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^{35}Cl NMR study of spin dynamics in $Sr_2CuO_2Cl_2$

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Measurements of the ^{35}Cl nuclear-spin–lattice relaxation rate (NSLR) are reported for $Sr_2CuO_2Cl_2$ around the antiferromagnetic transition temperature $T_N = 260 \pm 0.5$ K. The temperature dependence of the Cu^{2+} spin correlation length $\xi(T)$ is obtained indirectly by using the conventional description of NSLR and scaling arguments and compared with the $\xi(T)$ obtained in La_2CuO_4 by neutron scattering. In both systems $\xi(T)$ follows the two-dimensional Heisenberg behavior renormalized by quantum fluctuations except close to T_N where a crossover to a power-law T dependence is observed in $Sr_2CuO_2Cl_2$.

The discovery of the superconducting properties of layered CuO_2 materials has greatly revived the interest in the magnetic properties of two-dimensional (2D) Heisenberg antiferromagnets (AF). $Sr_2CuO_2Cl_2$ is a layered perovskite with body-centered-tetragonal K_2NiF_4 structure providing a good prototype for the study of the correlated spin dynamics in 2D $S = \frac{1}{2}$ systems, to be compared with the analogous properties in the high-T_c superconductors.

The structural and magnetic properties of $Sr_2CuO_2Cl_2$, studied in a number of recent papers by x-ray scattering, neutron scattering, susceptibility, and muon spin rotation,[1–3] are almost identical to the ones in La_2CuO_4, except for two important differences: (i) While the latter undergoes an orthorhombic distortion, the Cl-substituted material remains tetragonal down to at least 10 K. This fact is believed to explain the different behavior of the susceptibility near T_N for the two systems. (ii) $Sr_2CuO_2Cl_2$, although potentially suitable for electron-type doping and superconductivity has not led to any successful superconductor, in contrast with Sr- and Ba-doped La_2CuO_4. One should stress that Cl replaces the apical oxygen in the CuO_6 octahedra, which is still under consideration as the driving mechanism for high-T_c superconductivity.

In La_2CuO_4 neutron-scattering data yielded[4,5] a Cu^{2+} spin correlation length ξ that has been fitted, in the paramagnetic phase, by a theoretical model[6] for the 2D Heisenberg $S = \frac{1}{2}$ system that includes a reduction of ξ from quantum fluctuations:

$$\xi/a = C_\xi \exp(2\pi\rho_s/k_B T) , \quad (1)$$

where C_ξ is a constant of the order of unity and $\pi\rho_s \simeq J$ (for $S = \frac{1}{2}$); J is the nearest-neighbor exchange energy for Cu^{2+} spin in the Heisenberg Hamiltonian

$$H = 2J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j ,$$

where the sum is over nearest-neighbor pairs.

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are local probes of time correlations of local fields. Whenever the slowing down of the local fluctuations is related to the increase of the spatial correlations, the nuclear-spin–lattice relaxation rate can be used to measure indirectly the correlation length. For example, ^{139}La NQR relaxation rates in slightly Sr-doped La_2CuO_4 were used to investigate the effect of reduction of $\xi(T)$ by the mobile charge defects.[7,8]

The ^{35}Cl nucleus ($I = \frac{3}{2}$) offers a suitable tool to probe the microscopic static and dynamical effects occurring in the CuO_2 planes. In this paper we present the results of a ^{35}Cl NMR study in $Sr_2CuO_2Cl_2$, with the aim of deriving the correlation length and spin dynamics of Cu^{2+} magnetic moments to be compared with the corresponding behavior in the other prototype La_2CuO_4.

The sample was prepared in polycrystalline form, as described in Ref. 1. An unsuccessful search for $^{63,65}Cu$ NQR and NMR signals, both in the paramagnetic and AF phases, was performed. The lack of a detectable signal is most likely due to a very short T_2, analogously to the case of La_2CuO_4.[7]

