Revisiting the chain magnetism in Sr$_{14}$Cu$_{24}$O$_{41}$: Experimental and numerical results

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We study the magnetism of the hole doped CuO$_2$ spin chains in Sr$_{14}$Cu$_{24}$O$_{41}$ by measuring the Electron Spin Resonance (ESR) and the static magnetization $M$ in applied magnetic fields up to 14 T. In this compound, the dimerized ground state and the charge order in the chains are well established. Our experimental data suggest that at low temperatures the Curie-like increase of $M$ as well as the occurrence of the related ESR signal are due to a small amount of paramagnetic centers which are not extrinsic defects but rather unpaired Cu spins in the chain. These observations qualitatively confirm recent ab initio calculations of the ground state properties of the CuO$_2$ chains in Sr$_{14}$Cu$_{24}$O$_{41}$. Our complementary quantum statistical simulations yield that the temperature and field dependence of the magnetization can be well described by an effective Heisenberg model in which the ground state configuration is composed of spin dimers, trimers, and monomers.

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I. INTRODUCTION

Hole doped antiferromagnets with an inhomogeneous ground state have attracted much attention in recent years. A prominent example is provided by high temperature (high-$T_c$) superconductors in which low dimensionality, $s = 1/2$ quantum magnetism, and charge degrees of freedom are intimately related. In particular, a nonuniform distribution of charges in the Cu-O planes of the high-$T_c$ layered cuprates seems to play an important role in establishing the superconductivity. The quasi one-dimensional (1D) edge-sharing CuO$_2$ chain compounds such as (Sr,Ca,La)$_{14}$Cu$_{24}$O$_{41}$, Na$_{1+x}$CuO$_2$, or Ca$_{2+y}$Y$_{2-x}$Cu$_5$O$_{10}$ constitute another class of cuprates with charge inhomogeneities. The interplay of spin and charge degrees of freedom in one dimension, as is evidenced by both theoretical and experimental results, is even more pronounced as compared to the layered 2D situation, yielding unusual ground states and novel excitations both in the spin and charge sectors.

In this work we focus on the low-temperature magnetic properties of the so-called “telephone number” compound Sr$_{14}$Cu$_{24}$O$_{41}$, where a composite structure with CuO$_2$ spin ladders and CuO$_2$ spin chains is realized. Magnetically, the ladders do not contribute significantly at low temperature due to a large spin gap of $\Delta \sim 380$ K. A remarkable property of this compound is self-doping, i.e. the material is intrinsically hole doped with 25% of holes per Cu site. As most of the holes are localized in the chains their concentration in this subunit is very high, close to 60% per Cu in the chain formula unit (c.f.u.). This influences strongly the magnetism of the spin chain resulting in an inhomogeneous ground state. Two Cu spins which are separated by a hole site couple antiferromagnetically (AF). If they are surrounded by two localized holes at both sides they form almost independent dimers. Such a dimerized nonmagnetic state in the chain subsystem of Sr$_{14}$Cu$_{24}$O$_{41}$ is experimentally well established. The occurrence of charge order, which is an important ingredient of the dimer scenario in Sr$_{14}$Cu$_{24}$O$_{41}$, is supported e.g. by NMR and ESR data. In a very recent numerical study Gelle and Lepetit (GL) highlight that structural modulations due to the pseudoperiodicity of the chains and the ladders might be crucial for the electron localization and for the occurrence of the dimer state. Remarkably, these calculations suggest that the ground state is not perfectly dimerized even in the limiting case where all holes are located in the chains. Ideally, in that case, where six out of the ten sites in the chain unit cell are holes, the remaining four spins could be coupled to two AF dimers with no free spins left. In contrast to that, GL arrive at the surprising result that it is energetically favorable if a few spins are left unpaired. Then the stable configuration corresponds to 1.7 dimers and 0.5 free spins per c.f.u., respectively. Therefore, the occurrence of a Curie contribution to the magnetic susceptibility of Sr$_{14}$Cu$_{24}$O$_{41}$ at low temperatures, which has originally been attributed to the free spins, might be an intrinsic property of the hole doped Heisenberg Cu-O spin chain due to the distortion by structural modulations.

