Magnetization of hole-doped CuO_2 spin chains in $Sr_{14-x}Ca_xCu_{24}O_{41}$

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We report on magnetization measurements of $Sr_{14-x}Ca_xCu_{24}O_{41}$, with $0 \leqslant x \leqslant 12$, in magnetic fields up to 16 T. The low-temperature magnetic response of the CuO_2 spin chains changes strongly upon doping. For $x=0$, the ground state with nearly independent dimers is confirmed. A reduction of the number of holes in the chains through Ca doping leads to an additional contribution to the magnetization, which depends linearly on the magnetic field. Remarkably, the slope of this linear contribution increases with the Ca content. We argue that antiferromagnetic spin chains do not account for this behavior but that the hole dynamics might be involved.

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I. INTRODUCTION

Introducing charge carriers in a quantum antiferromagnet causes frustration of the magnetic interactions and degeneracy of the ground state. This degeneracy can be lifted by charge order (CO) which evolves on the background of the quantum antiferromagnet. One remarkable example is the formation of spatial spin and charge modulations in the high-T_C cuprates.[1] Another class of low-dimensional cuprates where spin and charge correlations determine the electronic and magnetic properties are the intrinsically doped CuO_2 spin chain systems which comprise edge-sharing chains like $Sr_{14-x}Ca_xCu_{24}O_{41}$ and $Na_{1+x}CuO_2$. In the latter, at commensurate doping levels, a one-dimensional (1D) Wigner lattice occurs where charge order on the chains is determinded by long-range Coulomb interaction.[2] Charge order is also known for the spin chains in $Sr_{14}Cu_{24}O_{41}$. In the chains of these compounds, there is a nonmagnetic dimer ground state related to static charge order on the chains. The presence of CO is well established, e.g., by NMR and ESR data.[3,4] Its presence, however, is intimately connected to the number of holes on the chains. Reducing the number of holes in the chains by Ca doping yields a decrease of the stability of CO.[4–6] Here, we show that the static dimer spin gap Δ_d, which is present in $Sr_{14}Cu_{24}O_{41}$, is even more strongly affected by the Ca doping than the CO. We show that in $Sr_{14-x}Ca_xCu_{24}O_{41}$, with $x \neq 0$, at low temperature there is a finite susceptibility which is not Curie-like. If there is a gap for this additional contribution to the magnetization, it is much smaller than the dimer gap Δ_d. Remarkably, susceptibility due to the low-energy response increases with the Ca content, i.e., the lower the number of holes, the larger the magnetic susceptibility.

II. BACKGROUND

The compounds $Sr_{14-x}Ca_xCu_{24}O_{41}$ have an incommensurate layered structure of two alternating subsystems.[7] In these subsystems, two quasi-1D magnetic structures are realized that are oriented along the c axis, i.e., $S=\frac{1}{2}$ Cu_2O_3 spin ladders and CuO_2 spin chains. For the low-temperature magnetic response, the ladders do not contribute significantly since they exhibit a nonmagnetic ground state and a large spin gap of $\Delta \approx 380$ K for the whole doping series $Sr_{14-x}Ca_xCu_{24}O_{41}$.[8–10] Thus, the low-temperature magnetic response of these compounds is determined by the weakly coupled CuO_2 spin chains. The chains consist of edge-sharing CuO_4 plaquettes containing Cu^{2+} ions with $S=\frac{1}{2}$ in the undoped case. The Cu—O—Cu bonding angle amounts to $\sphericalangle \sim 93$ deg.[7] For nearest neighbor spins, this results in a ferromagnetic (FM) superexchange.[11] The compounds $Sr_{14-x}Ca_xCu_{24}O_{41}$, however, are intrinsically hole doped with six holes per formula unit. Similar to the high-T_C cuprates, the holes are expected to be mainly of O:2p character and to form Zhang-Rice singlets.[12,13] In $Sr_{14}Cu_{24}O_{41}$, the holes are mainly located in the chains.[13] The magnetic coupling of next nearest neighbor Cu spins via a hole is antiferromagnetic. Below $T \approx 240$ K, charge ordering is observed[3,5] and a dimerized ground state with a spin excitation gap $\Delta \approx 130$ K develops.[5,14,15] It is well established that the dimers are formed by second neighbor spins separated by a hole. Dimers are separated from each other by two subsequent holes. Another important aspect of $Sr_{14-x}Ca_xCu_{24}O_{41}$ is the mutual distortion of the two subsystems due to the incommensurate structure. There is a pseudoperiodicity of ten chain units for seven ladder units which yields a modulation of each subsystem with respect to the periodicity of the other one. Since the magnetic interactions are very sensitive to a variation of the bonding length and the bonding angle, these modulations have a strong impact on the magnetic properties. It was shown that these modulations govern the low-energy properties of the compounds, through the localization of the magnetic electrons. In particular, the structural distortions favor the formation of dimers in $Sr_{14}Cu_{24}O_{41}$.[16]

