Spin dynamics in hole doped $S=\frac{1}{2}$ chains and ladders from NMR and susceptibility measurements in $Sr_{14-x}Na_xCu_{24}O_{41}$

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The authors report on NMR-NQR, dc susceptibility and resistivity measurements in $Sr_{14-x}Na_xCu_{24}O_{41}$ for $0\leqslant x\leqslant 2$. The analysis of the dc susceptibility points out that only a small fraction of Cu^{2+} spins are involved in the dimerization of $Cu(1)O_2$ chains while the remaining spins possibly form Zhang-Rice singlets with the localized holes. The role of structural distortions, evidenced either in NQR spectra or by anomalies in the resistivity measurements, in assisting the dimerization is discussed. The introduction of extra holes by Na^+ doping is observed to slightly decrease the $Cu(1)^{2+}$ uniform static susceptibility at low temperatures, to reduce the amplitude of the gap between singlet and triplet states in the $Cu(2)_2O_3$ two-leg-ladders and to increase the conductivity. The amplitude of the gap in the dimerized chain, derived either from dc susceptibility or $^{23}Na1/T_1$ was found to be the same, while a discrepancy is found in the estimate of the amplitude of the gap in the ladders by the same two techniques. [S0163-1829(98)05018-8]

I. INTRODUCTION

The discovery of high-temperature superconductivity has brought a renewed interest in the study of low-dimensional cuprates[1] and the search for superconductivity in the quasi-one-dimensional (quasi-1D) ones $[(Sr,Ca)_{14}Cu_{24}O_{41}]$ has recently proven to be successful.[2] This fact appears of major interest and could lead to a reexamination of the properties of high-T_c superconductors (HTSC's) in the frame of a quasi-1D scenario, particularly if a phase separation takes place.[3,4] Namely, HTSC's could be considered not as randomly disordered 2D compounds but as compounds where the strong correlation causes the segregation of the itinerant holes along stripes or rivers[5,6] which separate hole-depleted antiferromagnetic (AF) spin-ladder structures. In particular, the gap in the spin excitations observed in the normal state of underdoped HTSC's should not be associated to the one expected for randomly frustrated 2D quantum AF (Ref. 7) but to that existent when an even number of chains are paired to form an $S=1/2$ spin ladder.[8] All these conjectures, however, are speculative ones at the moment and further extensive investigation of either pure or hole doped quasi-1D cuprates and a comparison with normal state properties of HTSC's is required.

$Sr_{14}Cu_{24}O_{41}$ is the parent of this new family of quasi-1D superconductors and its structure comprises $Cu(1)O_2$ chains and $Cu(2)_2O_3$ two-leg ladders.[9] $Cu(1)^{2+}$ spins dimerize around 80–100 K and the origin of this dimerization is still under debate.[10] On the other hand, the comprehension of the properties of spin excitations in the two-leg ladders could be considered almost complete if it was not for the discrepancy by almost a factor 2 in the value of the gap derived from dc susceptibility and NMR measurements.[11] The chains are intrinsically doped by six holes due to the three excess O^{2-} ions present in the stoichiometry. By doping this system with Ca^{2+} an increase in the chemical pressure was obtained, a more efficient transfer of holes to the ladders was observed and a superconducting state was realized.[2]

In this paper we report on the modifications of the spin dynamics in the chains and in the two-leg ladders of $Sr_{14}Cu_{24}O_{41}$ after the introduction of extra holes by Sr^{2+} for Na^+ susbstitution. By varying the Na^+ content we expect to vary the concentration of holes in the ladders, due both to an increase in the chemical pressure and to the heterovalent nature of the substitution. ^{23}Na nuclei are also excellent NMR probes and allow one to achieve further information on the $Cu(1)O_2$ chains spin dynamics. In the following, through a quantitative analysis of susceptibility data we will show that only a small fraction of $Cu(1)^{2+}$ spins dimerize around 80–100 K, the remaining spins possibly forming Zhang-Rice singlets[12] with the localized extra holes even at room temperature. ^{23}Na nuclear spin-lattice relaxation rate $1/T_1$ at low temperatures is determined by the spin dynamics in the $Cu(1)O_2$ dimerized chains. At temperatures above $\simeq$100 K ^{23}Na $1/T_1$ shows an anomalous behavior which cannot be explained in the frame of the simple $S=1/2$ chain dimerization scenario. The possible effects of structural distorsions on ^{23}Na relaxation is then discussed, particularly in the light of the anomalies observed in the temperature dependence of the resistivity and of the $^{63}Cu(2)$ nuclear quadrupolar frequency. The high temperature behavior of $^{63}Cu(2)$ NMR $1/T_1$ is driven by the two-leg ladder spin dynamics and one observes that the amplitude of the gap between singlet and triplet states decreases with Na^+ doping, pointing out that

extra holes are introduced in the $Cu(2)_2O_3$ ladders. The same behavior was deduced from the analysis of dc susceptibility measurements. However, at variance with the situation observed in the dimerized chain, the amplitude of the gap derived from this technique is smaller than the one derived from $1/T_1$.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

$Sr_{14-x}Na_xCu_{24}O_{41}$ ($x=0,0.7,2$) was prepared by solid state synthesis starting from high purity CuO, $Na_2C_2O_4$, and $SrCO_3$. The starting materials were weighted in the required stoichiometric ratio, suspended in acetone and mixed overnight. The acetone was evaporated and the resulting powder was pressed isostatically at 2000 bars to yield a compact pellet. The pellet was then heated in a platinum crucible at 800 °C in a pure oxygen flux for 76 h with two intermediate grinding and pressing steps. The completion of the chemical reaction and the homogeneity of the as prepared material was checked by x-ray powder diffraction and microscopic [optical scanning electron microscope and electron microprobe analysis (EMPA)] inspection. According to the EMPA microanalysis, during the synthesis no loss of Na occurs when the reaction is carried out at 800 °C. A sizeable evaporation of NaO takes place only if the temperature is raised over 850 °C. We point out that using this procedure we did not succeed in increasing the Na^+ content above $x=2$. The stoichiometry of the oxygen content of the as prepared materials was measured by following the weight loss occurring in the reaction at 500 °C with a flowing mixture of hydrogen in argon (7% H_2) with a TA Thermal Analyst 2000 apparatus equipped with a thermogravimetric analyzer attachment. A platinum pan was employed as a sample holder. The x-ray diffraction patterns were found in agreement with the indexing scheme reported in Ref. 13. Resistivity measurements were performed by a standard four probes technique.

