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Mobility of holes and suppression of antiferromagnetic order in $La_{2-x}Sr_xCuO_4$

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We have measured the static magnetic susceptibility and the resistivity of Zn ($0 \leqslant z \leqslant 0.25$) and Sr ($0 \leqslant x \leqslant 0.03$) doped La_2CuO_4. Our data clearly show that Zn impurities lead to an increase of the Néel temperature T_N in weakly hole doped compounds. This increase of T_N correlates with an increase of the resistivity. The analysis of our data strongly suggests that the hole mobility is the most important source for the strong suppression of antiferromagnetic order in $La_{2-x}Sr_xCuO_4$. [S0163-1829(99)50102-1]

Doping of the parent compounds of high-temperature superconductors with charge carriers has a pronounced influence on both the antiferromagnetic (AF) order and the electronic transport properties. La_2CuO_4 for example is an insulator with AF order below a Néel temperature of $T_N^0 \sim 300$ K.[1] In $La_{2-x}Sr_xCuO_4$ (LSCO) this long-range magnetic order is almost completely destroyed by doping the CuO_2 planes with the small amount of $\sim 2\%$ holes ($x \sim 0.02$).[2] In contrast, a much weaker influence on the magnetic order is observed when the Cu spin lattice is diluted by nonmagnetic Zn ions.[3] In this case an impurity content as large as 30–40% is required to destroy the AF order which is in fair agreement with the theoretical predictions by the site percolation theory for a two-dimensional (2D) square lattice.[4] In contrast the situation is less clear in the case of doping with charge carriers. While it is well known that doped holes strongly disturb the antiferromagnetic bonds in the CuO_2 planes[5] and that there is a strong coupling between the hole motion and the AF correlations, the detailed mechanism of the rapid suppression of T_N upon hole doping is poorly understood. It has been argued that the strong suppression of AF order in lightly hole doped La_2CuO_4 is related to a segregation of the holes into quasi-one-dimensional, antiphase domain boundaries which lead to an in-plane anisotropy of the magnetic exchange.[6,7] A similar scenario has been recently derived from a comparative study of Sr- and Li-doped La_2CuO_4.[8] In particular, it was pointed out in this study that the magnetic properties do not correlate with the electrical transport properties.[8] Based on this observation it is argued that the strong suppression of AF order is caused by the motion of AF domains which are surrounded by charged, antiphase boundaries, i.e., due to collective hole phenomena.[8]

We have investigated in more detail the relationship between hole mobility and antiferromagnetic order by measuring the magnetic and electronic transport properties of La_2CuO_4 doped by both Sr and Zn in the AF phase. Here, the Zn doping is used to reduce the mobility of the holes introduced by the Sr doping. Our data show a clear correlation between the degree of the hole localization and the magnetic ordering temperature T_N. In particular, we find that Zn doping increases T_N in lightly hole doped La_2CuO_4 due to the localization of the charge carriers.

Using a standard solid state reaction[9] four series of polycrystalline $La_{2-x}Sr_xCu_{1-z}Zn_zO_4$ samples with different nominal compositions were prepared: one with a fixed Sr content ($x = 0.017$) and various Zn doping ($0 \leqslant z \leqslant 0.25$), and another with a fixed Zn concentration ($z = 0.15$) and various Sr doping ($0 \leqslant x \leqslant 0.03$). For comparison we show in addition results on $La_{2-x}Sr_xCuO_4$ and $La_2Cu_{1-z}Zn_zO_4$, i.e., samples doped either with Sr ($0 \leqslant x \leqslant 0.023$) or with Zn ($0 \leqslant z \leqslant 0.25$). To reduce the excess oxygen all samples have been annealed for 72 h at 625 °C in pure N_2 atmosphere. Within a series of samples with identical x (z) the differences of the Sr (Zn) content are smaller than $\Delta x \sim \pm 0.001$ ($\Delta z \sim \pm 0.01$). In order to obtain this necessary accuracy of the Sr content, a complete series of samples with different z was prepared from the same mixture of La_2O_3 and $SrCO_3$. The error of x was checked by measuring T_N of different samples with identical compositions (e.g., for $z = 0$).

