Magnetic-field-driven $x \approx 1/8$ anomaly of superconductivity in $La_{2-x-y}Sr_xMn_yCuO_4$

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Dependence of superconducting transition temperature T_c(y) on an applied magnetic field B is investigated in $La_{2-x-y}Sr_xMn_yCuO_4$ with $0 \leqslant y \leqslant 0.05$ and $x+y=0.15$. A strong linear decrease of T_c with increasing B is observed around the manganese concentration $y=0.025$, which correlates with the $x \approx 1/8$ anomaly in $La_{1.875}Sr_{0.125}CuO_4$. At this value of y the number of Mn^{3+} pairs, the effective Bohr magneton number p_{eff}, and the antiferromagnetic Curie temperature Θ attain their maxima, suggesting that local magnetic order of the Mn system is responsible for the observed effect.

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The key structural elements of the copper oxide superconductor $La_{2-x}Sr_xCuO_4$ (LSCO) are CuO_6 octahedra, each of them having a Cu atom in the center of the conducting CuO_2 plane. In the high-temperature tetragonal phase I4/mmm the apical oxygens are located on the c axis, one below and one above the Cu atom. The CuO_2 planes can be well characterized in terms of two-dimensional Heisenberg antiferromagnetic (AF) interactions between the Cu moments.[1] Superconductivity is observed in the low-temperature orthorhombic phase (LTO) where the CuO_6 octahedra are tilted so that the line connecting the apex oxygens deviates a few degrees from the c axis.[2] Using x-ray- and neutron-diffraction measurements Crawford *et al.*[3] found that in $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ (LNSCO) the superconducting critical temperature T_c decreases in a sequence of structural transitions: LTO $\rightarrow Pccn \rightarrow$ LTT, where LTT is a low-temperature tetragonal phase. They also reported existence of a local minimum of $T_c(x)$ at $x \approx 1/8$ in LNSCO as well as in LSCO, attributing it tentatively to charge wave instability of the Fermi surface. A similar conclusion was made by Nakamura and Uchida[4] who observed in LNSCO a discontinuous jump of various transport coefficients at $x \approx 1/8$.

The mechanism behind the $x=1/8$ anomaly and its connection to superconductivity has become a long-standing problem. In layered cuprates the kinetic energy of charge carriers competes with the superexchange interactions between neighboring Cu spins.[5] This competition leads to spatial segregation of the holes, forming antiphase domain walls between stripes of antiferromagnetically correlated Cu spins.[6] As a result of lattice commensuration effects the charged domain walls can freeze at the doping concentration $x=1/8$ in the LTT phase.[7] Tranquada *et al.*[8,9] have presented neutron-diffraction results for LNSCO suggesting that above a critical Nd concentration the charge order is stabilized by modification in the CuO_6 tilt pattern. However, referring to nuclear-quadrupole-resonance experiments[10,11] which show no anomaly at $x=1/8$, Ichikawa *et al.*[6] arrived at a conclusion that the anomalous suppression of T_c at $x=1/8$ is caused mainly by local AF order. Although the charge stripes in LSCO are considered to be disordered and dynamic[12] a small dip of T_c can be observed by magnetization measurements in this material for $x=1/8$ too.[13]

In this work we investigate magnetic and superconducting properties of ceramic $La_{2-x-y}Sr_xMn_yCuO_4$ (LSMCO) with $0.08 \leqslant x \leqslant 0.15$, $0 \leqslant y \leqslant 0.07$, and $x+y=0.15$, obtained by substitution of Mn^{3+} ($R=0.0645$ nm Ref. 14) for La^{3+} ($R=0.136$ nm, Ref. 14). The samples were made by using the conventional solid-state preparation method with several treatments at 1200 °C in air, and intermediate grindings. Finally the samples were pelletized and heated for 22 h in air. For pure LSCO prepared in this way, the value of T_c was 37 K. The values of $T_c(x,y)$ are determined as the points where the extrapolation of the steepest portion of the Meissner (field cooled) susceptibility $\chi_M(T)$ crosses the $\chi_M=0$ line.[13] For comparison, similar measurements were made on the shielding (zero-field cooled) susceptibility $\chi_S(T)$. Lattice structure and possible long-range magnetic correlations of the samples were investigated with the high-resolution G4.2 neutron powder diffractometer ($\lambda=2.3426$ Å) at LLB, Saclay, France, recording the diffraction patterns from 1.5 K to the room temperature over the angular range of $3 \leqslant 2\theta \leqslant 172°$. The diffraction data were analyzed with the FULLPROF program.

