Spontaneous Magnetization and Antiferromagnetic Correlations of the CuO_2 Chains in $Sr_{0.73}CuO_2$

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We have studied magnetic properties of the novel quasi-one-dimensional cuprate $Sr_{0.73}CuO_2$, containing edge-sharing CuO_2 chains. This compound can be described as an alternating-chain Heisenberg antiferromagnet. The CuO_2 chains are hole doped with a high hole concentration ($\sim 0.6/CuO_2$), and each hole renders the CuO_2 unit nonmagnetic. The experiments reveal that $Sr_{0.73}CuO_2$ develops a long-range magnetic order at 12 K with a small spontaneous ferromagnetic moment $M_s = 3.2(2) \times 10^{-3} \mu_B/\mathrm{Cu}$. The observation of long-range magnetic order in CuO_2 chains doped with a substantial number of holes is very surprising. [S0031-9007(98)05749-4]

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For many decades, spin chains have attracted much attention in condensed matter physics. Because of the enhanced quantum fluctuations in one-dimension (1D), they exhibit various interesting quantum magnetic phenomena, which have no analogy in higher dimensions. Some examples are the appearance of the Haldane gap in Heisenberg chains with integer spins [1], the observation of the spin-Peierls transition in CuO_2 chains in the inorganic compound $CuGeO_3$ [2], and the spin gap formation in pairs of antiferromagnetic (AF) $S = \frac{1}{2}$ chain (two-leg ladders) [3,4]. An important issue is the effect of hole doping on these systems. For example, it was predicted theoretically that charge carriers doped into the ladder may lead to a superconducting or charge density wave state [5].

Recently, hole doping of CuO_2 chains was achieved in $Sr_{14}Cu_{24}O_{41}$ [6,7]. The structure of $Sr_{14}Cu_{24}O_{41}$ [8,9] consists of two unique subcells. One contains a simple chain of copper ions which are coupled by nearly 90° Cu-O-Cu bonds, the other consists of two-leg ladder chains of copper ions coupled by nearly 180° Cu-O-Cu bonds. Magnetic susceptibility measurements [7] show that doped holes go mostly onto the chains, and each hole causes approximately one CuO_2 unit to become nonmagnetic, probably due to the Zhang-Rice singlet formation [10]. Moreover, magnetic susceptibility and electron paramagnetic resonance (EPR) measurements showed that the simple chain unexpectedly has a spin gap in the excitation spectrum, which originates from a dimerized state [6]. The mechanism of the chain dimerization is not clear at the moment. However, it is clear that the holes added to the compound play a very important role in the spin gap formation [7].

The presence of both ladders and chains in $Sr_{14}Cu_{24}O_{41}$ complicates the unambiguous interpretation of the experimental data. Whereas holes seem more likely to go onto the chains [7], there is still some debate on how many of them move onto the ladders. The respective role of the ladders and chains will be understood better if one can study their properties separately. Very recently, a new member of the 1D hole-doped cuprates with the chemical formula $Sr_{0.73}CuO_2$ was synthesized under high oxygen pressure [11]. This compound is related closely to the $Sr_{14}Cu_{24}O_{41}$ phase, but is made only of edge-sharing CuO_2 chains. The formal valency of copper in the CuO_2 chain is $+2.54$. Thus, $Sr_{0.73}CuO_2$ provides a unique possibility to study the properties of hole-doped CuO_2 chains without complications arising from the presence of ladders.

In this Letter, we report the results of dc magnetic susceptibility and EPR measurements on polycrystalline $Sr_{0.73}CuO_2$. It is found that the CuO_2 chains in this compound are hole doped and can be described as an alternating-chain Heisenberg antiferromagnet similar to $Sr_{14}Cu_{24}O_{41}$. However, in contrast to $Sr_{14}Cu_{24}O_{41}$, we observe that the chains in $Sr_{0.73}CuO_2$ exhibit long-range magnetic order below $T_c \sim 12$ K with a small ferromagnetic moment. This is, to our knowledge, the first example of the appearance of long-range magnetic order when a substantial number of holes are introduced into CuO_2 chains.