The ^{35}Cl NMR signal, detected at $H_0 = 5.8$ and 8.2 T, is characteristic of the $(+\frac{1}{2} - \frac{1}{2})$ central line transition, with satellite lines spread by first-order quadrupole interaction in powders. The width of the ^{35}Cl central line transition as a function of temperature is shown in Fig. 1. Well above T_N the line width must be determined by nuclear dipolar interactions and, if present, second-order quadrupole effects. The observed width is consistent with a quadrupole interaction $\nu_Q \leq 0.5$ MHz for axial symmetry. A point-charge calculation of the electric-field gradient performed on the basis of the crystal structure and assuming nominal charges $(+2e)$ at the Cu and Sr atoms and $(-2e)$ at the O atoms yields $\nu_Q \cong (1 - \gamma_\infty)20$ kHz which is, alone by itself, of the order of magnitude of the experimental finding for a reasonable antishielding factor

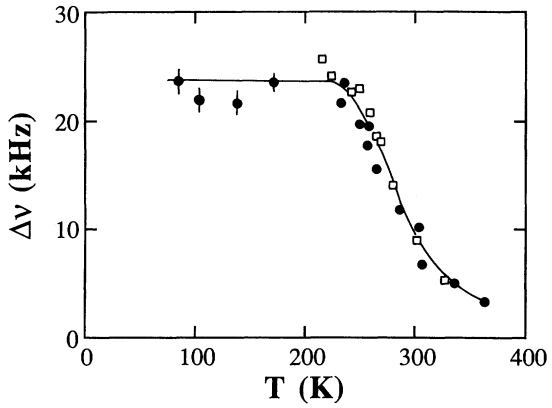

FIG. 1. Full width at half intensity of the ^{35}Cl central NMR line vs temperature in $Sr_2CuO_2Cl_2$ as obtained from the Fourier transform (FT) of the free induction decay. Identical results are obtained from the FT of half of the echo signal. (●) $H_0=5.8$ T, (□) $H_0=8.2$ T.

$(1-\gamma_\infty)=25$. This indicates that the Cu-Cl bond is largely ionic.

The result is consistent with the ^{17}O NMR results in La_2CuO_4 where it is found that the apical O sites have a $\nu_Q \cong 0.2$ MHz, considerably smaller than for the O sites in the CuO_2 planes.[9] As shown in Fig. 1, the full width at half intensity of the line increases on crossing T_N (=260 K, see below), reaching a value $\Delta\nu \simeq 24$ kHz for $T \leq 200$ K. No measurable shift is observed below T_N indicating that the transferred hyperfine interaction between the ^{35}Cl and Cu^{2+} spins is small. The broadening observed below T_N can be entirely accounted for by the anisotropic dipolar interaction of ^{35}Cl nucleus with the ordered Cu^{2+} magnetic moments. The dipolar field H_{dip}, evaluated assuming the AF arrangement given in Ref. 2, is $|H_{dip}| = 340(\mu/\mu_B)$ G.

In concluding about the NMR static properties, the lack of transferred hyperfine field is consistent with the weakness of the quadrupole interaction at the chlorine site and both are indicative of a weakly covalent character of the CuCl bond. Further work in a single crystal is under way to better elucidate these aspects, which, however, are not directly relevant for the study of the correlated spin dynamics.

The relaxation transition probability W driving the ^{35}Cl nuclear-spin-lattice relaxation can be extracted from the multiexponential recovery of the free-induction decay or of the echo amplitude following a two-pulse sequence. By assuming that the dominant relaxation mechanism is of magnetic rather than of quadrupolar origin, one has a recovery law for the central-line signal $s(t)$ given by

$$[s(t)-s(\infty)]/s(\infty)=c_1\exp(-2Wt)+c_2\exp(-12Wt).$$

The coefficients $c_{1,2}$ depend on the initial conditions following the saturating irradiation. For irradiation of the central line by a single pulse $c_1=0.1$ and $c_2=0.9$ (case 1); for irradiation of the central line only, with a pulse sequence much longer than W^{-1}, $c_1=0.4$ and $c_2=0.6$ (case 2). Finally, for irradiation and complete saturation of both the central and satellite lines, $c_1=1$ and $c_2=0$ (case 3). In our case the satellite lines are spread over a frequency range which allows only for partial irradiation. Thus we observe a gradual modification of the recovery law from case (2) to case (3), as function of the number of the pulses in the saturating sequence. By studying the recovery law under variable irradiation conditions a reliable estimate of $2W$ has been obtained.