Standard dc susceptibility measurements were performed with a SQUID magnetometer, directly providing the magnetization M of the sample in an applied field H. Hereafter we will call susceptibility the quantity $\chi=M/H$, which does not necessarily correspond to $(dM/dH)_H$.[14] In particular, we find that on increasing the field intensity M slightly saturates (see the inset to Fig. 5 later on).

NMR and NQR measurements have been performed by using standard rf pulse sequences. $^{63}Cu(2)$ NMR-NQR spectra were obtained by recording the echo intensity on sweeping the irradiation frequency. ^{23}Na NMR spectrum of the central line was derived directly from the Fourier transform of half of the echo signal, obtained for a long delay $\tau\simeq100$ μs between the pulses in order to avoid contamination from $^{63}Cu(1)$ NMR signal. This procedure was used also during ^{23}Na T_1 measurements. The $^{63}Cu(2)$ NQR frequency strongly depends on temperature[14] and the corresponding spectrum [see Fig. 1(a)] lightly broadens with increasing Na doping x. The NMR measurements were performed in powders aligned with the b axis parallel to the magnetic field. For this orientation $^{63}Cu(2)$ NMR spectrum is characterized by a well defined central line, corresponding to $^{63}Cu(2)$ nuclei, shifted by $\simeq1.3\%$ from a less intense spectrum corresponding to $^{63}Cu(1)$ NMR line.[14] ^{23}Na central line is also well defined and its width is around 10 kHz, instead of the ~40 kHz observed for the unoriented powders. This linewidth is close to the one expected on the basis of an estimate of the quadrupolar coupling frequency ν_Q from point charge calculations. In particular, if Na^+ replaced Sr^{2+} ions, one would obtain $\nu_Q\simeq2.8$ MHz, with an asymmetry parameter $\eta\simeq0.6$, and a corresponding powder spectrum for the central ^{23}Na NMR line with a linewidth around 30 kHz. ^{23}Na NMR linewidth in the oriented powders is observed to increase on decreasing temperature in a Curie-like form, evidencing the presence of randomly distributed unpaired spins [Fig. 1(b)].

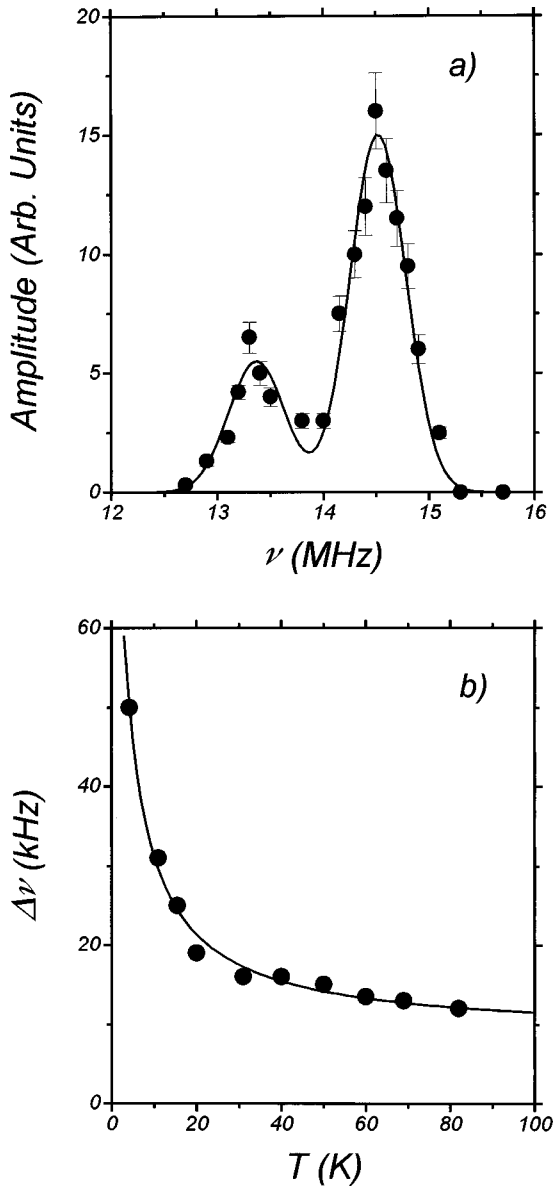

FIG. 1. (a) $^{63,65}Cu(2)$ NQR spectrum for the $x=2$ sample at $T=77$K. (b) Temperature dependence of the full width at half intensity of the central ^{23}Na NMR line for the $x=2$ sample in a field $H_o=5.9$ T along the b axis.

The recovery of $^{63}Cu(2)$ nuclear magnetization after inversion of the population between the $\pm1/2$ levels obeys the characteristic double exponential law $y(t)=0.1\exp(-2Wt)+0.9\exp(-12Wt)$, with $2W\equiv1/T_1$ [Fig. 2(a)]. For ^{23}Na a double exponential recovery law is also observed