Details of the synthesis and structural analysis of $Sr_{0.73}CuO_2$ are given in [11]. The structure of $Sr_{0.73}CuO_2$, shown in Fig. 1, is incommensurate in one direction and consists of two sublattices: One contains Sr atoms and the other one forms Cu-O chains. The translation periods of these two sublattices are different, and the atoms arrange in a way to minimize their free energy. This is reached with uniform Sr-O bond lengths which leads to the structural modulation of the Cu-O chains along the a axis with a wavelength of about 10 Å and an amplitude of 0.35 Å [11]. The magnetic susceptibility was measured using a Biomagnetic Technologies Inc. SQUID magnetometer. The

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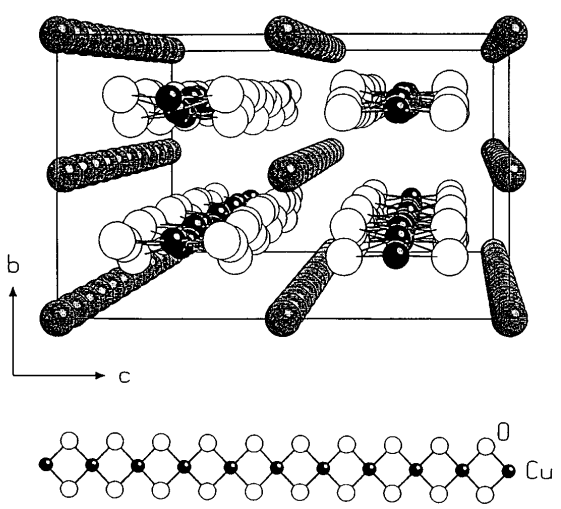

FIG. 1. Perspective view of the crystal structure of $Sr_{0.73}CuO_2$ along the a axis. A 1D CuO_2 chain is shown separately at the bottom.

EPR measurements were performed with an X-band BRUKER ER-200D spectrometer.

Perhaps the most peculiar feature of $Sr_{0.73}CuO_2$ is the small spontaneous ferromagnetic moment observed at low temperatures. Figure 2(a) shows field-cooled susceptibility curves at low temperatures measured in different magnetic fields. Below $\sim$10 K, a sudden jump in the magnetization is observed, indicating ferromagnetic order. The transition is sharp at low fields and becomes broader at higher fields. The magnetization versus field isotherms are shown in Fig. 2(b). Above $\sim$15 K, $M(H)$ is linear, passes through the origin, and is reversible within the experimental uncertainty. At lower temperatures, $M(H)$ acquires a distinctly different character showing a very large dM/dH at very low fields and a linear increase at higher fields. There is also a small hysteresis of magnetization at low fields. The extrapolation of the high field linear behavior to the $H = 0$ kOe results in the ferromagnetic component M_s with a magnitude which is strongly dependent on temperature: $M(T, H) = M_s(T, 0) + \chi H$. At $T = 5$ K, M_s corresponds to a ferromagnetic moment of $3.2(2) \times 10^{-3} \mu_B$/Cu.

We performed EPR measurements to study the magnetic properties of $Sr_{0.73}CuO_2$ on a microscopic level. Figure 3(a) shows the EPR signal observed at different temperatures. The powder averaged spectra with $g_\parallel = 2.21(1)$ and $g_\perp = 2.015(5)$ are characteristic for Cu^{2+} ions in an axial crystal-electric field [12]. The g value and linewidth of the EPR signal are temperature independent. However, below $\sim$15 K, two new lines split from the main EPR line [Fig. 3(a)]. With decreasing temperature, one line splits from the $g_\parallel$ peak and shifts to lower fields, while the other line splits from the $g_\perp$ peak and shifts to higher fields. It is remarkable that the EPR line splits at the same temperature where the sharp increase of the magnetization was detected [see Fig. 2(a)], and the