The results for $T_1^{-1}=2W$ as a function of temperature are shown in Fig. 2. Within the experimental error the results for T_1 appear independent from the magnetic-field strength, indicating that the fluctuation frequency of the Cu^{2+} spin dynamics remains much greater than the Larmor frequency. Thus the peak in T_1^{-1} vs T occurs at the transition temperature[10] and one derives $T_N=260\pm0.5$ K. Below T_N, the relaxation rate W drops rapidly as expected for ordered magnetic materials.[11] In the paramagnetic phase one has a critical enhancement of W on ap-

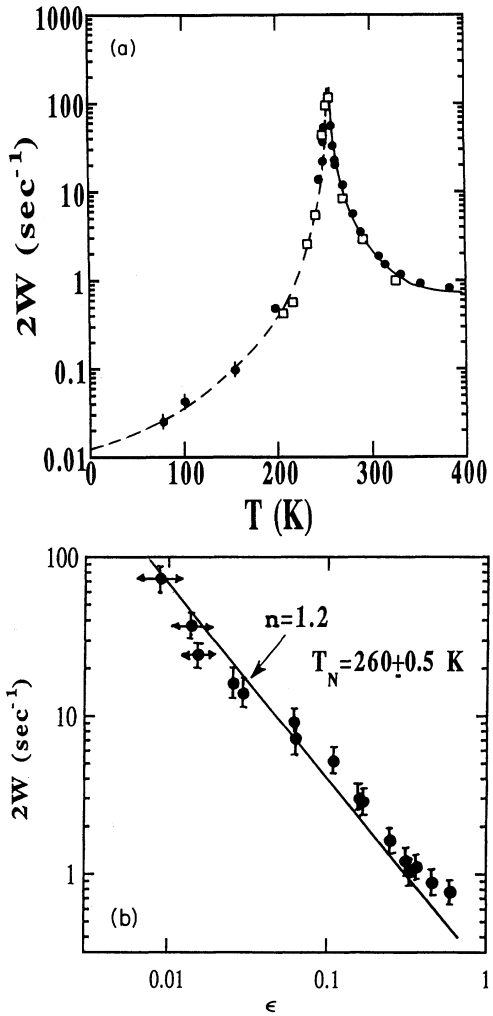

FIG. 2. (a) ^{35}Cl spin-lattice relaxation rate $2W$ vs temperature in $Sr_2CuO_2Cl_2$; (●) $H_0=5.8$ T, (□) $H_0=8.2$ T. The AF transition temperature, estimated from the peak in $2W$ is $T_N=260\pm0.5$ K. The dashed and solid lines are aids to the eye. (b) $2W$ is plotted vs reduced temperature $\epsilon=(T-T_N)/T_N$ and compared with a power-law behavior with critical exponent $n=1.2$.

proaching T_N, indicative of the divergent behavior of the magnetic correlation length and the corresponding slowing down of the correlated spin dynamics.[10]

In order to discuss quantitatively the critical spin dynamics in the paramagnetic phase we relate the ^{35}Cl relaxation rates to the correlation functions of the Cu^{2+} spin components $S_\alpha(t)$.[11] For fluctuations faster than the Larmor frequency one writes

$$2W = \tfrac{1}{2}\gamma^2 \int \langle \mathbf{h}_+(t)\cdot\mathbf{h}_-(0)\rangle dt \,, \tag{2}$$

where $\mathbf{h}(t)$ is the effective local field at the nuclear site. For a nucleus-electron hyperfine Hamiltonian including the dipolar part which should be relevant here (see previous section) and by assuming isotropic fluctuations of the S_α components (Heisenberg model), Eq. (1) can be rewritten in terms of the collective spin components $S_\mathbf{q}$ in the form[10]

$$\begin{aligned} 2W &= \tfrac{1}{2}\gamma^2 \frac{1}{N}\sum_\mathbf{q} |\mathbf{h}_\mathbf{q}|^2 \int \langle S_\mathbf{q}^+(0) S_\mathbf{q}^-(t)\rangle dt \\ &= \gamma^2 \frac{1}{N}\sum_\mathbf{q} |\mathbf{h}_\mathbf{q}|^2 |S_\mathbf{q}|^2/\Gamma_\mathbf{q} \end{aligned} \tag{3}$$