At low temperatures all investigated samples ($x \leqslant 0.03$) are insulators. It is well established that the electrical resistivity in this nonmetallic regime is described within the variable range hopping (VRH) model as $\rho(T) \propto \exp((T_0/T)^{\alpha})$, where T_0 is a characteristic temperature controlled by the mobility of the holes and the exponent α depends on the dimensionality of the VRH process.[10] As shown in Fig. 1 the resistivity ρ of $La_{1.983}Sr_{0.017}Cu_{1-z}Zn_zO_4$ is well described assuming an exponent $\alpha = 1/3$ which corresponds to a two-

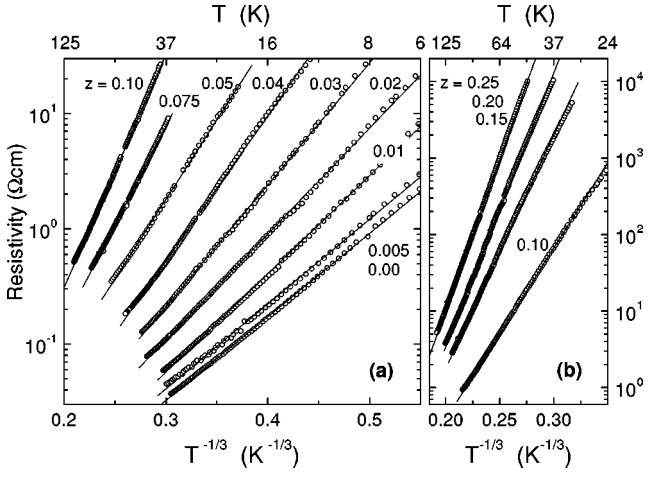

FIG. 1. Resistivity of $La_{1.983}Sr_{0.017}Cu_{1-z}Zn_zO_4$ plotted on a logarithmic scale vs $T^{-1/3}$ for $z \leqslant 0.1$ (a) and $z \geqslant 0.1$ (b). The characteristic temperature T_0 is obtained from the linear fits to the data (solid lines).

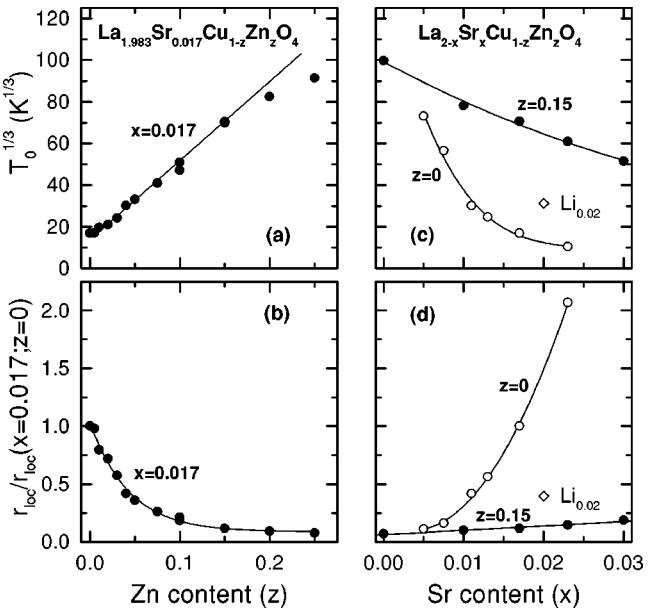

FIG. 2. T_0 and localization radius r_{loc} of $La_{2-x}Sr_xCu_{1-z}Zn_zO_4$ normalized to the value found for $x=0.017$ and $z=0$ as a function of Zn (left) and Sr (right) doping. The solid lines are guides to the eye. Values for $La_2Cu_{0.98}Li_{0.02}O_4$ ($\diamond$) are extracted from $\rho(T)$ data in Ref. 14.

dimensional hopping at elevated temperatures.[11] The general trend of $\rho(x,z)$ as a function of doping is an increase with decreasing x and increasing z, respectively. In the case of 2D VRH the characteristic temperature T_0 is related to the localization radius r_{loc} of the holes via

$$T_0=\frac{13.8}{k_B N(\epsilon_F) r_{loc}^2}, \tag{1}$$

where $N(\epsilon_F)$ is the density of states at the Fermi energy.[10] Measurements of the electronic specific heat yield that $N(\epsilon_F)$ does not vary significantly in the doping regime of our experiments.[12] Therefore, we neglect a possible weak dependence of $N(\epsilon_F)$ on x and z in our qualitative discussion of the localization radius r_{loc}.