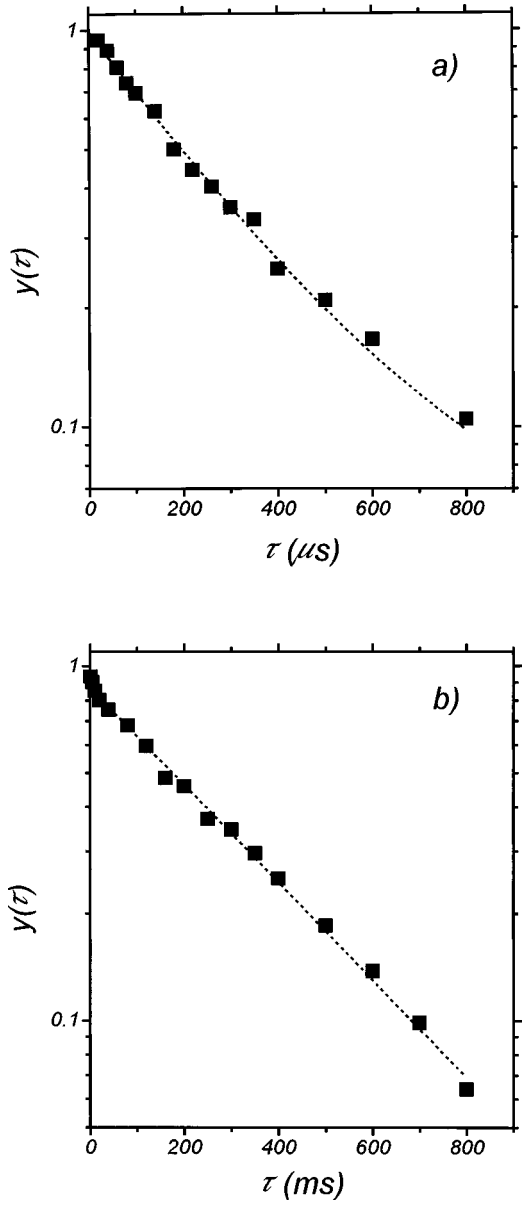

FIG. 2. (a) Recovery of ^{63}Cu(2) nuclear magnetization after inversion of the population between the $\pm 1/2$ levels in NMR. (b) Recovery of ^{23}Na nuclear magnetization after inversion of the population between the $\pm 1/2$ levels in NMR.

but with the coefficients of the exponentials which differ from the ones reported above, possibly due to the partial irradiation of the satellite lines. Then, the long decay component $[\exp(-2Wt)]$ allows for an accurate estimate of $1/T_1$ [see Fig. 2(b)]. The weight of the two exponentials changes as a function of temperature possibly due to modifications in the electric field gradient at the ^{23}Na site, as observed also for ^{63}Cu(2).[14] On the other hand, in NQR ^{63}Cu(2) recovery law is characterized by a single exponential $y(t)=\exp[-k(\eta)Wt]$, where $k(\eta)$ is a factor which depends on the asymmetry parameter η and in the case of ^{63}Cu(2) one has $k(\eta\simeq 0.6)\simeq 5.6$ (Ref. 14) (see Fig. 3). Below $\simeq$90 K some slight deviation from the above recovery laws can be observed.

The decay of ^{63}Cu(2) echo intensity, on increasing the delay τ between the rf pulses, is the one expected in the case

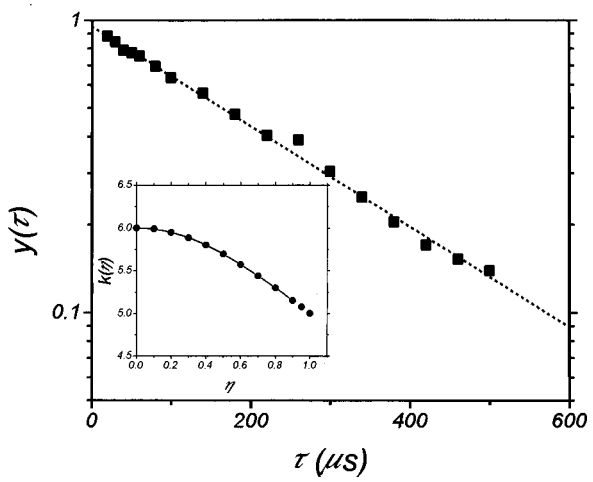

FIG. 3. Recovery of ^{63}Cu(2) nuclear magnetization after saturation of the population on the $\pm 1/2$ and $\pm 3/2$ levels in NQR. In the inset the dependence of the coefficient $k(\eta)$ in the exponential recovery is reported as a function of the asymmetry parameter η.

of a relevant contribution from indirect nuclear dipole interaction and one has that[15]

$$E(2\tau)=E(0)\exp[-(2\tau/2T_{2G}^2)]\exp(-2\tau/T_{2R}), \quad (1)$$

where $1/T_{2R}=(1/T_1)_\perp+(a/T_1)_\parallel$, with $a=3$ for NMR when the central line is irradiated and $a=2$ in NQR. $\perp$ and $\parallel$ indicate the direction of the magnetic field with respect to the b axis. Since for ^{63}Cu(2) the decay of the echo is strongly dominated by the Gaussian term the uncertainty in deriving $1/T_1$ anisotropy $[(T_1)_\parallel/(T_1)_\perp\simeq 3.9]$,[14] influenced by small misalignments, is not relevant for the estimate of T_{2G}.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Resistivity and dc susceptibility

The temperature dependence of the resistivity (ρ) is reported in Fig. 4. For all samples the trend of ρ vs temperature is similar and evidences two different regimes, below and above a crossover temperature $T_\rho\simeq 130$ K. At this temperature one observes a characteristic kink (see the inset to Fig. 4) which is peculiar of structural distortions.[16] Above T_ρ an activated behavior is observed with an energy barrier E_a^h decreasing with increasing x (see Sec. IV). At T_ρ a sharp increase of the energy barrier to a value E_a^l is observed, as shown by the plot of the derivative of the $\ln(\rho)$ (see the inset to Fig. 4). The occurrence of structural distortions could play an important role in the dimerization of $Cu(1)O_2$ chains since it can modify the Cu(1)-O-Cu(1) bonding angle and the corresponding superexchange coupling.[14] In fact, if the Cu(1)-O-Cu(1) bonding angle remained around 90°, as at room temperature,[9] it would be difficult to justify a superexchange coupling along the $Cu(1)O_2$ chains giving rise to a dimerization gap $\Delta_D\simeq 140$ K (see in the next paragraph).

The temperature dependence of the dc susceptibility is due to a dominant contribution from $Cu(1)^{2+}$ spins and its trend is the one expected in the case of spin dimerization with a broad maximum around 100 K, as first pointed out by Matsuda and Katsumata.[10] $Cu(2)^{2+}$ spins in the ladder are

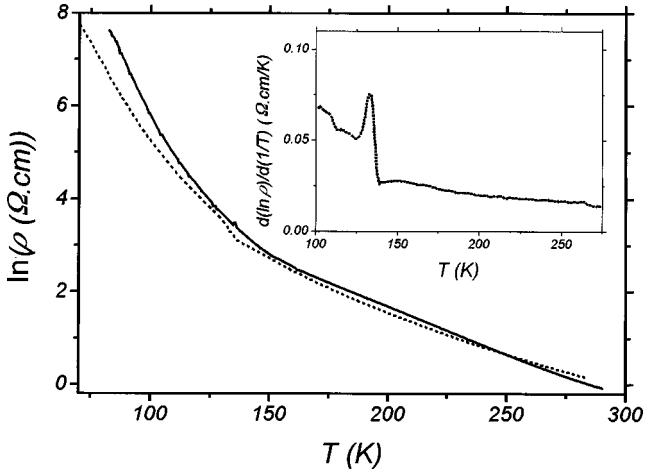

FIG. 4. Temperature dependence of the resistivity for the $x=0$ (solid line) and $x=2$ (dotted line) samples. In the inset we report the derivative of $\ln(\rho)$ with respect to $1/T$ for the $x=2$ sample where a clear peak around a temperature T_ρ is observed.