where $|S_\mathbf{q}|^2$ is the mean square amplitude and $\Gamma_\mathbf{q}$ is the decay rate of the collective spin fluctuations, while $\mathbf{h}_\mathbf{q}$ is the Fourier transform of the lattice functions which couple the Cl nucleus to the Cu^{2+} spins $S_i(t)$. Since the hyperfine field at the ^{35}Cl site does not cancel for an AF arrangement of the Cu^{2+} spins, one expects the main contribution to the ^{35}Cl relaxation rate to come from AF fluctuations.[10] By expanding the $\mathbf{h}_\mathbf{q}$ factor around the value corresponding to the critical wave vector describing the staggered order below T_N and by using conventional scaling arguments[12] for the q dependence of the in-plane correlated fluctuations, Eq. (3) becomes

$$2W = (\gamma h_{\rm eff})^2 \frac{1}{N}\sum_\mathbf{q} \frac{\xi^{2-\eta} f(q\xi)}{\omega_e \xi^{-z} g(q\xi)} \,, \tag{4}$$

where $h_{\rm eff}$ is the static field at the Cl site resulting from the Cu^{2+} configuration of the ordered magnetic structure while $\mathbf{q}$ is the 2D wave vector measured with respect to $q_{\rm AF}$. In Eq. (4), we have written $|S_\mathbf{q}|^2$ in terms of the correlation length (in lattice units) while the decay rate of the fluctuations has been expressed by a scaling form in terms of the Heisenberg exchange frequency ω_e: $\Gamma_q = (\omega_e/\xi^z) g(q\xi)$, z being a characteristic dynamical scaling exponent, and $f(q\xi)$ and $g(q\xi)$ are homogeneous functions of the product $x = q\xi$. By transforming the q summation in Eq. (4) into a 2D integral and taking into account the convergence of $\int [f(x)/g(x)]dx$ to a number of the order of unity, one finally has

$$2W = (\gamma h_{\rm eff})^2 \frac{1}{\omega_e} \xi^{z-\eta} \,. \tag{5}$$

It is noted that in the high-temperature limit of no correlation [$\xi \to 1$ from Eq. (1)], Eq. (5) reduces to the well-known result for paramagnets.[11] With $\omega_e = [(8/3)]J^2 ZS(S+1)]^{1/2}/\hbar \simeq 3\times 10^{14}$ rad s^{-1} for $J = 860$ K (Ref. 2) and $Z = 4$ (number of nearest-neighbor magnetic ions), and with $(h_{\rm eff})^2 = \sum h_i^2 \approx 10^6$ G^2 for the estimated value of the uncorrelated Cu^{2+} dipolar field at the Cl site, one has $(2W)_{T\to\infty} \simeq 2\times 10^{-2}$ s^{-1}. Since this value is much smaller than the experimental data at the highest temperature measured (i.e., $2W \simeq 0.75$ s^{-1}), one can infer that correlation effects are already relevant for $T \leq 400$ K. In the discussion which follows we derive $\xi(T)$ from Eq. (5) assuming that dynamical scaling is obeyed. It should be stressed that only scattering experiments directly measure spatial correlations. The consistency of NQR results with neutron-scattering results is an indication that dynamical scaling is valid in the system investigated.

The divergence of the relaxation rate for $T \to T_N^+$ is of the form $2W \propto (T - T_N)^{-n}$, with $n = 1.2 \pm 0.1$, as shown in Fig. 2(b). This critical behavior is close to the one observed in the ^{19}F NMR linewidth in the 2D Heisenberg model system K_2MnF_4.[13] From Eq. (5) and setting $\xi \propto (T - T_N)^{-\nu}$ one has $n = \nu(z - \eta)$. It has been argued[14] that the large value of n should be ascribed to a crossover, close to T_N, towards an anisotropic Heisenberg system. Thus a value of $(z - \eta)$ of the order 2 appears reasonable for the dynamical critical exponent. By using $(z - \eta) = 2$, from the experimental data for $2W$, on the basis of Eq. (5), one can extract the temperature dependence of ξ shown in Fig. 3. In this derivation we have estimated $h_{\rm eff} = 360(\mu/\mu_B)$ G and $\mu = 0.35\mu_B$.[2] This value of the hyperfine field was calculated as explained above, and it corresponds to the short-range AF correlated spin arrangement equivalent to the long-range order observed below T_N by neutron scattering.[2] The temperature dependence of ξ for $Sr_2CuCl_2O_2$ is compared in Fig. 3 with the corresponding value of ξ for La_2CuO_4 obtained from neutron scattering.[4,5] The remarkable agreement between the absolute values of the two sets of data has to be considered