The aim of our paper is thus twofold. First, we...
show experimental magnetization and electron spin resonance (ESR) data which give strong indications that a small amount of free spins, that gives rise to a finite magnetization and to an ESR signal at low temperatures, is not extrinsic but mainly reside in the chain subunit of Sr$_{14}$Cu$_{24}$O$_{41}$. This finding qualitatively supports the model calculations by GL in Ref. 17. Secondly, we present our own quantum statistical simulations which rely on the numerical diagonalization of an effective Heisenberg Hamiltonian. This Hamiltonian, which depends parametrically on hole positions and on the screened Coulomb interaction between them, also yields an inhomogeneous ground state configuration of spins and holes. It turns out that the ground state is dominantly built of the aforementioned dimers, but also contains weakly coupled monomers and/or trimers which not only leads to the Curie-like behavior of the magnetization at low temperatures, but also yields a nearly perfect quantitative description of the low-temperature magnetic response of the Cu spin chain. The very good agreement also suggests that other arrangements of spins and holes are well gaped from the ground state configuration.

II. EXPERIMENTAL RESULTS

In this section we present ESR and magnetization measurements on a high quality single crystal of Sr$_{14}$Cu$_{24}$O$_{41}$. For ESR experiments an X-Band Bruker ESR spectrometer has been used, which operates at a frequency of 9.5 GHz. The magnetization data have been collected with a homemade vibrating sample magnetometer (VSM) in external magnetic fields up to 14 T and with a SQUID magnetometer in a field of 1 T. The single crystal grown by the floating zone technique has been previously thoroughly characterized by measuring the magnetization, the thermal expansion, and the inelastic neutron scattering cross section, and the ESR response.

In order to recall the magnetic properties of Sr$_{14}$Cu$_{24}$O$_{41}$ we show in Fig. 1(a) the temperature dependence of the magnetization $M(T)$ of our single crystal in a magnetic field of $B = 1$ T applied parallel to the crystallographic c-axis (chain direction). The $M(T)$ dependence can be very well fitted with Eq. (1) comprising two terms, the magnetization $M_{\text{dimer}}$ of AF coupled dimers in a concentration $N_D$ with an exchange constant $J/k_B = -134$ K, and the Curie magnetization $M_{\text{Curie}}$ to a small concentration $N_S$ of free spins (see, e.g. Ref. 16).

$$M(T) = M_{\text{dimer}} + M_{\text{Curie}} = N_a g^2 \mu_B^2 B \left[ \frac{T}{T + 3 + \exp(-J/k_BT)} \right] + \frac{2N_D}{4T} \left[ \lambda M + \frac{2N_D}{T} \lambda M \right].$$

The very good agreement of the experimental $M(T)$ curve with Eq. (1) give evidence of the dimerized ground state which in addition has been proven for our sample by inelastic neutron scattering and thermal expansion measurements. In Fig. 1(b) we present the magnetization versus applied magnetic field, $M(B)$, at temperatures of 20 K, 15 K, 10 K, 4.2 K, and 2.5 K, respectively. At all temperatures the dependence of $M$ on $B$ can be nicely fitted as a sum of the temperature independent contribution $\chi_0 B$ owing to diamagnetism and Van-Vleck paramagnetism of the Cu ions and a Brillouin function $B_s=\frac{1}{2}$ describing the magnetization of free $s=1/2$ spins with a concentration $N_S$.

$$M(B) = \chi_0 \cdot B + \frac{1}{2} N_s g_e \mu_B \cdot B_s \left( \frac{g\mu_B(B + \lambda M)}{2k_BT} \right).$$