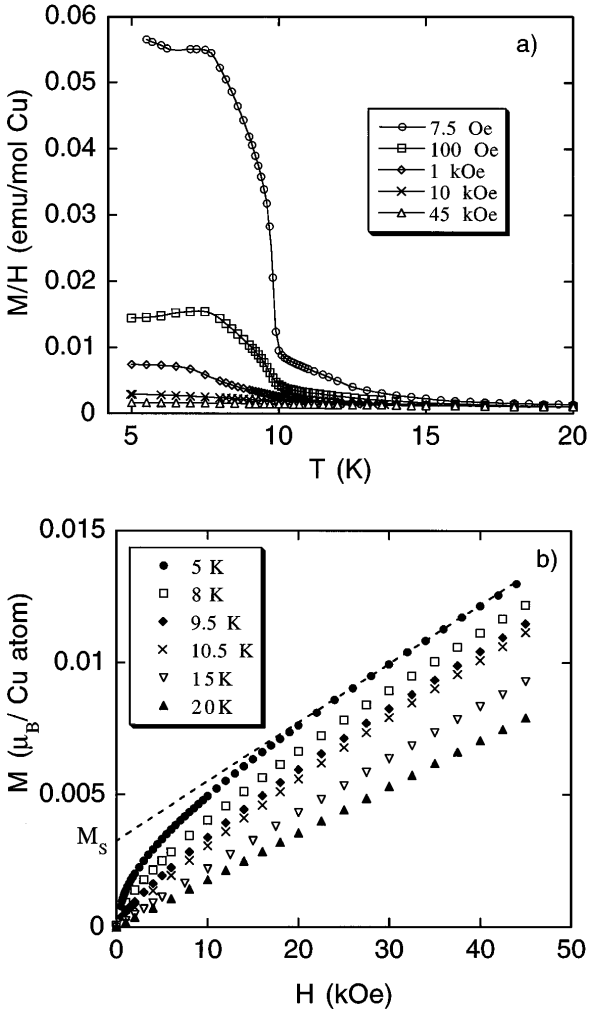

FIG. 2. (a) Field-cooled susceptibility curves for $Sr_{0.73}CuO_2$ at low temperatures measured in different magnetic fields. The solid lines are guides to the eye. (b) Magnetization versus applied magnetic field at various temperatures.

splitting is significantly larger than the linewidth. This demonstrates that, below T_c, a well defined internal field develops in $Sr_{0.73}CuO_2$ due to 3D long-range magnetic order. The temperature dependence of the EPR line splitting, which represents a measure of the internal magnetic field present in the sample, is shown in Fig. 3(b). The solid lines correspond to a power-law fit $(1 - T/T_c)^\beta$ with $T_c = 12.05(5)$ K and $\beta = 0.34(5)$.

It is important to note that the observed EPR signal originates from bulk Cu^{2+} ions. In fact, the concentration of Cu^{2+} ions calculated from the EPR intensity agrees well with the Cu^{2+} concentration obtained from susceptibility measurements. Furthermore, the temperature dependence of the EPR integral intensity closely follows the temperature dependence of magnetic susceptibility (see Fig. 4). All of this suggests that the EPR signal originates from bulk paramagnetic centers and not from impurities. As seen in Fig. 3(a), despite the extra peaks which appear below T_c, the unsplit EPR line persists down to the lowest

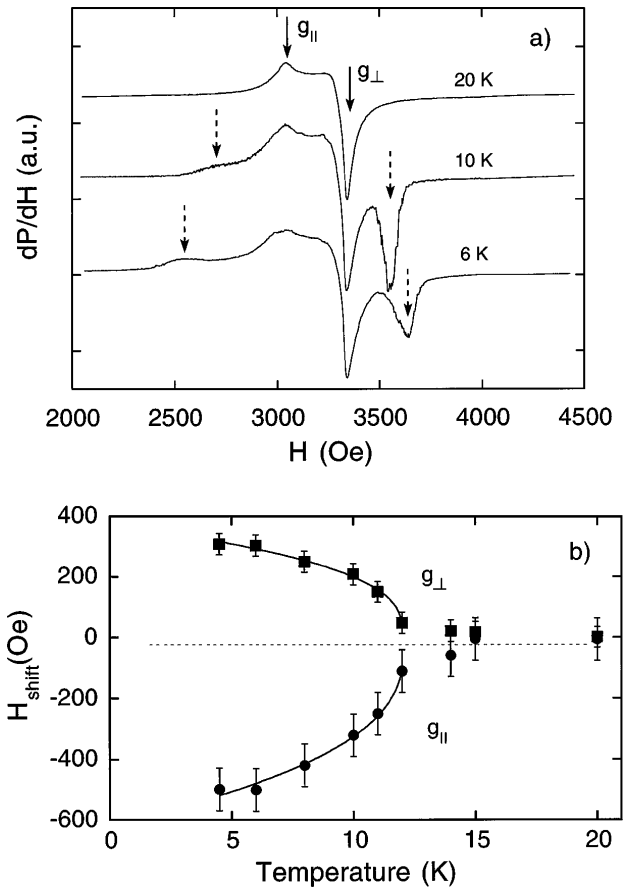

FIG. 3. (a) EPR spectra of $Sr_{0.73}CuO_2$ at various temperatures. The dashed arrows mark two extra peaks which split from the main EPR line below the magnetic transition temperature $T_c \sim 12$ K. (b) Temperature dependence of the position of the extra peaks relative to the $g_{\|}$ and $g_{\perp}$ components. The solid lines correspond to a power-law fit $(1 - T/T_c)^{\beta}$ with $T_c = 12.05(5)$ K and $\beta = 0.34(5)$.