The substitution of Ca^{2+} for Sr^{2+} leads to a partial charge transfer into the ladder subsystem owing to chemical pressure.[13,17] Upon Ca doping, the charge order is suppressed[4–6] and the dimer state becomes unstable.[14,15] For

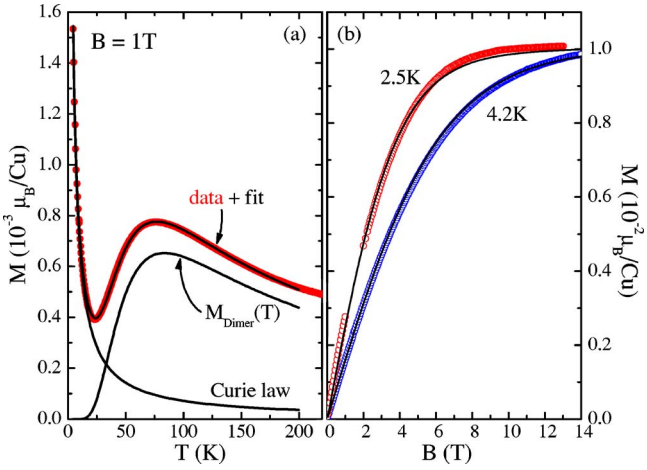

FIG. 1. (Color online) Magnetization of $Sr_{14}Cu_{24}O_{41}$ for a constant magnetic field $B=1$ T versus temperature (a) and for $T=2.5$ K ($T=4.2$ K) versus applied magnetic field (b). B was applied along the c axis. Lines are fits to the data (see the text).

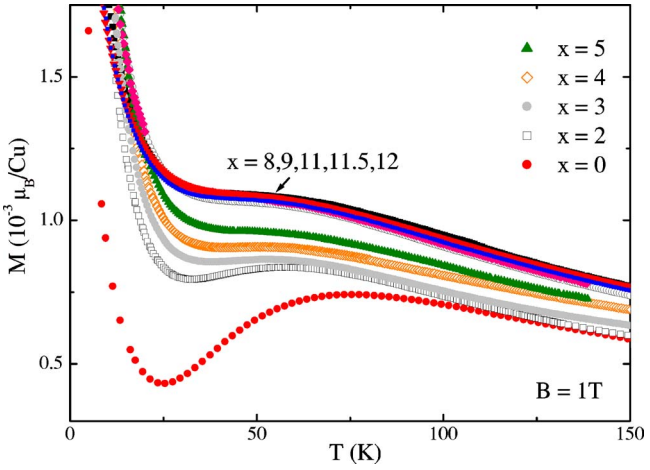

FIG. 2. (Color online) Magnetization of $Sr_{14-x}Ca_xCu_{24}O_{41}$ with $0 \leqslant x \leqslant 12$ in a magnetic field of $B=1$ T parallel to the c axis.

$Sr_{14-x}Ca_xCu_{24}O_{41}$, with $x \geqslant 11$, long range antiferromagnetic order is found at low temperatures (<2.5 K).[18,19] This magnetic order is related to a specific charge order with alternating spins and holes on the chains.[4] It is a remarkable fact that in this doping regime the compounds become superconducting upon the application of a hydrostatic pressure of ~ 3 GPa.[20,21]

III. EXPERIMENTAL AND RESULTS

A. Experimental

We report on magnetization measurements of $Sr_{14-x}Ca_xCu_{24}O_{41}$ single crystals, with $x=0,2,3,4,5,8,9,11,11.5,12$, in external magnetic fields up to 16 T. We used a vibrating sample magnetometer (VSM) and a SQUID magnetometer. We studied crystals of approximately 200 mg mass grown by the floating zone technique.[22] The samples were cut perpendicular to the c axis (parallel to the chains) and to the b axis (perpendicular to the CuO_2 plaquettes), respectively. Our samples have been previously characterized by diverse methods, such as magnetization and thermal expansion,[5] electrical and thermal transport,[6,10] inelastic neutron scattering,[15] and ESR.[4]