The values for $T_0^{1/3}$ and the normalized localization radius r_{loc} are summarized in Fig. 2. Let us first focus on the data obtained for $La_{1.983}Sr_{0.017}Cu_{1-z}Zn_zO_4$ shown in Figs. 2(a) and 2(b). A clear increase of T_0, i.e., an increasing localization, is observed with increasing Zn doping. The localization radius r_{loc} determined from T_0 using Eq. (1) strongly decreases with increasing z and saturates for Zn doping $z \gtrsim 0.15$.

The corresponding results for T_0 and r_{loc} for the samples with fixed Zn content $z=0.15$ and variable Sr concentration $x \leqslant 0.03$ are shown in Figs. 2(c) and 2(d) (full symbols). With increasing Sr content $T_0^{1/3}$ (r_{loc}) decreases (increases), i.e., the holes become more mobile. However, we stress that for this high Zn content r_{loc} stays small even for the largest Sr doping ($x=0.03$). Indeed, our findings for $z=0.15$ markedly differ from the behavior in pure $La_{2-x}Sr_xCuO_4$, i.e., for $z=0$, which is also shown in Figs. 2(c) and 2(d) (open symbols). In the latter case there is a much stronger increase of the hole mobility (r_{loc}) with increasing x.

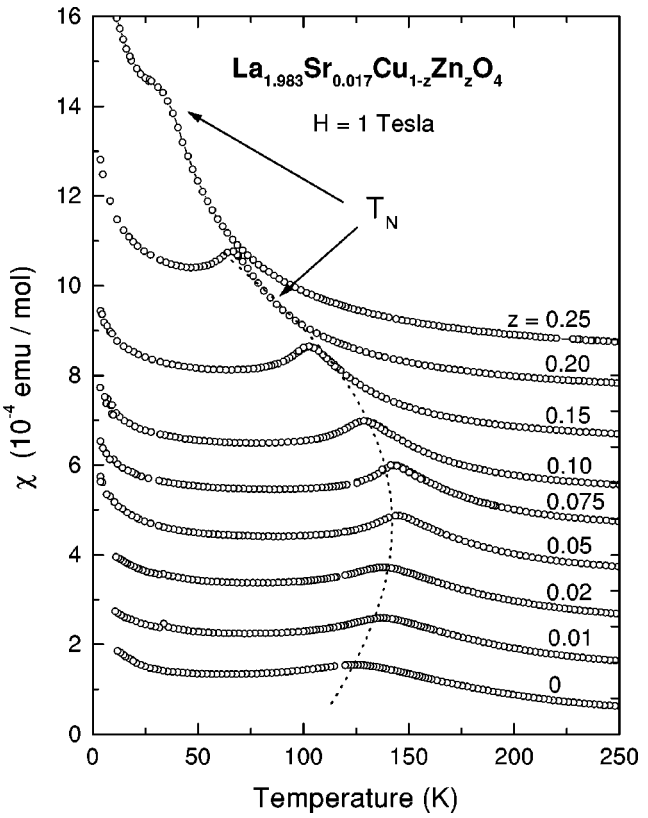

FIG. 3. Static magnetic susceptibility ($H=1$ Tesla) vs temperature of $La_{1.983}Sr_{0.017}Cu_{1-z}Zn_zO_4$ for different Zn doping. The dotted line is a guide to the eye to emphasize the nonmonotonous dependence of T_N on Zn doping. The curves are displaced vertically by 1×10^{-4} emu/mol for clarity.