With a $g$ factor of $g_c = 2.04$ (see below) one obtains $\chi_0 \approx 1 \cdot 10^{-5}$ emu/Mol Cu, the mean field parameter $\lambda = 0$ and $N_S \approx 0.01$/Cu. We note that the magnetization at $T = 2.5$ K saturates in a field of $B = 14$ T at a very small value of about $1 \cdot 10^{-2}$ $\mu_B$/Cu justifying that the magnetic response at low temperature is caused by about 1% of free $s = 1/2$ spins while there is no response from the remaining 99% of the spins. Moreover, we emphasize that the determination of $N_S$ from our high field magnetization data is much more straightforward and accurate as compared to the conventional analysis of the low temperature contribution to $M(T)$ using the $M_{\text{Curie}}$
term in Eq. (1). Therefore, precise knowledge of $N_S$ from
the analysis of $M(B)$ curves allows for an accurate
determination of the number of dimers $N_D$. Substituting
$N_S = 0.01$/$Cu$ in the $M_{Curie}$ term in Eq. (1) one ob-
tains from the fit to the experimental $M(T)$ dependence
$N_D = 0.0738$/$Cu$. Thus the number of magnetic Cu sites
amounts to $N_S + 2N_D \approx 3.78$ /Cu. In our $Sr_{14}Cu_{24}O_{41}$
single crystal which differs from a previous less precise
estimate that employed the analysis of $M(T)$ curves of
polycrystalline samples).

We note that the concentrations of dimers and free
spins, $N_D$ and $N_S$, respectively, are significant observ-
ables in the recent \textit{ab initio} calculations of the low energy
electronic properties of the Cu-O chain in $Sr_{14}Cu_{24}O_{41}$
by GL.\textsuperscript{17} Therefore, the accurate determination of $N_D$
and $N_S$ from our magnetization data provides an im-
portant check for the relevance of the GL model with respect
to the low energy physics of $Sr_{14}Cu_{24}O_{41}$. Comparison of
our data with the numerical results shows that the num-
ber of dimers $N_D$ found in our analysis roughly agrees
with the calculations of GL for the case that all holes are
localized in the chains, $N_D^{GL} = 0.0708$ /Cu. The number
of free spins $N_S$, however, is smaller than theoretically predicted $N_S^{GL} = 0.021$ /Cu by a factor of two. This is
surprising because the experimental value $N_S$ comprises
not only the response owing to the imperfect dimeriza-
tion of the spin chain, but also should include the re-
sponse of paramagnetic defects which may occur in real
crystals. Thus, theoretical calculations should yield a
smaller number of free spins than experimental data. Be-
sides the quantitative discrepancy this comparison sug-
gests that, at least in the framework of the GL model,
the free spins in a concentration $N_S \approx 0.01$ /Cu found
in our $Sr_{14}Cu_{24}O_{41}$ single crystal are not \textit{extrinsic} para-
magnetic defects but mainly reside in the spin chain.\textsuperscript{24}
This suggestion is corroborated with the analysis of the
anisotropy of the ESR signal and of the magnetization.

Detailed studies of the ESR response from the spin
chains in the family of the “telephone number” com-
 pounds have been published in Refs. \textsuperscript{16,17} Here we present the ESR data of the $Sr_{14}Cu_{24}O_{41}$ single crystal
in the low temperature regime. Below 20 K the ESR sig-
nal is mainly due to the free spins, which also contribute
to the Curie-like increase of the magnetization, compare
Fig. 1(a). At higher temperatures the ESR response is
dominated by the dimer spins which are thermally acti-
vated. The evolution of the $g$ factor of the ESR signal in
the crossover regime around 20 K is shown in Fig. 2. The
g factor of the Cu spins in a dimer is anisotropic with the
values $g_c = 2.045$ for the magnetic field $\vec{B}$ parallel to the
chain direction (c-axis) and $g_b = 2.284$ for the magnetic
field $\vec{B}$ perpendicular to the plane of the chains (b-axis),
respectively. These $g$ factors are temperature independ-
ent. The anisotropy of the $g$ tensor is determined by
the crystal field splitting of the Cu orbital state of $e_g$

