N (10–20 K) found in the present system and $T_N \sim 420$ K observed for Cu(2) site in oxygen deficient Y-Ba-Cu-O samples, is not yet clear.

All the 2:1:2:6 compounds exhibit normal paramagnetic behavior and adhere closely to the Curie-Weiss Law over the major portion of the measured temperatures. The magnetic susceptibility above T_N can be well described by $\chi=\chi_0+C/(T-\Theta)$ where χ_0 is the temperature-independent part of the susceptibility, C is the Curie constant, and Θ is the Curie-Weiss temperature. Least-square fit for the curves shown in Figs. 3 and 4 yield the parameters listed in Table I. The paramagnetic effective moments derived from C for pure $La_2MCu_2O_6$ are $0.43\mu_B$ and $0.61\mu_B$ per Cu for $M=$La and Sr, respectively. The valence of Fe in 2:1:2:6, determined by Mössbauer studies is 3^+ in a high spin state $S=\frac{5}{2}$. Assuming $P_{\text{eff}}=5.9\mu_B$ for Fe^{3+} we can extract the Fe concentration N(Fe) in the Fe-doped $La_2CaCu_2O_6$ material, using the relation $8C=N(\text{Fe})5.9^2+[1-N(\text{Fe})]0.43^2$. We obtain $N(\text{Fe})=0.011$ which is within the experimental error of the nominal Fe constant -1%. Figure 3 illustrates the large contribution of Fe to the magnetic moment of the system.

Of particular interest is the paramagnetic parameters obtained for $La_{1.6}Sr_{0.4}CaCu_2O_6$ (Table I). From the Curie constant we derive $P_{\text{eff}}=1.10\mu_B$ (per Cu atom) which corresponds to a fraction of 64% spin-$\frac{1}{2}$ local moments of the Cu^{2+} ions ($1.7\mu_B$). It means that the large Curie-Weiss contribution to the susceptibility is intrinsic to this compound and does not arise from impurity phase, since such a large concentration of an impurity phase would be easily visible in the x-ray diffraction pattern.

One should also notice the large $\chi_0=(2.1\times10^{-3}$ emu/mole Oe) value obtained in $La_{1.6}Sr_{0.4}CaCu_2O_6$. If

$$\chi_0=\chi_c+\chi_L+\chi_p$$

where χ_c is the core diamagnetism, χ_L is the diamagnetism orbital contribution term due to the conduction electrons, and χ_p is the Pauli paramagnetism term due to the conduction electron. By neglecting χ_c (which is in the order of 10^{-6}) and assuming[15] that $-\chi_L=1/3\chi_p$, we obtain $\chi_c \propto \chi_p$, where χ_p is directly proportional to the density of states $N(0)$ at the Fermi level. The large χ_0 which means large $N(0)$ for this compound may be correlated with the existence of superconductivity in this material prepared under high oxygen atmosphere.

E. Specific-heat measurements

Because Mössbauer and magnetic studies suggest long-range magnetic order of Cu moments, we also measured the specific heat C_p of 2:1:2:6 parent compounds. Figure 5(a) shows C_p curves for $La_2MCu_2O_6$ at $H=0$ and the inset exhibits the usual presentation of C_p/T vs T^2.