In the following we will show that this strong influence of the Zn doping on the hole mobility as revealed from our resistivity data clearly correlates with the magnetic properties. In Fig. 3 the magnetic susceptibility χ is plotted for some representative $La_{1.983}Sr_{0.017}Cu_{1-z}Zn_zO_4$ samples with a fixed Sr content $x=0.017$ and different Zn concentrations ($0 \leqslant z \leqslant 0.25$). The susceptibilities are similar to that of the canted antiferromagnet La_2CuO_4.[13] The paramagnetic state at high temperatures is characterized by a Curie-Weiss-like increase of χ with decreasing T, followed by a well defined peak which indicates the transition to AF order at T_N. At very low temperature a Curie-like upturn due to small amounts of paramagnetic moments (e.g., uncompensated Cu spins) is visible. Without Zn doping, $T_N=125$ K is observed which is significantly below T_N of pure La_2CuO_4 due to the Sr doping ($x=0.017$). The remarkable feature of Fig. 3 is the fact that additional Zn doping initially does not lead to a further reduction of T_N. In contrast, T_N even increases up to $T_N=144$ K for $z=0.05$. Only for $z>0.05$, T_N starts to decrease again. Note that a large Zn concentration of $z \simeq 0.1$ is required to reach $T_N=125$ K measured for $z=0$.

A similar study of the influence of Zn doping on T_N has been performed for $x=0$, i.e., for samples without doped holes. A comparison of the T_N obtained for these two sets of samples is given in the phase diagram shown in Fig. 3(a). For $x=0$, the well-known linear decrease of $T_N(z)$ with increasing z is observed. The distinction to our findings for the lightly hole doped compounds is apparent. However, note

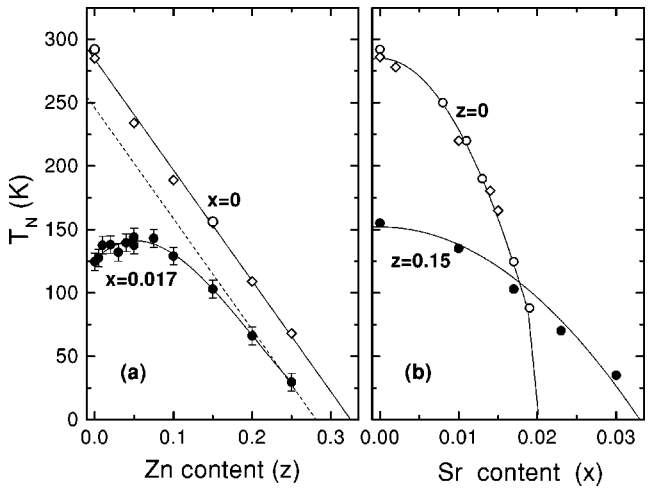

FIG. 4. (a) Néel temperature T_N as a function of the Zn content for samples with $x=0.017$ (●) and $x=0$ (○, ◇). Error bars show the scatter of T_N for different samples with identical nominal compositions. (b) T_N as a function of the Sr content for samples with $z=0.15$ (●) and $z=0$ (○, ◇). The solid lines are guides to the eye. The dashed line in (a) represents an extrapolation of the linear part of the $T_N(x=0.017,z)$ curve to small z. Samples marked with (◇) are additionally doped by Eu which is irrelevant in the context of this paper.

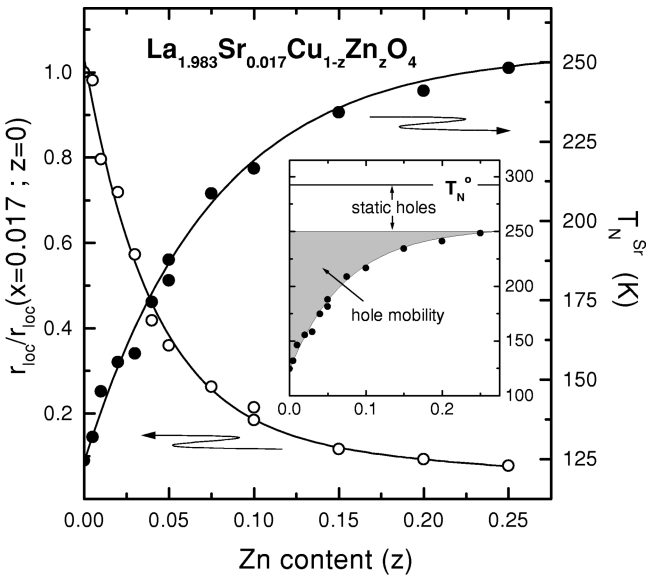

FIG. 5. Néel temperature T_N^{Sr} corrected for the influence of Zn doping (●) (see text) and normalized localization radius r_{loc} (○) of $La_{1.983}Sr_{0.017}Cu_{1-z}Zn_zO_4$ vs the Zn content. Inset: separation of the contributions of static holes and the mobility of holes to suppression of T_N. T_N^0 denotes the ordering temperature of pure La_2CuO_4.