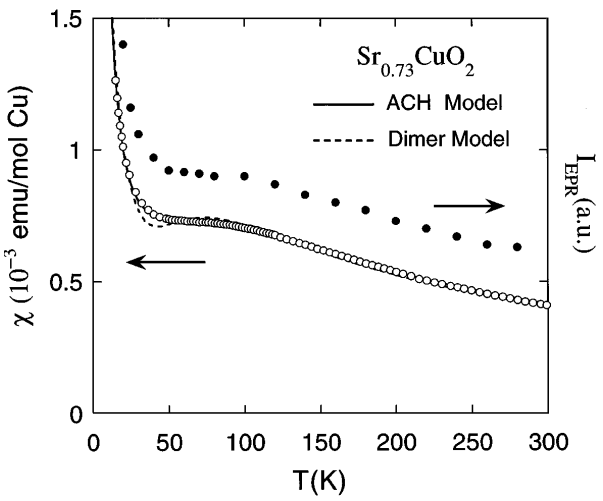

FIG. 4. Temperature dependence of the magnetic susceptibility (left axis) and EPR intensity (right axis) of $Sr_{0.73}CuO_2$. The solid and dashed lines represent best fits of the susceptibility data to the alternating chain Heisenberg (ACH) and dimer model, respectively.

measured temperatures. However, the line position and g factor anisotropy is the same as for the EPR line observed above the magnetic transition, suggesting that this EPR line does not originate from the free moments in another phase, but from those in the main phase which do not take part in magnetic order or because the internal magnetic field is canceled at these sites. Simple estimations show that the intensity of this line is only about 30% of the total EPR intensity at low temperatures. It means that at least 70% of the sample volume orders magnetically. This is in agreement with preliminary zero-field muon spin relaxation measurements on the same sample which confirmed a sharp magnetic transition below 10 K and show that at least 90% of the sample volume undergoes magnetic order [13].

Thus, magnetic susceptibility and EPR measurements provide evidence that, below $T_c \sim 12$ K, a long-range magnetic order with a small spontaneous FM moment $M_s = 3.2(2) \times 10^{-3}\mu_B$/Cu occurs in $Sr_{0.73}CuO_2$. Such a weak-ferromagnetic (WF) moment may result from spin-canted AF due to the Dzyaloshinski-Moriya [14,15] antisymmetric exchange. As was mentioned above, the copper-oxygen chains in this compound are wave modulated along the a axis forming infinite corrugated ribbons, which can allow an antisymmetric superexchange term in the spin Hamiltonian. It is worth noting that WF with $M_s \sim 10^{-3}\mu_B$/Cu was also observed in the 2D AF copper oxides La_2CuO_4 [16] and Gd_2CuO_4 [17].

Let us consider the temperature dependence of magnetic susceptibility χ in the paramagnetic regime. $\chi(T)$ data of $Sr_{0.73}CuO_2$ above 15 K are shown in Fig. 4. The susceptibility shows a broad plateau near 80 K, followed by a strong upturn below 50 K. The plateau resembles the broad maximum also observed in $Sr_{14}Cu_{24}O_{41}$, which is ascribed to the formation of a gap in the spin excitation spectrum [6,7]. In $Sr_{0.73}CuO_2$, the gap feature is significantly smeared out because of the large Curie term at low temperature. This behavior was also observed in $Sr_{14}Cu_{24}O_{41}$ with oxygen nonstoichiometry [18] or when doped with Ca [19]. While the broad peak is a characteristic feature of linear chain Heisenberg antiferromagnets (LCHA) [20,21], the Curie-like increase at low temperatures may arise from finite length chains with an odd number of spins [20], isolated spins, and/or other paramagnetic impurities. Following the approach used for $Sr_{14}Cu_{24}O_{41}$ [7], we assume that the observed $\chi(T)$ consists of three terms:

$$\chi(T) = \chi_0 + \chi_{\mathrm{CW}}(T) + \chi_{\mathrm{chain}}(T), \qquad (1)$$

where χ_0 is the temperature-independent term, $\chi_{\mathrm{CW}}(T)$ is the Curie-Weiss susceptibility $\chi_{\mathrm{CW}} = C/(T - \Theta)$ with a Curie constant $C = N_{\mathrm{F}} g^2 \mu_{\mathrm{B}}^2/4k$ (N_F is the number of free $S = \frac{1}{2}\,Cu^{2+}$ spins) and $\chi_{\mathrm{chain}}(T)$ is the LCHA susceptibility.