strongly coupled forming singlets and their contribution is rather small, however, not negligible for $T \gtrsim 200$ K. Therefore, one can write the total spin susceptibility as

$$\chi = (10/24)\chi_D + (14/24)\chi_L , \tag{2}$$

where χ_D is the susceptibility of the dimerized $Cu(1)O_2$ chains and χ_L that of the ladder. The coefficient in front of each term gives the percentage of $Cu(1)^{2+}$ and $Cu(2)^{2+}$ spins per formula unit. Both terms can be written in the form

$$\chi_{D,L} = \frac{N_A g^2 \mu_B^2}{k_B T} \frac{z_{D,L}(T,\Delta_{D,L})}{1+3z_{D,L}(T,\Delta_{D,L})} . \tag{3}$$

For a chain of noninteracting dimers[17] one has $z_D = \exp(-\Delta_D/T)$, while for a two-leg ladder in the isotropic limit ($J_\parallel = J_\perp = J = 2\Delta_L$, $J_\parallel$ being the superexchange coupling along the chains and $J_\perp$ in the rungs) and for $J \gg T$, one has $z_L \simeq 0.4\sqrt{T/2\Delta_L}\exp(-\Delta_L/T)$.[18]

From a quantitative analysis of the susceptibility data at low temperatures ($T \leqslant 200$ K), one immediately realizes that only around 35% of the spins in the $Cu(1)O_2$ chain contributes to the susceptibility. This fact indicates that in the chains, at relatively high temperatures, there are $Cu(1)^{2+}$ spins forming singlets. As first suggested by Carter *et al.*,[19] on the basis of analogous measurements, this could be related to the formation of strongly bound Zhang-Rice singlets,[12] formed by the $Cu(1)^{2+}$ spins and the extra holes intrinsically present in this compound. If one supposes that there are n_h of these localized holes in the chain, per formula unit, the dc susceptibility should be reduced by a factor $(10-n_h)/10$. Then one has

$$\chi = \frac{10-n_h}{24}\chi_D + \frac{14}{24}\chi_L . \tag{4}$$

By fitting the low temperature (for $T<130$ K χ_L is negligible) experimental data for the $x=0$ and $x=2$ compounds with just the first term of the above equation one can derive n_h and Δ_D. One finds that $\Delta_D \simeq 140$ K, weakly sample dependent, while the number of localized holes in the chain

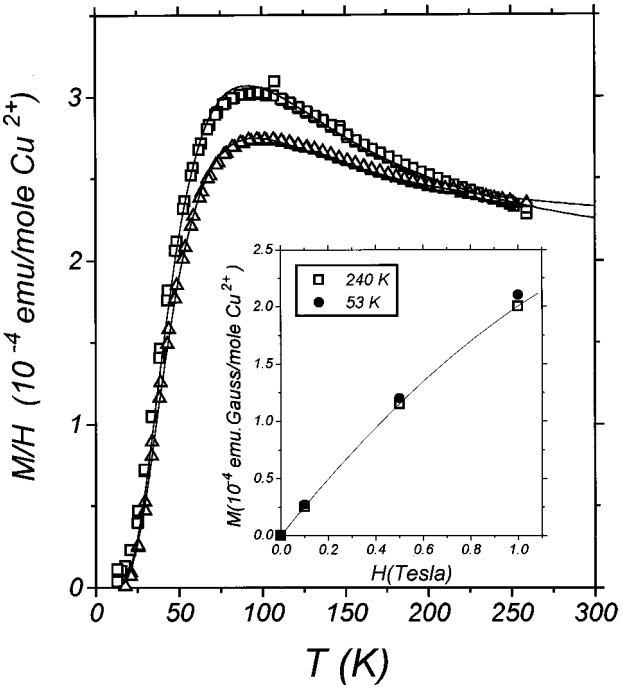

FIG. 5. Temperature dependence of the dc susceptibility for the $x=0$ (squares) and $x=2$ (triangles) samples. A low-temperature Curie-Weiss contribution $\chi_{CW} = C/(T-\Theta)$ has been subtracted from the raw data, with $C(x=0)=0.015$ emu K/mole Cu^{2+}, $C(x=0.02)=0.0167$ emu K/mole Cu^{2+}, $\Theta(x=0)=-1.23$ K, and $\Theta(x=0.02)=-1.14$ K. The solid lines give the best fit according to Eqs. (3) and (4) over all the temperature range. In the inset we show the field dependence of the magnetization at two different temperatures for the $x=0$ sample. The line is a guide to the eye.

increases from $n_h=6.4$ to $n_h=7$ on increasing x. Keeping these two parameters fixed one can estimate Δ_L from the fit of the data over all the temperature range with Eqs. (3) and (4) (see Fig. 5). One has $\Delta_L \simeq 500$ K for $x=0$, while $\Delta_L \simeq 420$ K for $x=2$. It should be mentioned that a similar value for the gap of the $x=0$ sample can be determined directly from $^{63}Cu(2)$ NMR shift data.

The value for n_h derived for the pure compound is in good agreement with the value $n_h=6$ that one would expect on the basis of previous considerations on the oxygen stoichiometry. From the same considerations, for $x=2$ one would expect a stronger increase of n_h. The fact that only a slight increase is observed suggests that part of the holes start to dope the $Cu(2)_2O_3$ ladders, causing the observed decrease in Δ_L. The observations in the previous paragraph suggest that the dimerization occuring at low temperatures involves a relatively small number of $Cu(1)^{2+}$ spins. The fact that Δ_D is independent on doping suggests that the dimers are weakly interacting and supports the use of the expression for z_D used in the analysis of the low-temperature dc susceptibility data.