B. $Sr_{14}Cu_{24}O_{41}$

In order to recall the magnetic properties of $Sr_{14}Cu_{24}O_{41}$, in Fig. 1(a) its magnetization is shown, in an applied magnetic field of $B=1$ T, as a function of temperature. In addition, we show in Fig. 1(b) the magnetization M, at low temperatures, versus B. The data confirm the dimerized ground state which has been observed in our sample by inelastic neutron scattering and thermal expansion data.[5,15] The data in Fig. 1(b) reveal a small value of the magnetization of about 1×10^{-2} μ_B/Cu, at $T=2.5$ K, in a magnetic field of $B=14$ T. Moreover, the susceptibility is also very small at high fields, as is evident from the weak dependence of M on B in this field regime. The data, therefore, show the magnetization due to about 1% of free spins while there is no response from the remaining 99% of the spins. This agrees with the fact that most of the spins are dimerized, but there are some uncompensated "defect" spins. Consequently, the data in Fig. 1(b) can be explained in terms of the magnetization of free spins with $S=\frac{1}{2}$. Applying the Brillouin function

$$M(B) = \chi_0 \cdot B + \frac{1}{2} N_S g_c \mu_B \cdot B_{1/2}\left(\frac{g\mu_B(B+\lambda M}{2k_B T}\right), \qquad (1)$$

with the mean field parameter λ and the g factor[4] $g_c=2.04$, to the data in Fig. 1(b) yields $\chi_0 \approx 1\times10^{-5}$ emu/mol Cu, $\lambda=0$ and $N_S \simeq 0.01$/Cu. Here, the linear term $\chi_0 \cdot B$ considers the Van Vleck magnetism of the Cu ions. The data in Fig. 1(b) provide the number N_S of free spins in our sample very accurately, which allows us to estimate their response versus temperature. Considering the Curie contribution due to the free spins and applying the model of independent dimers (cf. Refs. 5 and 23) to the data in Fig. 1(a) provides the dimer spin gap and the number N_D of dimers. The analysis yields a gap of $\Delta_d=134$ K and $N_D=0.0738$/Cu. In this analysis, the number of magnetic Cu sites amounts to $N_S+2N_D \approx 3.78$/f.u. in our $Sr_{14}Cu_{24}O_{41}$ sample.

C. $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($0 \leqslant x \leqslant 12$)

It is known that the application of chemical pressure through Ca doping leads to a hole transfer from the chains to the ladders in $Sr_{14-x}Ca_xCu_{24}O_{41}$, thereby destabilizing the charge ordered ground state which is present for $x=0$.[4,5,13] In our study, we concentrate on the effect of Ca doping on the low-temperature magnetic susceptibility. We note that the magnetic properties have been studied previously by investigating the temperature dependence of the magnetization of polycrystals at $B=1$ T.[23] These data of $Sr_{14-x}Ca_xCu_{24}O_{41}$, with $0 \leqslant x \leqslant 10$, have been analyzed in terms of the free dimer model. Qualitatively, our $M(T)$ data on single crystals are similar to those in, e.g., Refs. 23 and 24.

Figure 2 displays the magnetization data at a small magnetic field for $Sr_{14-x}Ca_xCu_{24}O_{41}$ with $0 \leqslant x \leqslant 12$. Obviously,

changing the Ca content significantly affects the properties at low temperatures. In particular, the signature of the dimer gap, a broad maximum of M around 75 K, which is very pronounced in $Sr_{14}Cu_{24}O_{41}$, becomes much weaker upon Ca doping. The data show that the magnetization of $Sr_{14-x}Ca_xCu_{24}O_{41}$, at $T \gtrsim 25$ K, increases upon doping for $x \leqslant 8$ and is nearly independent of the Ca content for larger x. Due to the fact that upon Ca doping, however, the Curie contribution significantly increases, these data do not answer the question of the existence of a spin gap for $x > 0$. In particular, it is possible to describe perfectly the data for $0 \leqslant x \leqslant 5$ in terms of the free dimer model by including the Van Vleck magnetism and the Curie contribution due to free spins. However, our magnetization data M vs B, which we present in the following, show that the dimer model is not valid for $x \neq 0$.