In Fig. 1(a) are shown the values of $T_c(x)$ (solid squares) determined from χ_M for a few LSCO samples ($y=0$) at $B=8$ mT. In agreement with Refs. 13 and 15 a small anomaly of T_c is observed around $x=0.125$ in this compound. The curves of $T_c(y,B)$ measured for LSMCO as a function of y at different values of B have complex shape above $y=0.015$ involving a broad valley between $y=0.015$ and 0.03 before total collapse of the superconductivity at $y=0.05$ in the field of 8 mT or at $y=0.02$ in the field of 100 mT. The most significant effect occurs around $y=0.025$ ($x=0.125$) where the T_c can be suppressed to zero by external magnetic field. As evident from Fig. 1(b), the magnetic field has no influence on T_c in $La_{1.85}Sr_{0.125}CuO_4$ (in the range of our measurements) but in LSMCO the values of $T_c(y,B)$ exhibit a linear decrease, $\Delta T_c=-0.4$ K/mT, with increasing B, before reaching a field where T_c falls quickly to zero. To avoid magnetic freezing of possible large clusters, the samples were warmed up to 300 K between the measurements at different magnetic-field values.

Among the 3d transition-metal elements, manganese has a special position as an atom, impurity ion, or material having high tendency of cluster formation. To understand the nature of the magnetic interactions brought about by doping LSCO with Mn, we investigate the magnetic susceptibility of

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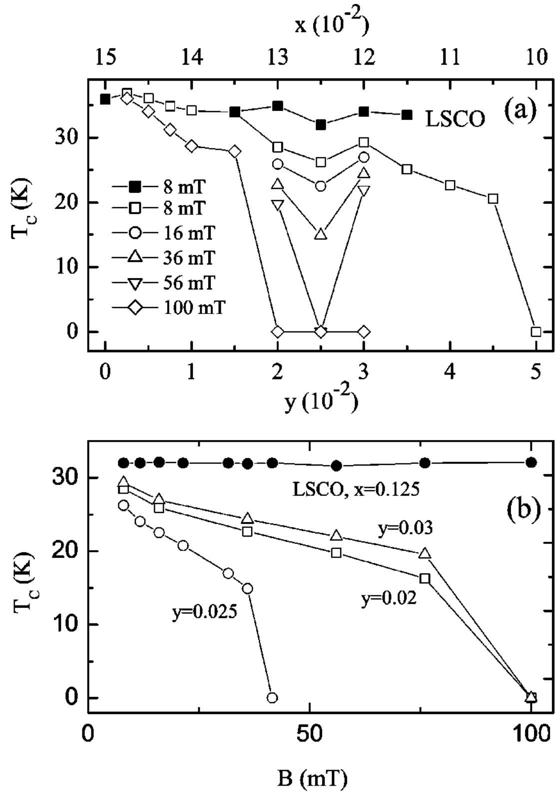

FIG. 1. (a) Dependence of the critical temperature T_c on the Mn concentration in $La_{2-x-y}Sr_xMn_yCuO_4$, determined in fields B between 8 mT and 100 mT. The solid squares give T_c for LSCO with different x. (b) Dependence of T_c on magnetic field in LSCO with $x=0.125$ and in LSMCO with $y=0.02$, 0.025, and 0.03. The solid lines are to guide the eye.