The susceptibility data for $Sr_{14}Cu_{24}O_{41}$ were successfully fitted by taking, for χ_{chain}, the susceptibility of

noninteracting dimers χ_D [7]: $\chi_D = 2N_D g^2 \mu_B^2 / k_B T[3 + \exp(J_D/k_B T)]$, where N_D is the number of dimers with spin $\frac{1}{2}$ and J_D is the dimer coupling. Applied to our case, this model gives a rather poor fit, as shown in Fig. 4. A better fit can be obtained taking into account the interdimer interaction by using the alternating chain Heisenberg (ACH) model. The Hamiltonian for this model may be written as [21,22]

$$H = J \sum_i (S_{2i} S_{2i+1} + \alpha S_{2i} S_{2i-1}), \qquad (2)$$

where J is the exchange integral between a spin and its right neighbor ($J > 0$ for AF exchange) and αJ is the exchange integral between a spin and its left neighbor. Parameter α measures the degree of alternation. In the limit $\alpha = 0$, the model reduces to the dimer model with pairwise interactions, whereas, for $\alpha = 1$, it reduces to the linear chain model [20]. There are no analytical solutions for the magnetic susceptibility of alternating Heisenberg chains. However, a useful closed-form approximation to χ_{ACH} has been suggested [22] to be

$$\chi_{\mathrm{ACH}} = \frac{N_{\mathrm{Ch}} g^2 \mu_B^2}{kT} \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3}, \qquad (3)$$

where $x = J/kT$ and N_{ch} is the number of Cu^{2+} spins contributing to the chain susceptibility. The values of parameters $A, B, \ldots, F$ were calculated numerically by Hall *et al.* [22]. A fit to the data using the ACH model (solid line in Fig. 4) yields $\chi_0 = 3(1) \times 10^{-5}$ emu/mol Cu, $J = 180(10)$ K, $\alpha = 0.6(1)$, $N_{\mathrm{ch}} = 0.32(1)$ spins per formula unit (f.u.), $N_F = 0.06(1)$ spins per f.u., and $\Theta = 0.35(5)$. For the calculations, we used $g = 2.08$ determined from our EPR measurements.

The total spin density per f.u., $N_{\mathrm{ch}} + N_F = 0.38$, is close to the expected Cu^{2+} concentration which is 0.46 as derived from the chemical formula. This means that each hole in the CuO_2 chain causes approximately one CuO_2 unit to become nonmagnetic [7]. It is very unusual that such a highly diluted compound, where only about 40% of the Cu ions are magnetic, exhibits long-range magnetic order with $T_c \sim 12$ K. This striking result remains to be understood.

Another interesting question is as follows: Can a spin gap similar to that in $Sr_{14}Cu_{24}O_{41}$ exist in $Sr_{0.73}CuO_2$. The ACH model with the obtained values $J = 180$ K and $\alpha = 0.6$ predicts a spin gap of about 105 K in $Sr_{0.73}CuO_2$ [23]. If a spin gap exists, χ_{chain} goes to zero as $T \rightarrow 0$, but, unfortunately, a large Curie contribution and ferromagnetism prevent us from following the behavior of χ_{chain} at low temperatures. Nevertheless, it is interesting to note that the susceptibility of $(Sr_{0.8}, Ca_{0.2})_{14}Cu_{24}O_{41}$ is well described also by the ACH model with $J = 135$ K and $\alpha = 0.6$ [24]. This indicates that the magnetic properties of the hole-doped chains in $(Sr, Ca)_{14}Cu_{24}O_{41}$ and $Sr_{0.73}CuO_2$ are similar. Inelastic neutron scattering experiments similar to those performed on $(Sr, Ca)_{14}Cu_{24}O_{41}$ [24,25] would be important to establish the existence of a spin gap in $Sr_{0.73}CuO_2$.

In summary, we have studied the magnetic properties of the novel hole-doped 1D cuprate $Sr_{0.73}CuO_2$ by magnetic susceptibility and EPR measurements. We find that in this compound, in contrast to $Sr_{14}Cu_{24}O_{41}$, long-range magnetic order with a small spontaneous ferromagnetic moment occurs below $T_c \sim 12$ K. However, the microscopic mechanism of this magnetic order is not clear at the moment. At higher temperatures, $Sr_{0.73}CuO_2$ and $Sr_{14}Cu_{24}O_{41}$ show similar magnetic properties: The CuO_2 chains in both compounds are diluted highly magnetically by holes which render the CuO_2 unit nonmagnetic. In addition, the values of the AF exchange integrals J are close. The magnetic susceptibility data are well described by the ACH model, indicating a possible dimerization of the CuO_2 chains with an excitation gap $\sim$105 K. We plan to perform inelastic neutron scattering experiments to clarify this point. If a spin gap is present in $Sr_{0.73}CuO_2$, this compound will be the second example of a material with coexistence of a spin gap state and long-range magnetic order. The coexistence of these qualitatively different magnetic states was observed recently in the Si or Zn doped spin-Peierls compound $CuGeO_3$ [26,27].

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