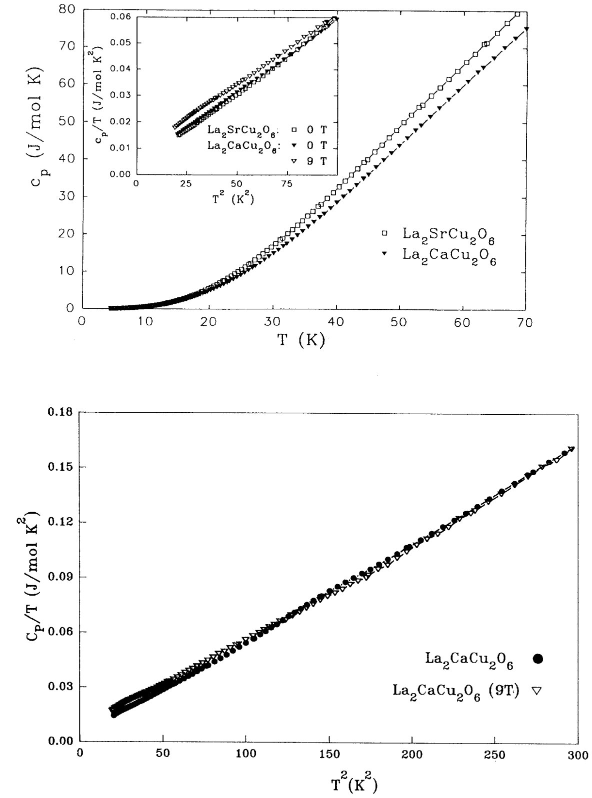

FIG. 5. (a) Specific-heat curves for $La_2MCu_2O_6$ at $H=0$. Note the absence of any anomaly at T_N in both materials. The inset shows C_p/T vs T^2 curves for $M=$Ca at $H=0$ and 9T, and for $M=$Sr at $H=0$ at the low temperature range. (b) C_p/T vs T^2 curves for $La_2CaCu_2O_6$ at $H=0$ and 9 T at temperatures well above $T_N=13.5$ K.

The specific heat for $La_2CaCu_2O_6$ was also measured in applied magnetic field of 9 T. We found that in the vicinity of T_N, as well as in the high-temperature regime, there is hardly a change between the zero field and applied field measurements [Figs. 5(a) and 5(b)]. However, at low temperatures a slight enhancement of the heat capacity can be observed at 9 T [inset of Fig. 5(a)]. There is no anomaly in the C_p curves of either compound, as would be expected for an antiferromagnetic system. This is not the case in other related cuprates such as $R_2Cu_2O_5$ where R = Y or Lu, which order antiferromagnetically at $T_N = 10$ and 17 K, respectively, and a sharp peak in C_p shows up at T_N.[16] This finding implies that the magnetic anomaly does not originate from long-range AFM ordering, but rather from a spin-glass-like behavior. In that respect, the difference between the FC and the ZFC obtained for $La_2SrCu_2O_6$ (Fig. 4) is well understood. However, (1) the absence of such a difference for $La_2CaCu_2O_6$ (Fig. 3), (2) the ac measurements which do not show a frequency dependence of the peak at T_N and (3) the sharp sextets obtained at 4.1 K in the Mössbauer spectra [Fig. 2(e)] all exclude the spin-glass state assumption. In the low-temperature region, the extrapolation of the nearly linear C/T vs T^2 plots gives a small but finite intercept, which indicates a linear contribution of T to the heat capacity. The data in the temperature range from 4 to 16 K were fitted with $C_p = \gamma T + \beta T^3 + \delta T^5$ [where γ is the electronic specific-heat contribution and β is the phonon contribution from which the low temperature of the Debye temperature $\Theta(0)$ is derived]. This yields $\gamma = 4.3 \pm 0.3$ and 8.5 ± 0.3 mJ/mol K^2 for M = Ca and $H = 0$ and 9 T, respectively, and $\gamma = 4.1 = 0.3$ mJ/mol K^2 for M = Sr [Fig. 5(a)]. Nonzero values of the specific-heat linear term have been reported for other cuprates materials in their normal state.[17] Although it is well known that below 6 K the Debye approximation for the high-T_c cuprates is valid, our $\Theta(0)$ values obtained from the fitting procedure is given for comparison. The corresponding $\Theta(0)$ values are 343 ± 10 and 351 ± 10 K for M = Ca and Sr, respectively. These values are similar to the average initial Debye temperatures for $YBa_2Cu_3O_z$ (410 ± 35 K) and $La_{2-x}Sr_xCuO_6$ (390 ± 40 K).[18]

Figure 5(b) exhibits the C_p/T vs T^2 curves of $La_2CaCu_2O_6$ at $H = 0$ and $H = 9$ T for the high-temperature range, well above $T_N = 13.5$ K. Note the extremely small anomaly in slope of the C_p/T curve for $H = 0$ at about (180 K^2) which vanishes in the $H = 9$ T curve. The result of this figure is the absence of an anomaly in the specific heat that corresponds to the antiferromagnetic behavior shown in Figs. 3 and 4. According to the thermodynamic arguments of Fisher,[19] the magnetic contribution of the specific heat C_M for an AFM material is related to the ZFC susceptibility as $C_M = A\,\partial/\partial T(T\chi(T))$. This relation implies that any anomaly in the susceptibility will be associated with a similar anomaly in the specific heat. Using this relation and the data of the susceptibility of $La_2CaCu_2O_6$ at 100 Oe, we have estimated C_M as about 2 J/mol K at T_N. On the other hand, using the ac susceptibility data, which exhibit only a rather broad and washed out maximum at T_N, we obtain nearly a constant magnetic contribution to C_M over the entire range up to 40 K, which is of the order of 100 mJ/mol K. In both cases the estimated magnetic contribution to the heat capacity is much larger than the experimental resolution. Nevertheless this was not detected in the experiment, and the intriguing question remains as to why in $La_2MCu_2O_6$ materials the C_p curves do not show an anomaly in T_N.