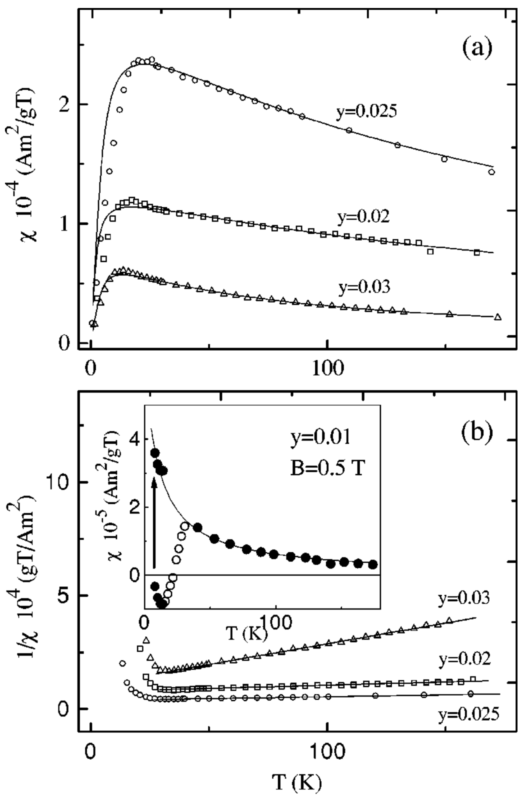

FIG. 2. (a) Temperature dependence of χ in LMSCO having $y=0.02$, 0.025, and 0.03, with fits to Eq. (1) (solid lines). (b) The values of $1/\chi$ determined from the data in (a) with fits to Eq. (2) (solid lines). The influence of superconductivity is shown by upturns of the low-temperature ends of the $1/\chi$ curves. The inset to the figure gives the values of $\chi(T)$ for the sample with $y=0.01$ (closed circles) after correction against superconductivity (open circles) at the lowest temperatures (arrow). The solid line is the fit to the Curie law. The measurements are made with a superconducting quantum interference device magnetometer.

LSMCO in the normal state. In Fig. 2(a) are shown a few experimental $\chi(T)$ curves together with fits calculated in terms of Mn^{3+} ions using a cluster Hamiltonian:[16]

$$\chi=n\frac{g^2\mu_B^2}{3k(T-\Theta)}\frac{\sum_s s(s+1)(2s+1)\exp(-E_s/kT)}{\sum_s (2s+1)\exp(-E_s/kT)}, \tag{1}$$

where n is the number of Mn-Mn pairs, Θ is the Curie-Weiss temperature, $g=2$ is the Landé g factor, $E_s=\varepsilon_s-g\mu_B mH$, where m is the magnetic quantum number, ε_s is the energy in zero magnetic field, μ_B is the Bohr magneton, and k is the Boltzmann constant.

Fitting the data of $1/\chi$ in Fig. 2(b) with the Curie-Weiss law

$$\chi-\chi_0=\frac{C}{T-\Theta}, \tag{2}$$

where χ_0 is a contribution of the background, $C=N_{Mn}p_{\mathrm{eff}}^2\mu_B^2/3k$ is the Curie constant, and N_{Mn} is the number of the manganese ions, we get the effective Bohr magneton number $p_{\mathrm{eff}}(y)$ varying between 4.9 and 34 and $\Theta(y)<0$.

As shown in the inset of Fig. 2(b), by suppressing the superconductivity with an external magnetic field of 0.5 T a weak paramagnetic susceptibility [$\sim\chi_0$ in Eq. (2)] (solid circles) becomes visible in the sample with $y=0.01$. Due to partial masking of the data by superconductivity the measured values of χ diminish upon lowering the temperature in the region below 34 K (open circles) until an upturn is observed as a result of a steep increase of the paramagnetic contribution. From the fit with the Curie law we get for this sample $p_{\mathrm{eff}}=4.6$ which is 94% of the spin ($S=1, L_z=0$) value 4.9 of Mn^{3+} ion. This may be related to a low-symmetry crystal-field component lifting the degeneracy of the ground state of $Mn^{3+}(d^4, t_{2g}^3e_g^1)$ ions.[17,18] Local changes of the surroundings is very likely when a Mn^{3+} ion with smaller radius replaces La^{3+} in the lattice.[19]