that this difference reduces with increasing Zn content. Indeed, for large Zn contents $z \gtrsim 0.15$ the slope dT_N/dz is about the same for the two sets of samples. Thus, it is evident from the measured $T_N(z)$ dependences that for the hole doped samples with $x=0.017$ there is a kind of threshold value $z \sim 0.15$ for the Zn doping. Above this value T_N is consistent with a simple spin dilution, whereas for smaller Zn doping there is an apparently different mechanism controlling T_N for compounds with a finite hole content.

To obtain further insight into the effect of Zn and Sr doping on T_N in La_2CuO_4 we have studied the susceptibility of samples with a fixed Zn content $z=0.15$ and various Sr concentrations in the range $0<x<0.03$. The Néel temperatures of these samples monotonously decrease with increasing x as shown in Fig. 4(b) (full symbols). A quite remarkable result is obtained when comparing these findings to the well-known $T_N(x)$ dependence of samples without Zn doping [open symbols in Fig. 4(b)]. In the absence of holes, i.e., for $x=0$, T_N is much smaller in the Zn-doped compound as expected due to the dilution of the Cu spin system. However, the decrease of T_N with increasing Sr concentration is much weaker in the Zn-doped compounds and, finally, T_N of these samples is significantly larger than for the samples without Zn doping. The extrapolated critical Sr content for which $T_N=0$ is as large as $x_c \simeq 0.033$ for $z=0.15$ and therefore clearly exceeds the corresponding value $x_c \simeq 0.02$ of samples without Zn. A comparison of these experimental findings for T_N in Fig. 4(b) to the results of the resistivity measurements on the same samples shown in Fig. 2(d) indicates a relationship between T_N and r_{loc}: a strong decrease of T_N with increasing x seems to correlate with a strong increase of r_{loc} which is only present for $z=0$.

In order to clarify this relationship between r_{loc} and T_N we consider again the series of Zn-doped samples with a fixed Sr content of $x=0.017$. Both, the resistivity and the susceptibility data strongly suggest that one has to distinguish two regimes of Zn doping. There is a strong doping regime for $z \gtrsim 0.15$ where the degree of localization does not change significantly as a function of the Zn content, i.e., the mobility of holes is already reduced to its minimum. In this doping regime T_N decreases linearly with the Zn content z which can be interpreted in terms of simple spin dilution. In contrast to that, the charge mobility is strongly affected by the Zn doping in the weak doping regime $z \lesssim 0.15$ as signaled by the strong decrease of r_{loc} in Fig. 2(b). In the same range of doping the unusual nonmonotonous change of T_N as a function of the Zn content is observed [see Fig. 4(a)]. Hence, in the low doping regime Zn doping plays a twofold role. On the one hand it reduces T_N due to the creation of static spin holes in the Cu spin lattice (spin dilution). However, on the other hand it causes a localization of the mobile holes thus reducing the effect of Sr doping on the AF order. The superposition of these two effects causes the nonmonotonous change of T_N with increasing z.