![FIG. 2: Temperature dependence of the $g$-factor along c- and b-axis, respectively, as obtained from ESR data. Dashed lines extrapolate $g$ of the dimers. Below $\sim 20$ K, the response is due to small deviations from the perfectly dimerized state.](image)

and $t_{2g}$ symmetry

$$g_c = 2 - \frac{8 \cdot \lambda}{\Delta_{yz,zz}}, g_b = 2 - \frac{2 \cdot \lambda}{\Delta_{xy}} \ .$$

(3)

Here $\lambda = -0.1$ eV is the spin-orbit coupling constant
and $\Delta_{yz,zz}$ and $\Delta_{xy}$ are the energy differences between
relevant orbital states.\textsuperscript{26} The anisotropy of the $g$ tensor
above $\sim 20$ K is temperature independent and is typical
for a Cu ion in an approximately square planar coordi-
ation of the oxygen ligands,\textsuperscript{16,26} i.e. the coordination
occurring in the chain of $Sr_{14}Cu_{24}O_{41}$. Remarkably, be-
low 20 K the $g$ factor for both orientations changes only
slightly giving strong indication that the ESR response at
low $T$s comes from a paramagnetic Cu ion having a very
similar environment to that of the chain Cu ions. A small
change in the anisotropy of the $g$ factors can be explained
by a slightly different charge distribution around a free
Cu spin which has in the chain two neighboring holes,
both to the left and to the right hand side, whereas a Cu
spin in a dimer has only one neighboring hole on the one
side and two holes on the other side, compare also Fig. 3.

The fact that the free spins exhibit the similar
anisotropy as the dimerized ones is confirmed by our
magnetization data. Our analysis of $M(T)$ shows that
the ratio of the Curie constants which describe the re-
sponse of the free spins along b- and c-axis amounts to
$C_b/C_c = g_b^2/g_c^2 \approx 1.25$. This ratio agrees well with our
ESR data. This fact is illustrated by Fig. 3 in which
$M/g^2$ is shown for $B$ parallel to the b-axis and the c-axis,
respectively. After being corrected for the anisotropy of
the $g$ factor the magnetization data for two orientations
coincide almost perfectly in the whole temperature range.
Note that in our analysis we have also considered the
anisotropy of the Van-Vleck magnetism which is related to
the anisotropy of the $g$ factors as\textsuperscript{26}.
Curie-like response in Sr strongly suggest that the free spins which cause the chains of Sr while GL assume slightly more than 60% of holes in the result of structural modulations. As noted above, the occurrence of such free spins in the hole doped chain confirms the results of GL in Ref. 17, which predict the paramagnetic defects but reside in a not perfectly dimerized state and the smaller experimental value of calculated number of paramagnetic defects in the dimerization. Thus our experimental study qualitatively evidenced for trimers in spin chains with less than 60% hole concentration. This ansatz is similar to a simple Born-Oppenheimer description where the electronic Hamiltonian (here spin Hamiltonian) depends parametrically on the positions of the classical nuclei (here hole positions). Each configuration \( \hat{c} \) of holes and spins defines a Hilbert space which is orthogonal to all Hilbert spaces arising from different configurations. The Hamilton operator \( \hat{H}(\hat{c}) \) of a certain configuration \( \hat{c} \) is of Heisenberg type, i.e.

\[
\hat{H}(\hat{c}) = \sum_{\hat{c}} \left( \hat{H}(\hat{c}) + V(\hat{c}) \right)
\]

\[
\hat{H}(\hat{c}) = -\sum_{u<v} J_{uv}(\hat{c}) \hat{s}_u(\hat{c}) \cdot \hat{s}_v(\hat{c})
\]

\[
V(\hat{c}) = \frac{e^2}{4\pi\varepsilon_0 \varepsilon_r \varepsilon_0} \frac{1}{2} \sum_{u \neq v} \frac{1}{|u - v|}.
\]

\( J_{uv}(\hat{c}) \) are the respective exchange parameters which depend on the configuration of holes: \( J < 0 \) describes antiferromagnetic coupling, \( J > 0 \) ferromagnetic coupling. For the theoretical results presented in this article three exchange parameters are used, see Fig. 4. The strongest and antiferromagnetic exchange \( J = -134 \) K is across one hole. The exchange across two holes \( J_{2h} = 15 \) K is ferromagnetic as is the exchange \( J_{NN} = 100 \) K of neighboring spins. Periodic boundary conditions are applied for the following calculations, i.e. large rings are considered instead of chains with open boundaries.