In order to clarify the origin of the low-temperature magnetization in $Sr_{14-x}Ca_xCu_{24}O_{41}$, we studied the field dependence of M at $T=2.5$ K. The data are displayed in Fig. 3. As already shown in Fig. 1, for $x=0$ the magnetization in high magnetic fields is nearly independent of B, i.e., the susceptibility $\partial M/\partial B$ is almost zero, indicating the spin gapped state. When the number of holes in the chains, however, is reduced through the Ca doping, the data show a finite slope of $M(B)$ in high magnetic fields. In particular, a finite slope is already observed for $x=2$. Remarkably, the slope of $M(B)$ increases monotonically upon Ca doping. This becomes even more apparent if the data are analyzed in terms of Eq. (1). The fitting procedure is illustrated in Fig. 4(b) for the example of $Sr_2Ca_{12}Cu_{24}O_{41}$. The experimental data are described in terms of a Brillouin function and a linear term, as displayed in the figure by the solid and the dashed line, respectively. The fitting yields a reliable result in the whole field range. We mention that, in contrast with $Sr_{14}Cu_{24}O_{41}$, for the sample with $x=12$, the Brillouin function does not describe entirely independent spins but a small mean field parameter of $\lambda \simeq 60$ (emu/mol Cu)$^{-1}$ is necessary to describe the data correctly. In order to demonstrate the effect of the magnetic field, also the temperature dependence of the static susceptibility M/B of $Sr_2Ca_{12}Cu_{24}O_{41}$ for $B=1$ T and $B=14$ T is shown in Fig. 4(a). These data confirm that, below ~ 20 K, the field dependence of M is nonlinear. For comparison, the susceptibility χ_0 which corresponds to the linear term in Eq. (1) is plotted in Fig. 4(a). We emphasize that, in the case $x=12$, $\chi_0 = \partial M_{lin}/\partial B$ is much larger than for $Sr_{14}Cu_{24}O_{41}$. Thus, in contrast with the undoped compound, where χ_0 is ascribed completely to the Van Vleck magnetism,[28] the linear term in Eq. (1) has a different physical origin. We also extracted χ_0 from M vs B measurements at higher temperatures, as it is illustrated by the diamonds in Fig. 4(a). The data imply that χ_0 is only very weakly temperature dependent for $T \leqslant 20$ K.[29]

The above-described fitting procedure has been applied to the $M(B)$ curves of all compositions under study. The resulting Brillouin function is displayed in Fig. 3 for each composition. It is apparent that the difference between the data and the Brillouin function, i.e., the linear contribution to $M(B)$, increases monotonically upon Ca doping. This major result of our study is visualized in Fig. 5(a), where the susceptibility χ_0 from Eq. (1) is plotted. In addition, we show the field derivative of the experimental magnetization data $\partial M/\partial B$ at $B \sim 14$ T. For $x \neq 0$, obviously, χ_0 is much larger than the Van Vleck magnetism. Hence, both the raw data and our analysis clearly show that, for $x \neq 0$, there is an additional magnetic contribution which gives rise to a linear field dependence of the magnetization in the accessible field range. This response is due neither to free spins nor to dimers. The free spins are nearly completely aligned in high magnetic fields, at low temperature. The spin gap of the dimers is much larger than the applied magnetic field, i.e., $\Delta_d/(g\mu_B) \gg 14$ T.

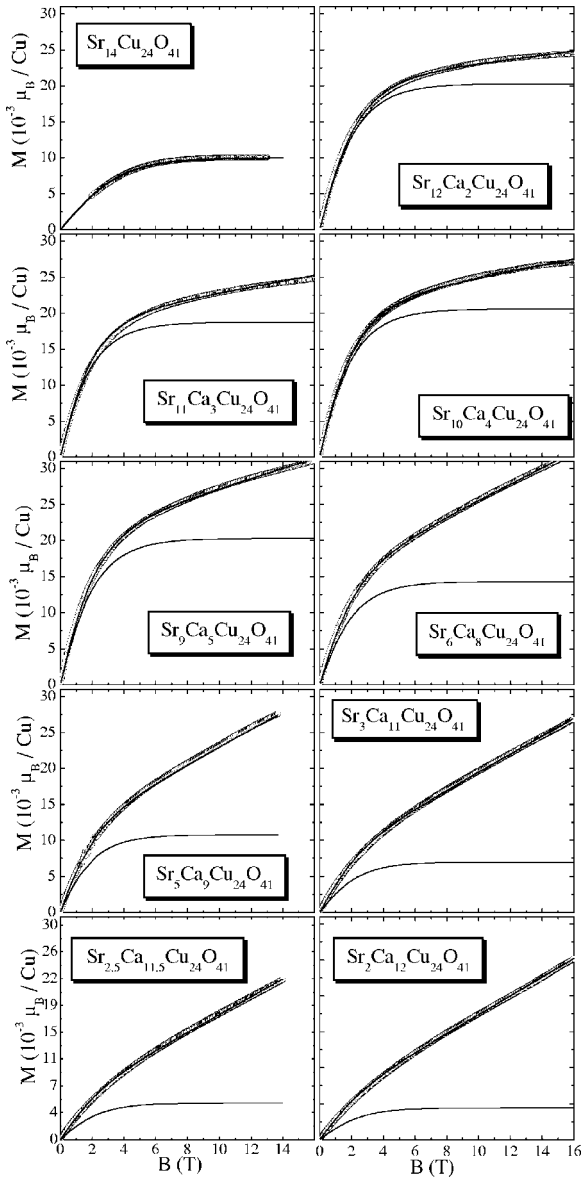

FIG. 3. Magnetic field dependence of the magnetization of $Sr_{14-x}Ca_xCu_{24}O_{41}$ with $0 \leqslant x \leqslant 12$ at $T=2.5$ K. The lines describe the response of nearly free spins (see the text).