In conclusion, we provide static magnetic measurements of the antiferromagnetic nature found in nonsuperconducting $La_2MCu_2O_6$ For M = Sr, $T_N = 18.5$ K and for M = Ca, $T_N = 13.5$ K was observed for undoped and for 1% Fe-doped samples. Thus the presence of 1% Fe does not alter the magnetic nature of the materials, and Fe serves as a reliable probe in the Mössbauer measurements. Once again the interplay between superconductivity and AFM order is displayed. The $La_{1.6}Sr_{0.4}CaCu_2O_6$ compounds which are not superconducting order antiferromagnetically at $T_N = 10.5$ K. The most striking result obtained is the absence of an indication to the magnetic order in the specific-heat measurements. The assumption of magnetic spin-glass-like nature is rejected, and the unexpected specific-heat data are not yet explained.

Note added in proof. We recently learned that our T_N values compare well with those obtained by Kinoshita and Yamada,[20] but disagree with μSR studies reported in Ref. 21.

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[1] N. Nishida *et al.*, Jpn. J. Appl. Phys. **26**, L1856 (1987).

[2] J. M. Tranquada *et al.*, Phys. Rev. Lett. **60**, 156 (1988); W. H. Li, J. W. Lynn, and Z. Fisk, Phys. Rev. B **41**, 4098 (1990).

[3] I. Nowik, M. Kowitt, I. Felner, and E. R. Bauminger, Phys. Rev. B **38**, 6677 (1988).

[4] I. Felner, I. Nowik, E. R. Bauminger, D. Hechel, and U. Yaron, Phys. Rev. Lett. **65**, 1945 (1990).

[5] I. Felner *et al.*, Phys. Rev. B **43**, 8737 (1991).

[6] T. Oashi *et al.*, Physica C **157**, 315 (1989); I. Nowik, I. Felner, and E. R. Bauminger, Phys. Rev. B **45**, 4912 (1992).

[7] N. Nguyen, L. Er-Rhahko, C. Michel, J. Choisnet, and B. Raveau, Mater. Res. Bull. **15**, 891 (1980).

[8] E. A. Hayri and J. Z. Lareze, Physica C **170**, 239 (1990).

[9] R. J. Cava *et al.*, Nature (London) **345**, 602 (1990).

[10] T. Sakurai *et al.*, Physica C **174**, 187 (1991).

[11] K. Kinoshita, H. Shibata, and T. Yamada, Physica C **176**, 433 (1991).

[12] C. Meyer, F. Hartmann-Boutron, Y. Gros, and P. Strobel, Physica C **181**, 1 (1991).

[13] D. Hechel, I. Nowik, E. R. Bauminger, and I. Felner, Phys. Rev. B **42**, 2166 (1990).

[14] R. J. Cava *et al.*, Physica C **172**, 138 (1990).

[15] T. P. Orlando, E. J. McNiff, Jr., S. Foner, and M. R. Beasley, Phys. Rev. B **19**, 4545 (1979).

[16] V. V. Moshchalkov *et al.*, J. Magn. Magn. Mater. **90-91**, 533 (1990).

[17] S. J. Collocott, R. Driver, and E. R. Vance, Phys. Rev. B **41**, 6329 (1990); N.E. Phillips *et al.*, Phys. Rev. Lett. **65**, 357 (1990).

[18] A. Junod, in *Physical Properties of High T_c Superconductors,* edited by D. M. Ginsberg (World Scientific, Singapore, 1990), Vol. 2, p. 13.

[19] M. E. Fisher, Philos. Mag. **7**, 1731 (1962).

[20] K. Kinoshita and T. Yamada, Phys. Rev. B **46**, 9116 (1992).

[21] E. J. Ansaldo *et al.*, Phys. Rev. B **46**, 3080 (1992).