As shown in Fig. 3(a) the values of $T_c(y)$ obtained from $\chi_M(T)$ and $\chi_S(T)$ agree quite well. A correlation is observed between the minimum of $T_c(y)$ at $y=0.025$ and the maxima of $n(y)$, $p_{\mathrm{eff}}(y)$, and $\Theta(y)$ in Figs. 3(b)–3(c). The strong fluctuation of p_{eff} and Θ as well as the values of the exchange constant J/k increasing from -0.6 K ($y<0.035$) to -4 K ($y=0.05$) [Fig. 3(d)] when y is increased are indica-

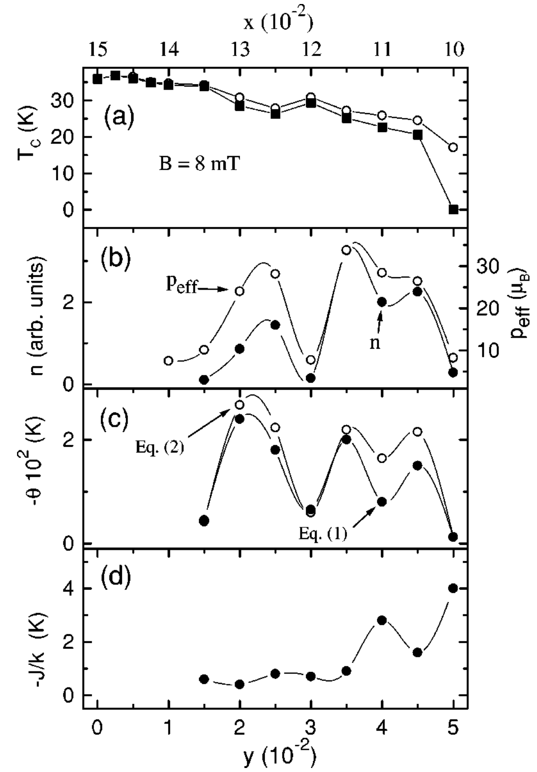

FIG. 3. (a) The values of T_c determined from χ_M (filled squares) and from χ_S (open circles) for LSMCO with different y. (b) The values of n obtained from best fits to Eq. (1) and those of p_{eff} obtained from the Curie-Weiss fits [Eq. (2)] with corresponding values of Θ shown in (c). (d) Dependence of the exchange constant $-J/k$ on y.

tions of cluster formation. The small values of J/k can be connected with small noninteracting clusters (chiefly pairs of Mn^{3+} ions) while higher values of J/k reflect formation of larger clusters with more collective interactions when the amount of Mn is increased.[20] However, no long-range magnetic correlations were observed in neutron-diffraction investigations of the samples.

The low-temperature LTT phase stabilizing the static stripes and competing with superconductivity has been observed by x-ray powder-diffraction measurements in $La_{1.85-y}Nd_ySr_{0.15}CuO_4$ between 32 K for $y=0.18$ and 84 K for $y=0.8$.[21] In the same material with $0.30<y<0.60$ magnetic order below 30 K was revealed by spontaneous muon spin rotation experiments.[22] In these compounds having a substantial amount of Nd ions replacing La^{3+} the magnetic interactions are explained by interplay of Nd moments with the net ferromagnetism arising from rotation of Cu moments away from the CuO_2 plane.[23] No traces of the LTT phase were observed by neutron-diffraction experiments between 2 K and 120 K in LSMCO containing a small amount of Mn $(y=0.025)$, suggesting that there is no static stripe order in our samples.