The unusually large value of χ_0 is almost isotropic. This is illustrated in Fig. 6, where the magnetization of $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$, at 2.5 K, is shown for B parallel to the a, b, and c axis, respectively. In order to study the anisotropy of

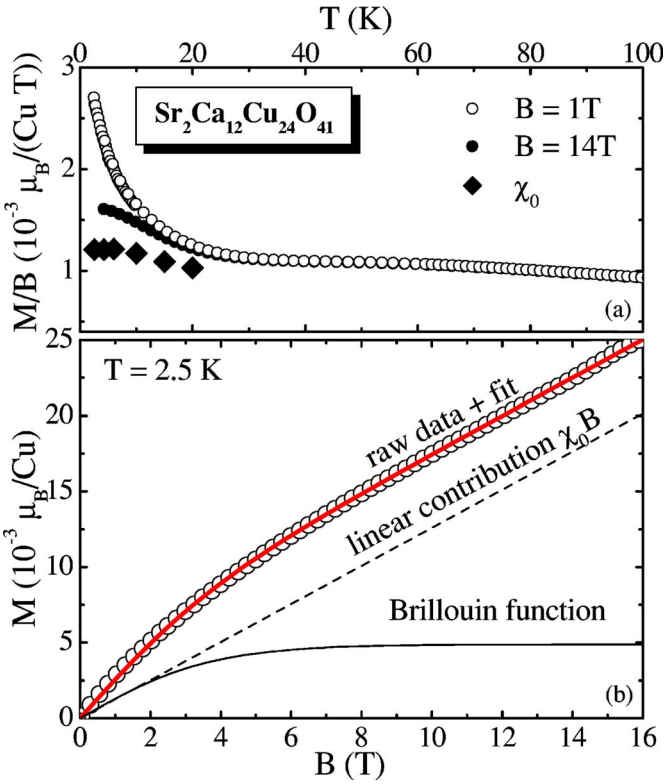

FIG. 4. (Color online) Magnetization of $Sr_2Ca_{12}Cu_{24}O_{41}$. (a) Temperature dependence of M/B for $B=1$ T and $B=14$ T. (b) Field dependence of M at $T=2.5$ K (cf. Fig. 3). The data are well described by a fitting function which considers a linear term (dashed line) and a Brillouin function (straight line). The diamonds in (a) correspond to the susceptibility $\partial M/\partial B$ of the linear term in (b).

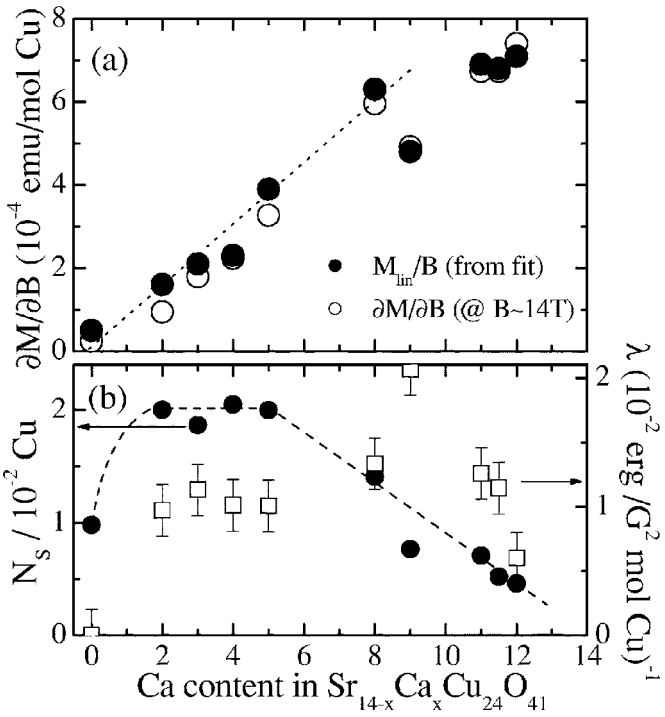

FIG. 5. Results of fitting the data of Fig. 3 with Eq. (1). (a) Linear term $\chi_0=M_{lin}/B$ from fit (full circles) and derivative of the raw data $\partial M/\partial B$ at $B\sim 14$ T (open circles). (b) Number of quasi-free spins N_S (circles) and mean-field parameter λ (squares). The lines are guides to the eye.

χ_0, the data are corrected for the anisotropy of the g factor and of the Van Vleck magnetism. Values of the g factor were taken from Ref. 4. Obviously, the magnetization is very similar for all field directions. The data imply $\Delta M/g_i^2 < 0.01\mu_B$/Cu, at 16 T, which is comparable to the error which originates from the uncertainty of the g factor.