B. ^{23}Na nuclear spin-lattice relaxation rate

Now we turn to the discussion of the spin dynamics in the chain probed by ^{23}Na NMR $1/T_1$. The temperature dependence of ^{23}Na $1/T_1$ for $H \| b$ is shown in Fig. 6. One observes an increase on decreasing temperature and then a sharp activated decrease at low temperatures. This tempera-

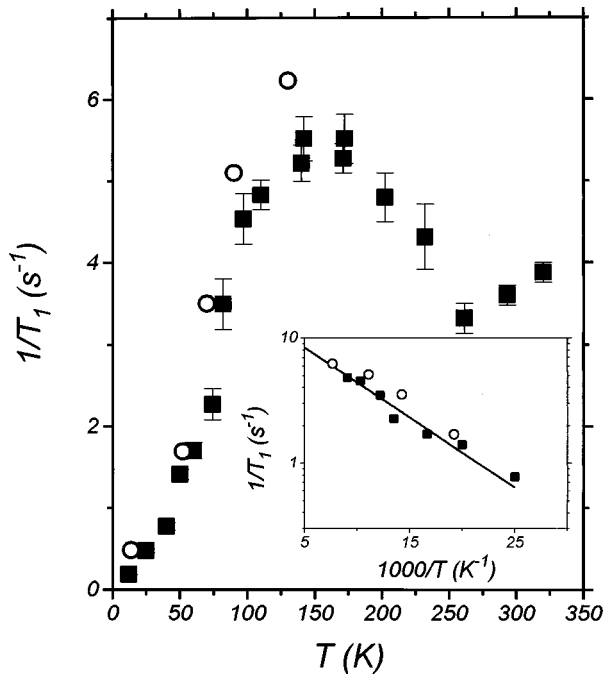

FIG. 6. Temperature dependence of ^{23}Na $1/T_1$ for the $x=0.7$ (circles) and $x=2$ samples (squares) in a magnetic field $H=5.9$ T along the b axis. In the inset the corresponding Arrhenius plot is shown for $T\lesssim 100$ K. The solid lines shows the activated trend for $\Delta_D=130$ K.

ture dependence is very similar to the one of the spin susceptibility and the activation energy estimated from the low-temperature trend is $\Delta_D\simeq 130$ K. This value is very close to the one derived from susceptibility measurements and points out that ^{23}Na nuclei below ~ 130 K probe essentially $Cu(1)^{2+}$ spin dynamics. Only at high temperatures the contribution from $Cu(2)^{2+}$ spin fluctuations to the relaxation start to be observed, giving rise to a smooth increase in ^{23}Na $1/T_1$. Nuclear spin-lattice relaxation rate can be expressed in terms of the components of the dynamical structure factor $S_{i=x,y,z}(\vec{q},\omega)=\int_{-\infty}^{\infty}\langle S_{\vec{q}}^{i}(t)S_{\vec{q}}^{i}(0)\rangle e^{i\omega t}dt(z\|H_0\|b)$, in the form

$$1/T_1=\frac{\gamma^2}{2N}\sum_{\vec{q}}\left[A_z(\vec{q})^2S_z(\vec{q},\omega_N)+A_\perp(\vec{q})^2S_\perp(\vec{q},\omega_e\pm\omega_N)\right] \tag{5}$$

with ω_e and ω_N the electron and nuclear Larmor frequencies, respectively. $A_{\perp,z}(\vec{q})$ are form factors describing the hyperfine coupling of the spin excitations at wave vector $\vec{q}$ with the nuclei. The coupling of ^{23}Na to $Cu(1)^{2+}$ spins will be assumed to be essentially of dipolar origin, considered the order of magnitude of $1/T_1$. Then, both terms of the above equations are present. In dimerized chains, two-leg ladders or Haldane gap systems, for low temperatures and low magnetic fields ($g\mu_B H/k_B\ll T\ll\Delta_{D,L}$), only the low part of the triplet magnon branch is populated. In that case, following Sagi and Affleck,[20] the nuclear relaxation is dominated by indirect $q\simeq 0$ processes which can be either intrabranch ($\Delta m_z=0$) ones, described by the first term of Eq. (5), or interbranch ($\Delta m_z=\pm 1$) ones where a simultaneous flip of the electron and nuclear spins occur [second term of Eq. (5)]. Then the temperature dependence of $1/T_1$ for $T\ll\Delta_{D,L}$ is an activated one, the value of $1/T_1$ increasing with the increasing population of triplet states.[18,20] One has

$$1/T_1\propto\frac{\gamma^2}{2NJ}\exp\left(-\frac{\Delta}{k_BT}\right)\{(A_z^2)_{q=0}[0.8909-\ln(\hbar\omega_N/k_BT)] + (A_\perp^2)_{q=0}[0.8909-\ln(\hbar\omega_e/k_BT)]\}. \tag{6}$$

At temperatures $T\gg\Delta$, $1/T_1$ reaches asymptotically the value

$$1/T_1=\frac{\gamma^2}{2}\frac{S(S+1)}{3}(A_z^2+A_\perp^2)\frac{\sqrt{2\pi}}{\omega_E} \tag{7}$$

with ω_E the Heisenberg exchange frequency which for an $S=1/2$ chain corresponds to $Jk_B/\hbar$. This is indeed the behavior observed for ^{63}Cu(2) in the $S=1/2$ AF two-leg ladder[14] and in $S=1/2$ dimerized chains,[21] however, it is not the one observed for ^{23}Na $1/T_1$ in $Sr_{14-x}Na_xCu_{24}O_{41}$ which between these two regimes shows a broad maximum.

The broad peak in ^{23}Na $1/T_1$ should not be associated to the slowing down of the spin fluctuations induced by hole diffusion since in that case a peak with higher intensity should be observed, even if one considers just a dipolar coupling of ^{23}Na nuclei to $Cu(1)^{2+}$ spins.[22,14] Furthermore, it would imply that the hopping rate of the holes in the chain is around nuclear Larmor frequency $\omega_N\simeq 4\times 10^8$ rad/s around 130 K, which is not compatible to the high activation energy ($E_a\gtrsim 0.2$ eV) derived from transport measurements (see Fig. 3).[22] Moreover the activated temperature behavior below 100 K should be characterized by a gap related to the hole itineracy [$1/T_1\propto\exp(-E_a/k_BT)$] and not to Δ_D, as it is found.