Subtracting the effect of spin dilution which is known from the findings for $La_2Cu_{1-z}Zn_zO_4$ (as well as from the high Zn doping regime for $x=0.017$) allows to determine the suppression of T_N due to the mobility of the holes. The result is plotted in Fig. 5 which shows $T_N^{\mathrm{Sr}}=T_N(x,z)+[T_N^0-T_N(0,z)]$ as a function of the Zn content z for the samples with $x=0.017$. Here, $T_N^0=292$ K is the Néel temperature of pure La_2CuO_4 and T_N^{Sr} is the Néel temperature corrected for the influence of the dilution of the Cu spin lattice due to Zn doping. That is, T_N^{Sr} represents the ordering temperature of ''hypothetical'' exclusively Sr-doped samples ($x=0.017$) with different degree of hole mobility as measured by r_{loc}. From a comparison of T_N^{Sr} and r_{loc} in Fig. 5 the crucial role of the hole mobility for suppression of AF order becomes apparent. The strong *reduction of* r_{loc} at small z corresponds well with a respective steep *increase of* T_N^{Sr} by more than 100

K. In the limit of strong localization (large z) both $T_N^{\mathrm{Sr}}(z)$ and $r_{loc}(z)$ tend to saturate. However, note that T_N^{Sr} is still by about 40–50 K less than T_N^0 as illustrated in the inset of Fig. 5. According to our analysis this remaining difference has to be attributed to the decrease of T_N due to quasistatic holes. This suppression which amounts to about 40–50 K for $x=0.017$ is still about three times stronger than that for a Zn content of $z=0.017$ in $La_2Cu_{1-z}Zn_zO_4$. The reason for this stronger influence is obvious, since a doped hole on an oxygen site does not only dilute the spin lattice, but also causes a ferromagnetic exchange between the adjacent Cu spins.[5] Nevertheless, only a small part of the decrease of T_N in LSCO can be explained with the presence of quasistatic holes. For a Sr content $x=0.017$ this fraction amounts to about 1/4 of the total suppression (see inset of Fig. 5). Therefore our data show that the charge mobility plays the most significant role in destruction of the AF order in LSCO with increasing x.

This main conclusion of our study seems to contradict the above-mentioned findings on Li-doped La_2CuO_4.[8] However, also for Li hole doping the resistivity decreases strongly for small concentrations.[14] From the resistivity data in Ref. 14 we have estimated T_0 and r_{loc} for a Li content of 2%. The results are included in Fig. 2. As expected the holes are less mobile than in LSCO. However, the localization radius in the Li-doped compound is significantly larger than in the case of quasistatic holes for high Zn contents. Accordingly, $La_2Cu_{1-y}Li_yO_4$ should be compared to $La_{2-x}Sr_xCu_{1-z}Zn_zO_4$ at intermediate Zn doping, where charge mobility is still the main source of the suppressed T_N. From the correlation between T_N^{Sr} and r_{loc} for the 1.7% Sr-doped samples shown in Fig. 5 and r_{loc} of the 2% Li-doped compound we estimate a Néel temperature of $T_N \simeq 175$ K. This value is in fair agreement with the measurements revealing $T_N \simeq 140$ K,[14] if we take into account the slightly larger hole content in the Li-doped sample, i.e., 2% instead of 1.7%. This agreement strongly confirms our data analysis in $La_{2-x}Sr_xCu_{1-z}Zn_zO_4$ and, moreover, gives further experimental evidence for a correlation between transport and magnetic properties in lightly hole doped La_2CuO_4. In this respect our findings do not support the conclusions in Ref. 8. According to our results there is no apparent contradiction to the assumption that the mobility of individual holes determines both the electrical resistivity and the suppression of the magnetic order.

In summary, the investigation of the static magnetic susceptibility and the electrical resistivity of $La_{2-x}Sr_xCu_{1-z}Zn_zO_4$ has revealed a clear correlation between the antiferromagnetic ordering and the mobility of the holes in these compounds. Localizing the holes by Zn doping increases T_N and finally leads to a situation which is similar to that in $La_2Cu_{1-z}Zn_zO_4$ where the AF order is only suppressed due to the dilution of the Cu spin lattice. From our data we conclude that the hole mobility is the most important source for the strong suppression of AF order in $La_{2-x}Sr_xCuO_4$.

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[11] We have also analyzed the data assuming $\alpha=1/4$ and $\alpha=1/2$. Whereas $\alpha=1/4$ also reasonably fits the data, strong deviations are found for $\alpha=1/2$. We stress that the main conclusion of our analysis does not depend on a particular model for ρ, i.e., the qualitative changes of the mobility as a function of x and z can also be extracted from, e.g., the temperature derivatives of ρ.

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