In addition to the surprising strong dependence of χ_0 on the Ca content, our analysis yields the doping dependence of the number of the quasi-free spins. These data are shown in Fig. 5(b). Starting from $x=0$, N_S increases sharply for $x=2$ and stays constant for $2\leqslant x\leqslant 5$. For higher Ca content, the amount of quasi-free spins decreases. This result confirms a study on polycrystalline samples with $0\leqslant x\leqslant 6$ and $x\geqslant 12.6$, where a similar doping dependence but larger values of N_S were observed.[18] As already mentioned, our analysis suggests that the spins which give rise to the Curie-like contribution are not completely free for $x\neq 0$, but they are ferromagnetically coupled. As displayed in Fig. 5(b), the mean-field parameter which we extract from the data is of the order of $\lambda\simeq 100$ (emu/mol Cu)$^{-1}$ for $x\neq 0$.

The central result of our experimental study is summarized in Fig. 5(a). For $Sr_{14}Cu_{24}O_{41}$, our data confirm the presence of the spin gap. For $x\neq 0$, however, we find a finite susceptibility χ_0 at $T=2.5$ K, which is not due to free spins. This unusual magnetic response is practically isotropic and increases linearly upon Ca doping in the range $0\leqslant x\leqslant 9$. For the example of $x=12$, it is only weakly temperature dependent.

We mention that our data do not prove that χ_0 is gapless. Our measurements at $T=2.5$ K would not detect a very small gap. Moreover, despite the fact that Eq. (1) provides a reliable description of the data in Fig. 4, in addition to the strong

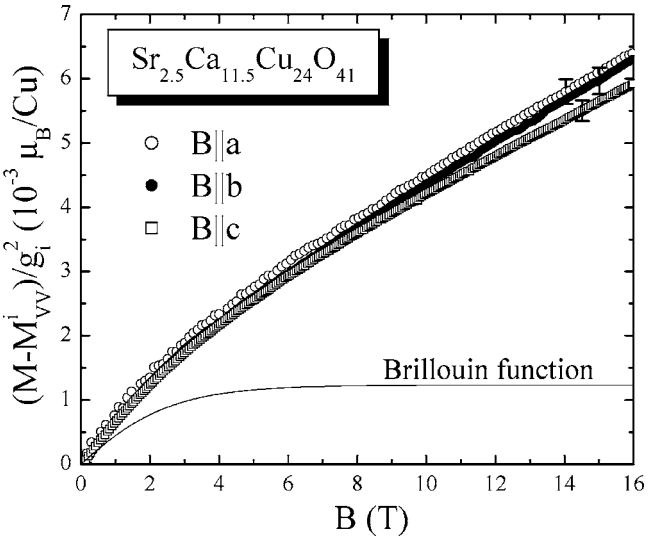

FIG. 6. Magnetization of $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ for B parallel to the a, b, and c axis, respectively. Data are corrected by the anisotropy of the g factor and the Van Vleck magnetism. Error bars show the uncertainty due to the correction.

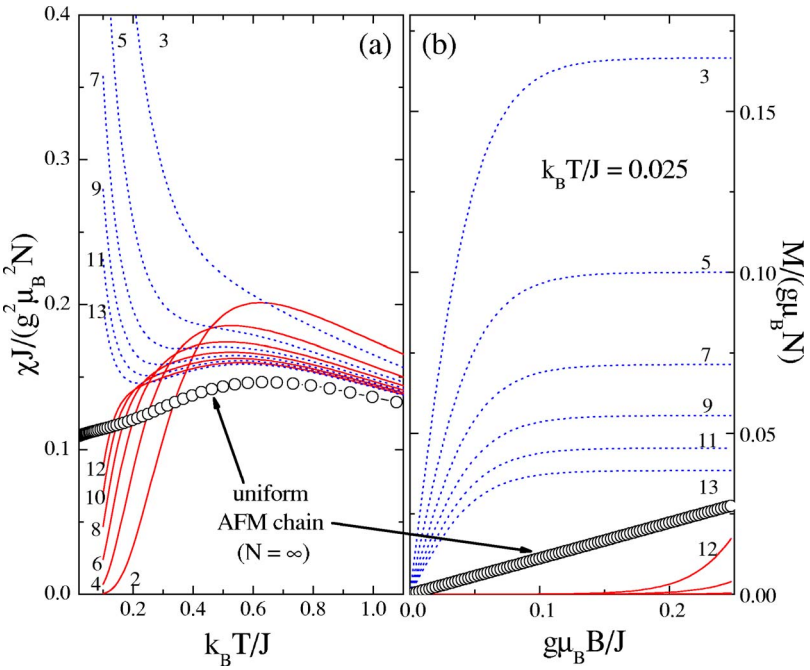

FIG. 7. (Color online) Susceptibility of finite $S=1/2$ spin chains with $2 \leqslant N \leqslant 13$ sites (a) versus temperature and (b) at $k_B T/J=0.025$ versus an external magnetic field (Ref. 25). For comparison, the data for a uniform AFM spin chain are plotted (Ref. 27).

field dependence of the Brillouin function there might be a weak field dependence of χ_0 at low magnetic fields, too. It is obvious, however, that at high fields the linear term in Eq. (1) describes the data correctly. Therefore, if a gap Δ_0 for χ_0 does exist, we estimate from our data that Δ_0 is of the order of only several Kelvin.