On the other hand, one could suspect that the maximum is due to structural distortions, which either progressively modify the hyperfine coupling or cause the slowing down of field fluctuations around a critical region.[23] The fact that the structure of this compound is rather soft has been already evidenced by the strong temperature dependence of the ^{63}Cu(2) nuclear quadrupole frequency, which changes by more than 20% over 500 K,[14] and by the anomalies in the resistivity around T_ρ. Remarkably, the broad maximum in ^{23}Na $1/T_1$ occurs around T_ρ. However, a structural transition usually gives rise to sharp singularities[23] and not to a broad maximum as the one observed. Therefore, we believe that the effect of the structural distortions on ^{23}Na $1/T_1$, if any, could be the one of progressively modifying the hyperfine coupling to $Cu(1)^{2+}$ spins. Nevertheless, to definitely exclude a dynamical origin of the maximum, a careful study of the field dependence of ^{23}Na relaxation rate is required.

C. ^{63}Cu(2) NMR-NQR relaxation rates $1/T_1$ and $1/T_{2G}$

Now we turn to the discussion of the temperature dependence of ^{63}Cu(2) $1/T_1$ (see Fig. 7). The hyperfine coupling tensor for ^{63}Cu(2) is essentially on site[14,24] and it is diagonal in the frame of reference of the crystallographic axes; therefore the first term in Eq. (5) is absent for $H\|b$. Around room temperature ^{63}Cu(2) $1/T_1$ probes the spin dynamics in the

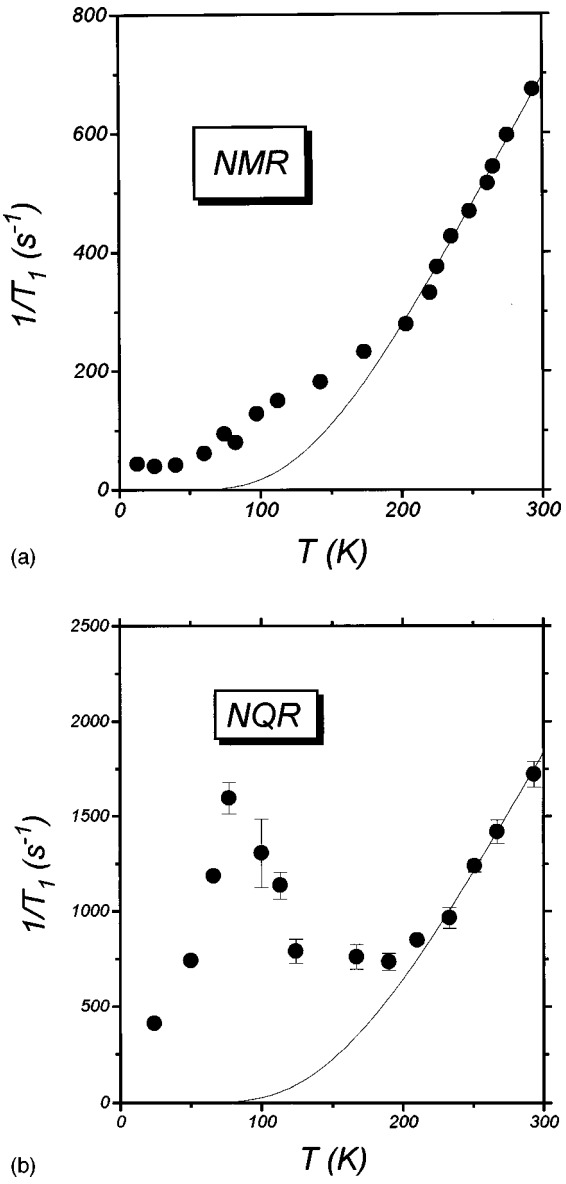

FIG. 7. (a) Temperature dependence of ^{63}Cu(2) $1/T_1$ for the $x=2$ sample in a magnetic field $H=5.9$ T along the b axis. The solid line describes the high-temperature activated trend. (b) Temperature dependence of ^{63}Cu(2) $1/T_1$ for the $x=0.7$ sample in NQR. The solid line describes the high-temperature activated trend.

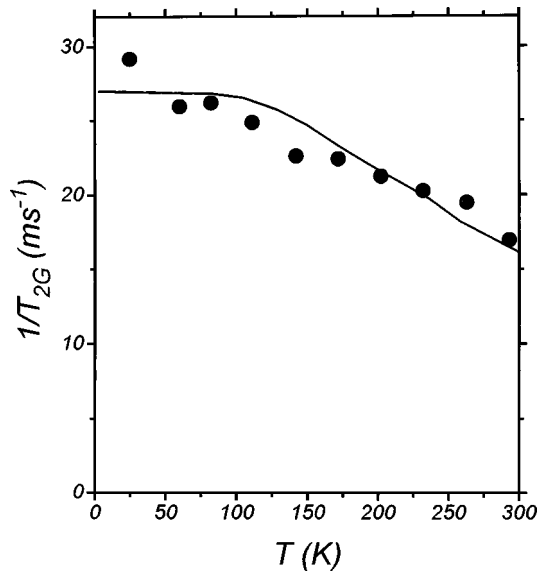

FIG. 8. Temperature dependence of ^{63}Cu(2) $1/T_{2G}$ for the $x=2$ sample in a magnetic field $H=5.9$ T along the b axis. The solid line shows the results from QMC calculations by Sandvik *et al.* (Ref. 31) for $J=850$ K and a transferred hyperfine coupling $B=-0.1A_z$.

ladders and, since the energy gap Δ_L is around 500–700 K, its temperature dependence is activated [see the second term in Eq. (6)]. It is interesting to notice that $1/T_1$ in NMR is reduced to nearly half of the value measured in NQR. This fact could be considered as an indication of the logarithmic divergence of $1/T_1$ on decreasing $\omega_e \pm \omega_N$ [see Eq. (6)]. Recently, by means of a careful Zeeman perturbed NQR study the divergence of ^{63}Cu(2) $1/T_1$ was confirmed to be logarithmic.[25] At low temperatures ($T \lesssim 150$ K) a broad peak superimposed to the activated trend is observed. This peak occurs at temperatures lower than the one observed in ^{23}Na $1/T_1$ and, therefore, should not be related to relaxation processes involving $Cu(1)^{2+}$ spin fluctuations, but rather to the slowing down of the spin fluctuations induced by holes.[26]