The distance between two nearest-neighbor Mn^{3+} ions in the pair bridging the apical oxygens is likely to be too long for direct Mn-Mn exchange interaction.[24] The magnetic properties of LSMCO with $y=0.025$, including the values of

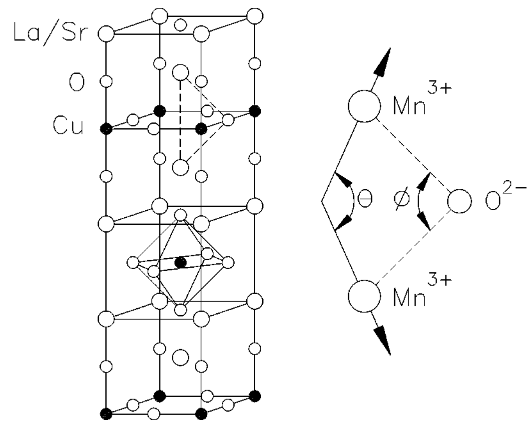

FIG. 4. The lattice structure of $La_{2-x}Sr_xCuO_4$. The dotted lines represent the three-site model where the Mn-Mn distance is 3.668 Å and the Mn-O distances are 2.63 Å, provided that the Mn^{3+} ions occupy exactly the positions of La^{3+} ions in the lattice. The angle ϕ is $\approx 90°$.

Θ and J/k (Fig. 3), resemble above T_c in many respects to those of the diluted magnetic semiconductors $Hg_{1-x}Mn_xTe$ $(J/k=-0.7)$ (Ref. 16) and $Cd_{1-x}Mn_xTe$ $(J/k=-0.55)$ (Ref. 20) for $x<0.1$. In these compounds the superexchange interaction is explained by d-sp band hybridization in a triangle formed by two Mn ions and one Te ion,[25] where the Mn-Mn distance is 3.668 Å and Mn-Te distance is 3.23 Å.[25] The magnitude of the canting between spins S_1 and S_2 is expressed by the angle $\theta_{12}\sim\pi-|D_{12}/J_{12}|$ where $J_{12}\propto\cos\phi^2$ is the AF superexchange interaction constant and $D_{12}\propto\cos\phi\sin\phi\hat{\mathbf{z}}$ is the Dzyaloshinsky-Moriya anisotropic exchange constant.[26] In the case $D_{12}\ll J_{12}$ we get $\theta_{12}\sim\pi$ corresponding to AF order. The same model has turned out to be applicable to MnO as well.[24] According to the band theory of magnetism in MnO the nearest-neighbor 90° Mn-O-Mn coupling is antiferromagnetic due to bonding of t_{2g} orbitals of one Mn ion and e_g orbitals of the other via the oxygen p orbitals.[27]

Referring to the "three-site model" valid to d^4, d^5, and d^6 configurations,[25] we propose tentatively that in LSMCO the observed antiferromagnetism originates from dominant superexchange interactions of Mn ions via oxygen on the intervening CuO_2 plane as shown in Fig. 4. The strong suppression of T_c by magnetic field at $y=0.025$ suggests an interaction between local AF order and mobile charge stripe domains, reducing the density of superconducting pairs by the polarization of the carriers due to hybridization of the manganese and oxygen orbitals in the CuO_2 plane. In terms of the spin-gap proximity-effect mechanism for superconductivity,[28] in underdoped materials T_c is determined by Josephson coupling between the stripes, rather than by the pairing scale. Accordingly, we can say that while the superconducting pairs may exist in the sample the phase coherence is reduced by magnetic field because of increasing interactions between the Mn ions.

To conclude, we have shown that in $La_{2-x-y}Sr_xMn_yCuO_4$ the value of the superconducting critical temperature T_c can be suppressed by application of an external magnetic field at all compositions of $y > 0.025$. The strongest effect is observed around $y = 0.025$ ($x = 1/8$), suggesting an interaction between the charge stripes and local antiferromagnetic order due to pairs and clusters of Mn^{3+} ions. No influence of magnetic fields up to 100 mT in the measurements was found on T_c in $La_{1.875}Sr_{0.125}CuO_4$. Our results encourage testing superconducting structures of alternating LSCO and LSMCO ($y = 0.025$) layers where the layer containing Mn^{3+} ions could be externally driven between superconducting and normal states by application of a modest magnetic field.

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