IV. DISCUSSION

The origin of the finite low-energy magnetic contribution χ_0 is not obvious. Since it is known that Ca doping reduces the number of holes in the chains, it is straightforward to assume that finite antiferromagnetic spin chains evolve upon Ca doping. The occurrence of finite spin chains, however, cannot explain our data. This is shown by exact diagonalization studies which calculate the magnetic response of antiferromagnetic $S=1/2$ spin chains with $2 \leqslant N \leqslant 13$ sites.[25] The temperature dependence of χ, which is displayed in Fig. 7, shows that for finite spin chains there is still a spin excitation gap. For chains with an even number of sites, the susceptibility $\partial M/\partial B$, at low temperature, becomes zero. For odd chains, there is a Curie-like upturn due to the uncompensated spin. Figure 7(a) once more illustrates that, in the presence of inevitable crystal defects which also yield to a Curie-like upturn even in the case of the uniform antiferromagnetic chain, it is not possible to detect finite susceptibility at low temperatures experimentally by $M(T)$ measurements in small magnetic fields. On the other hand, for even as well as for odd spin chains, at low temperatures, the susceptibility becomes essentially zero for larger magnetic fields $0 \ll g\mu_B B/J \ll 1$, as can be seen in Fig. 7(b). The data show that, at $g\mu_B B/J \simeq 0.15 \simeq 15$ T, the magnetic field is large enough to align the residual spins in the odd chains but too small to overcome the spin gap. Hence, finite spin chains do not account for our experimental observation of $\chi_0 \neq 0$ in Fig. 5(a), which evidences a finite slope in $M(B)$ at high magnetic fields. We mention that recent numerical results on the electronic structure of $Sr_{14-x}Ca_xCu_{24}O_{41}$ in Refs. 16 and 26 also do not explain the observed χ_0.

For a higher Ca content, $x \sim 12$, the scenario of an antiferromagnetic Heisenberg chain was suggested.[4] This scenario is based on the fact that for $x \sim 12$ one might expect a reduction of the hole content to $\sim 50\%$ in the chains, due to the charge transfer into the ladders. In this case, it was suggested that an antiferromagnetic chain of next nearest neighbor spins develops. The presence of a uniform antiferromagnetic spin chain straightforwardly explains the observation of $\chi_0 \neq 0$ since the spin excitations of the Heisenberg chain are gapless (cf. Fig. 7). Our data, however, cannot prove this scenario because we cannot describe both the temperature dependence and the field dependence of the magnetization in terms of a uniform Heisenberg chain by utilizing a common set of parameters for any compound under study. Moreover, the scenario of the Heisenberg chain should not account for $\chi_0 \neq 0$ at very small Ca contents. We recall that we observe an additional magnetic contribution χ_0 even for $Sr_{12}Ca_2Cu_{24}O_{41}$, where the number of holes is not supposed to be much smaller than in $Sr_{14}Cu_{24}O_{41}$. For $x=2$, a uniform Heisenberg chain is very unlikely and, in this case, another mechanism must account for a finite χ_0. We hence conclude that a simple 1D spin model based on either finite AFM spin chains or the uniform AFM Heisenberg chain does not explain the observed doping dependence of χ_0.

We now briefly discuss the fitting parameters N_S and λ in Eq. (1) [cf. Fig. 5(b)]. According to Ref. 16, for $x=0$, the Curie-like response is due to N_S single spins which are very weakly coupled to neighbored dimers. Introducing Ca ions leads to a smaller amount of holes in the chains. Thus, for a small Ca content, N_S (i.e., the number of single spins) increases. This trend, however, reverses for $x > 5$. Despite the fact that charge order and dimers are progressively destabilized,[4–6] the Curie-like response decreases for $x > 5$ (N_S decreases). As visible from numerical results in Fig. 7(b),