The high-temperature behavior allows us to estimate the amplitude of the gap Δ_L between singlet and triplet excitations in the ladders. One observes that the gap amplitude decreases on increasing x, implying that holes are being introduced in the ladders with Na^+ doping and perturbing the $S=0$ ground state. Accordingly one observes a decrease in the dc resistivity gap. This dependence on doping is analogous to the one observed by Kumagai *et al.*[27] and Magishi *et al.*[28] in Ca doped compounds, where the change in the chemical pressure promotes holes from the chains to the ladder. The amplitude of the gap Δ_L estimated from $1/T_1$ measurements, however, differs by a factor ~ 1.4 from the one estimated from dc susceptibility data. This difference was also observed in other two-leg ladder cuprates, as $SrCu_2O_3$,[11] however, it is not always present and there are $S=1/2$ two-leg ladders where it is not observed.[29] The origin of this discrepancy is still under debate and it will be briefly discussed in the last section.

^{63}Cu(2) transverse relaxation rate $1/T_{2G}$, derived from the decay of the echo amplitude [see Eq. (1)], is much higher than the one associated to the direct nuclear dipole interaction and is related to the indirect nuclear dipole coupling via the localized Cu^{2+} magnetic moments. In this case one can express the transverse relaxation rate in terms of the real part of the static spin susceptibility $\chi'_{zz}(q,0)$ along the quantization axis ($z \equiv b$)[15]

$$\left(\frac{1}{T_{2G}}\right)^2 = \frac{0.69}{\delta}\hbar^2\gamma^4\left\{\frac{1}{N}\sum_{\vec{q}} (A_z)_{\vec{q}}^4[\chi'_{zz}(\vec{q},0)]^2 - \left[\frac{1}{N}\sum_{\vec{q}} (A_z)_{\vec{q}}^2\chi'_{zz}(\vec{q},0)\right]^2\right\}, \quad (8)$$

with $\delta=4$ for NQR and $\delta=8$ for NMR when irradiating the central line. In Fig. 8 one observes that on decreasing temperature $1/T_{2G}$ progressively increases. By comparing the temperature depndence of ^{63}Cu(2) NMR $1/T_{2G}$ with the

quantum Monte Carlo (QMC) calculations by Sandvik *et al.*[30] we observe a reasonable agreement, provided one considers an isotropic superexchange coupling in the ladders $J\simeq 850$ K, i.e., a gap $\Delta_L\simeq 425$ K, and a small transferred hyperfine coupling. Therefore, from the measurement either of the q-integrated or uniform static susceptibility one derives a gap much smaller than the one estimated from T_1 data. It is interesting to mention that the ratio between $1/T_{2G}$ in NQR and in NMR is higher than the factor $\sqrt{2}$ expected from the difference in the constant δ [see Eq. (8)] for the two cases and keeps increasing on decreasing temperature.[14]

IV. SUMMARIZING REMARKS AND CONCLUSIONS

We have presented a series of NMR, dc susceptibility and resistivity measurements aiming at clarifying the modifications of the spin dynamics in $Cu(1)O_2$ chains and in $Cu(2)_2O_3$ ladders as a function of temperature and doping in $Sr_{14-x}Na_xCu_{24}O_{41}$. The transport and magnetic properties in the chains appear to be essentially the ones expected for weakly interacting dimers. In fact, the analysis of the susceptibilty evidences the presence of a rather small number of spins which dimerize while the other $Cu(1)^{2+}$ spins possibly form Zhang-Rice singlets with the localized holes. Therefore, $Cu(1)O_2$ chains should be rather considered as formed by dimers separated by an average distance around 4–5 lattice steps. This could also explain why the intensity of neutron scattering spectra shows a peak for wave vectors around 1/4−1/6 reciprocal lattice units.[31] The amplitude of the gap Δ_D between the $S=0$ and $S=1$ states was estimated either from the dc susceptibility or ^{23}Na $1/T_1$ data and a good agreement is observed. The amplitude $\Delta_D\simeq 140$ K does not vary with increasing doping (see Fig. 9), suggesting that the dimers are weakly interacting, thus supporting our analysis of the dc susceptibility. For a simple dimer, the spin correlation function and the charge transfer show singular behaviors as a function of the distance a between the spins.[32] In particular, on decreasing a one can show theoretically the existence of a sharp crossover from either an $S=1$ or a charge transfer state to an $S=0$ state. This could lead one to assert that for a system with a soft structure such as $Sr_{14-x}Na_xCu_{24}O_{41}$, the anomalies in the resistivity, followed at low temperatures by dimerization, can be explained in terms of these arguments.

Concerning the $Cu(2)_2O_3$ two-leg ladders we observe that the amplitude of the gap Δ_L, derived both from dc susceptibility and $1/T_1$ measurements decreases with increasing doping (Fig. 9). This trend is analogous to the one of the activation barrier E_a^h measured through dc resistivity (Fig. 9) and evidences a frustration of the AF correlations on increasing the hole itineracy. It is interesting to observe that the initial suppression rate for the gap $s=-d\Delta_L/dx$ is higher for Na-doped ($s\simeq 70$ K/Na^+ ion) than for Ca-doped samples ($s\simeq 45$ K/Ca^{2+} ion),[27,28] as expected for the heterovalent nature of the Sr^{2+} for Na^+ substitution.

Despite of the agreement in the trend vs x, the amplitude of the gap derived from $1/T_1$ and dc susceptibility differ by a factor ~1.4. This situation is similar to the one observed in other two-leg ladder cuprates but is at variance with the one observed in ladders where $J_\perp > J_\parallel$ (Ref. 29) or in dimers, as the ones formed by $Cu(1)^{2+}$ spins. Hereafter we will mention some of the possible origins for this discrepancy.