It is obvious that different configurations of spins and holes should also be energetically different. Besides their different magnetic ground state energies resulting from they also differ by their Coulomb interaction between the holes and possibly by the Coulomb interaction with the local environment. In the following we take the electrostatic hole-hole repulsion by means of a screened Coulomb potential into account. \( \varepsilon_0 = 2.75 \) Å is the distance between nearest neighbor sites on the ring. The accurate value of the dielectric constant \( \varepsilon_r \) is un-
known. Several attempts have been undertaken to estimate the dielectric constant which yielded values for $\varepsilon_r$ up to 30.27,29,30 If the interaction with the local – modulated17,31,32,33 – environment is neglected, it is necessary to assume a rather small dielectric constant $\varepsilon_r \lesssim 3$ in order to simulate the magnetization data. Under such conditions only the energetically lowest-lying spin-hole configuration $\vec{c}$ contributes to the magnetization for $T \lesssim 200$ K.

The assumption of a perfectly dimerized chain was studied in Ref. 19. In the following imperfect chains will be investigated. To this end Hamiltonian (2) is numerically completely diagonalized for the currently largest possible odd number of spins $N_s = 17$. The number of holes is chosen as $N_h = 25$ or $N_h = 26$ in order to yield about 60 % holes on the chain. Periodic boundary conditions are applied. It turns out that the ground state configurations are sequences of the building blocks shown in Fig. 5. In the case of $N_s = 17$ spins and $N_h = 26$ holes the resulting ground state sequence is $\vec{c}_{17,26} = sddd\ldots d$, i.e. it contains only dimers except for one single spin block. This ground state configuration is very similar to the one found using density functional theory calculations. In the case of $N_s = 17$ spins and $N_h = 25$ holes the chain consists of dimers and one block of three spins, i.e. it has the sequence $\vec{c}_{17,25} = tddd\ldots d$. In both cases other configurations of spins and holes are energetically well separated.

Having determined all energy eigenvalues and magnetic quantum numbers, the magnetization can be evaluated for the two ground state configurations. Figure 6 shows the resulting magnetization curves as a function of temperature for an applied field of $B = 1$ T. The solid curve displays the magnetization curve for $N_s = 17$ and $N_h = 26$, i.e. configuration $\vec{c}_{17,26} = sddd\ldots d$, whereas the dashed curve shows the result for $N_s = 17$ and $N_h = 25$, i.e. $\vec{c}_{17,25} = tddd\ldots d$. Both curves are rather close to the experimental data given by crosses.

The magnetization has also been determined as a function of applied field for two temperatures $T = 2.5$ K and $T = 4.2$ K. Figure 7 shows that both configurations, i.e. $\vec{c}_{17,26} = sddd\ldots d$ and $\vec{c}_{17,25} = tddd\ldots d$ reproduce the data with high accuracy.

**IV. CONCLUSION**

In this paper we present experimental as well as numerical evidence that the Curie-like contribution to the low-
temperature magnetization of Sr$_{14}$Cu$_{24}$O$_{41}$ is a genuine property of the CuO$_2$ chain subsystem. The hole-doped chains are not regular sequences of weekly interacting spin dimers, but instead they host a small percentage of almost free spins and/or spin trimers. This finding is in accord with recent density functional calculations. Nevertheless, our own simulational studies favor the occurrence of trimers instead of single spins which would be consistent with an intrinsic hole doping of the chains of less than 60% as was inferred from recent NEXAFS experiments.

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