however, from our magnetization data we cannot distinguish whether the Curie-like response is due to single free spins ("monomers") or due to the same number of trimers, quintumers, etc. For example, one expects a similar magnetic response for monomers and for a three times larger number of spins which are coupled to trimers. The parameter N_S hence measures the sum of all finite chain fragments with a Curie-like response, i.e., of finite chains with an odd number of spins. The fact that N_S decreases for $x>5$ therefore implies that defects (i.e., defects of the dimerized state) are not only individual spins but tend to form antiferromagnetic chain fragments. This assumption is confirmed by a recent numerical study,[26] which suggests the absence of individual free spins for $Sr_{14-x}Ca_xCu_{24}O_{41}$ with $x=13.6$ but implies larger spin clusters. In particular, the low-temperature spin configuration shown in Ref. 26 comprises neither single free spins nor spin clusters with an odd number of spins for $x=13.6$. This does not contradict our data since we extrapolate $N_S \sim 0.1$, for this doping level, which might be attributed to inevitable crystal imperfections. We mention that the decrease of N_S, for larger x, strongly confirms that, for $x=0$, the Curie-like response is not due to crystal imperfections but due to defects of the dimer state since the former should increase continuously upon Ca doping. Interestingly, the defects are ferromagnetically correlated in the case of $x \neq 0$, i.e., the mean-field parameter in Eq. (1), $\lambda > 0$ [see Fig. 5(b)]. The observation $\lambda \neq 0$ means that the defects of the dimer state, which at least for $x>5$, contain finite chain fragments with an odd number of spins (e.g., trimers), magnetically interact with each other. Quantitatively, applying

$$\lambda = \frac{2\tilde{J}}{N_A g^2 \mu_B^2} \tag{2}$$

yields a magnetic coupling of the order of $k_B\tilde{J} \sim 80$ K. Since the next nearest neighbor coupling via one hole is antiferromagnetic and the coupling via two holes is only weakly ferromagnetic,[15] the data thus suggest that the nearest neighbor coupling accounts for the observed ferromagnetic correlations. We therefore suggest that, for $x \neq 0$, finite chains with an odd number of spins reside on nearest neighbor chain fragments.

While the fitting parameters N_S and λ in Eq. (1) can be explained straightforwardly, we are not aware of any 1D spin model which can explain the unusual doping dependence of χ_0. It might be necessary to apply more advanced spin models, which, e.g., include the interchain coupling. We recall, however, that the additional contribution to the magnetization is isotropic. One might also speculate whether charge degrees of freedom are involved. This assumption is based on the observed doping dependence of χ_0. Figure 5(a) suggests a linear dependence of χ_0 on the Ca content up to $x \approx 8$. For larger x, χ_0 saturates. We recall that the dimerized ground state in $Sr_{14}Cu_{24}O_{41}$ is associated with a particular charge order. Ca doping leads to a charge transfer into the ladder subsystem, thereby destabilizing the charge order. It has been shown, by ESR,[4] transport,[6] and thermal expansion data,[5] that the charge ordering becomes progressively suppressed with increasing x and, for $x>8$, the CO seems to disappear. Apparently, the increase of χ_0 is associated with the destabilization of the dimer/charge ordered state upon Ca doping. This implies that the finite susceptibility χ_0 at 2.5 K cannot coexist with the charge ordering and charge mobility might be crucial for the observed phenomenon. On the other hand, our observation of $\chi_0 \neq 0$, at $T=2.5$ K, hence suggests a significant perturbation of the charge ordering, even at lowest temperatures.

V. CONCLUSION

The analysis of the temperature dependence of the magnetization of $Sr_{14-x}Ca_xCu_{24}O_{41}$ in $B=1$ T alone does not provide a correct understanding of the low-temperature magnetization, whereas the high magnetic field dependence of M at low temperatures is crucial. Our study of the high-field magnetization confirms the spin gap in the CuO_2 spin chains of $Sr_{14}Cu_{24}O_{41}$. The low-temperature magnetic response of the CuO_2 spin chains, however, strongly changes when the number of holes in the chains is reduced through Ca doping. We find an additional isotropic contribution to the magnetization, which linearly depends on magnetic fields between ~ 3 T and 16 T. Our data give evidence that, in $Sr_{14-x}Ca_xCu_{24}O_{41}$, with $x \neq 0$, at low temperature there is a finite susceptibility which is due neither to free spins nor to dimers. If there is a gap for this response, it is much smaller than the dimer gap Δ_d. Remarkably, the slope of the linear contribution increases with the Ca content, i.e., with the reduction of the number of holes in the chains. We argue that antiferromagnetic spin chains do not account for this behavior and possible field-induced dynamics of the holes might be relevant.

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[28] $\chi_{VV} \approx 1.2 \times 10^{-5}$ emu/mol Cu for $B \| c$.
[29] To subtract the susceptibility of the Curie-like spins, we applied Eq. (1) and considered $N_S \simeq 5 \times 10^{-3}$ spins/Cu to be temperature independent. In order to minimize the number of fitting parameters, we set $\lambda = 0$ since this does not affect the resulting value M_{lin}/B significantly.