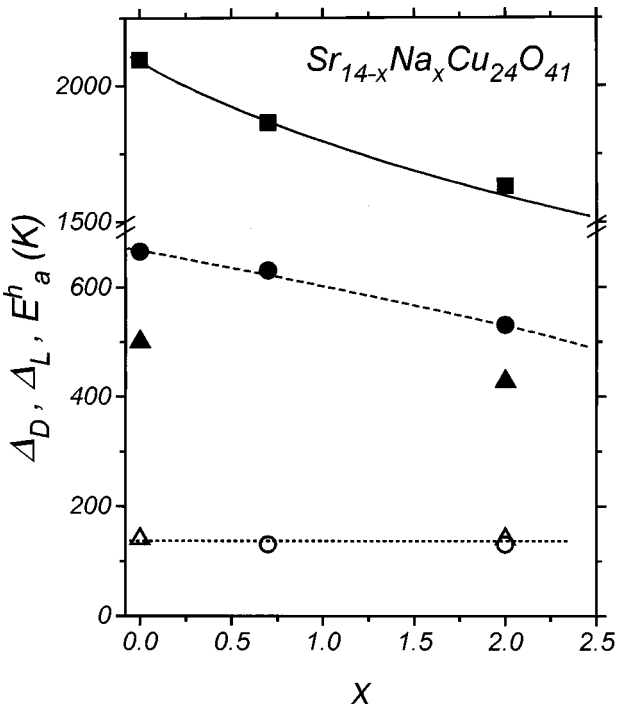

FIG. 9. Doping dependence of the high-temperature transport activation energy E_a^h (solid squares), Δ_L derived from $^{63}Cu(2)$ $1/T_1$ (solid circles), Δ_L derived from dc susceptibility measurements (solid triangles), Δ_D estimated from ^{23}Na $1/T_1$ (open circles), and Δ_D from dc susceptibility measurements (open triangles). The lines are guide to the eye.

Δ_L was estimated from the dc susceptibility data by using an expression based on a low-temperature expansion of the partition function. This approximation should be valid for $T\lesssim J/4$, i.e., in the isotropic limit $T\lesssim\Delta_L/2$.[18] Taking for Δ_L the values previously estimated, the above inequality implies that one can use this approximation as far as $T\lesssim 250$ K, well corresponding to the range where we carried out the analysis. According to Johnston[33] the small value of the gap measured by dc susceptibility is possibly due to a coupling $J_\perp < J_\parallel$ and the trend of χ vs T is also affected by the non-negligible coupling between adjacent ladders.[25] In further support for the existence of a small gap Δ_L we remark that $^{63}Cu(2)$ $1/T_{2G}$ data could be satisfactorily reproduced on the basis of QMC simulations[30] for a gap Δ_L around 450 K. Finally, recently, by means of neutron scattering measurements a value for the gap close to the one derived from static susceptibility measurements was found.[34]

Keeping this in mind one has to understand why $1/T_1$ measures a different gap or, in other terms, why Eq. (6) is not adequate to derive it. Recently Sachdev and Damle,[35] on the basis of a semiclassical approach to describe the spin excitations in quasi-1D gapped quantum AF, valid for $T\ll\Delta$, found that

$$1/T_1\propto\exp(-3\Delta/2T)\sqrt{\frac{T}{H}} \tag{9}$$

while

$$\chi \propto \exp(-\Delta/T)\sqrt{\frac{1}{T}}. \tag{10}$$

One notices that in this case the gap probed by $1/T_1$ and χ differs by a factor 1.5, very close to what is experimentally measured. However, it is not clear why this model should not apply to dimerized chains or to other ladder compounds[29] where the gap derived from susceptibility and $1/T_1$ is the same. It is interesting to notice that according to this model the low frequency spectral density should diverge as $\sqrt{1/H}$ as the field intensity H is decreased.

Another possibility is that one cannot neglect the damping of the triplet excitations on increasing temperature. In this case $1/T_1 \propto (1/\tau_T)\exp(-\Delta_L/T)$, with τ_T the temperature-dependent lifetime of the triplet excitations.[36] It is interesting to observe that if one considers a lifetime inversely proportional to the temperature $\tau_T \propto 1/T$ one finds a rather good agreement between the gap estimated from $1/T_1$ and the one derived from dc susceptibility, both for $x=0$ and $x=2$. The damping of the spin excitations in the temperature range of interest could be due to the lattice vibrations which are neglected in the derivation of Eq. (6). On the other hand, it is certainly negligible when considering the temperature dependence of the relaxation for two-leg ladders with small values for the gap.[29] Another possibility is that excitations around $q \simeq \pi$, involving three magnons,[20] can become more and more important as the gap decreases due to a reduction of $J_\perp$ with respect to $J_\parallel$. In that case the continuum of spin excitations moves to low energies and there is a higher density of states with energies $2\Delta_L$ which are involved in the 3-magnon processes. Then one should have an extra contribution of the form $(1/T_1)_{(3)} \propto \exp(-2\Delta_L/T)$. An agreement with the dc susceptibility measurements can still be found also in this case provided the amplitude of 3-magnon terms is 6 times larger than that of two-magnon processes. Finally we remark that Eq. (6) was derived on the assumption of a quadratic dispersion curve for $\kappa_x \rightarrow \pi/2$.[18] While this turns out to be a good approximation for $J_\perp \gg J_\parallel$, in the case $J_\parallel \gg J_\perp$ the dispersion curve becomes more and more linear around $\kappa_x \rightarrow \pi/2$ and deviations with respect to the $1/T \propto \exp(-\Delta/T)$ behaviors are found.[14]

In conclusion, we have evidenced through dc susceptibility and NMR $1/T_1$ measurements a dimerization of $Cu(1)O_2$ chains, involving only a few Cu^{2+} spins in the chain. The remaining $Cu(1)^{2+}$ spins possibly form Zhang-Rice singlets with the holes intrinsically present. The structural distortions evidenced in NQR spectra and resistivity measurements are believed to cause an increase in the superexchange coupling along the chain to values around $\Delta_D \simeq 140$ K. The introduction of extra holes by doping with Na^+ causes a reduction of the susceptibility at low temperatures which is tentatively associated to the formation of other Zhang-Rice singlets in the chain. Some extra holes are observed to dope the two-leg ladders and to cause a decrease in the spin gap and an increase in the conductivity. An anomalous behavior of ^{23}Na $1/T_1$, associated either to structural distortions or to dynamical effects, is evidenced. The difference in the gap estimated from $1/T_1$ and from measurements of the static susceptibility (χ or $1/T_{2G}$) in the ladders is related to the dynamics probed by $1/T_1$. The relationship between $1/T_1$ and Δ can differ from the one in Eq. (6) due to damping effects, to a non-negligible contribution from 3-magnon processes and, more in general, because of the form of the dispersion curve for $J_\parallel > J_\perp$.

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