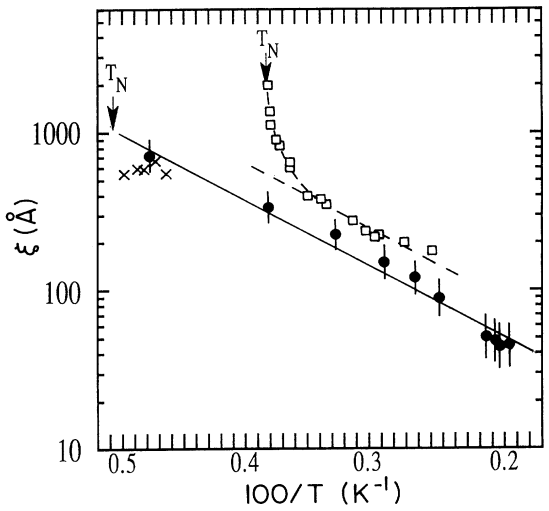

FIG. 3. (□) Correlation length ξ vs 100/T in $Sr_2CuO_2Cl_2$, obtained from the ^{35}Cl NMR relaxation rate as explained in the text. (●) correlation length derived from neutron scattering in La_2CuO_4 (Refs. 4 and 5); (×) correlation length estimated from ^{139}La NQR relaxation rate (Refs. 7 and 8), with the temperature renormalized to the $T_N = 195$ K of the sample studied by neutron scattering. The solid line corresponds to the theoretical behavior [Eq. (1)] with $2\pi\rho_s = 1000$ K and $C_\xi = 1.7$, $a = 3.95$ Å.

as partly fortuitous in view of the uncertainty in the evaluation of the effective hyperfine field in Eq. (5). On the other hand, the comparison of the temperature dependences of ξ is very enlightening. For $T \geq T_N + 17$ K, ξ vs T is well described by an exponential behavior [Eq. (1)], with approximately the same exponent, for both systems. For $\epsilon \equiv (T - T_N)/T_N \leq 7 \times 10^{-2}$ one can see, in $Sr_2CuO_2Cl_2$, the crossover from the 2D Heisenberg quantum behavior to a power-law behavior characteristic of a system approaching a phase transition. Regarding La_2CuO_4 no neutron-scattering data seem to be available in a comparable temperature range near T_N. The data for ξ in La_2CuO_4 obtained from ^{139}La NQR relaxation just above T_N do not show any critical enhancement, contrary to $Sr_2CuCl_2O_2$ (see Fig. 3).

In summary, the ^{35}Cl NMR investigation of the Cu^{2+} spin dynamics in $Sr_2CuO_2Cl_2$ has revealed an interesting behavior of the correlation length, which displays a crossover from 2D $S = \frac{1}{2}$ Heisenberg to a power-law behavior at $|T/T_N - 1| \leq 7 \times 10^{-2}$. The similarities of the magnetic properties of $Sr_2CuO_2Cl_2$ and the one of La_2CuO_4, already widely recognized,[1-3] is confirmed here also in regard the Cu^{2+} spin dynamics, except for the crossover effects. A crossover from 2D to 3D Heisenberg is very unlikely in $Sr_2CuO_2Cl_2$ in view of the small interplane coupling (smaller than La_2CuO_4).[2] A crossover from 2D Heisenberg to 2D anisotropic Heisenberg should occur when the reduced in-plane anisotropy satisfies $h_A(\xi/a)^2_{cr} \simeq 1$.[15] From Fig. 3, $(\xi/a)_{cr} \simeq 100$ and thus $h_A = (g\mu_B \times H_A/ZJS) \simeq 10^{-4}$. Both the Cu^{2+} dipolar interaction and the anisotropic exchange interaction in the plane are of the correct order of magnitude to explain the crossover.[16] The dipolar anisotropy would lead to a crossover from 2D Heisenberg to 2D Ising while the second kind leads to a 2D XY model. From the critical exponent extracted from NMR, i.e., $n = \nu(z - \eta) = 1.2 \pm 0.1$ (see Fig. 2), it does not seem possible to distinguish between 2D Ising or XY behavior. If a similar crossover is not present in La_2CuO_4, one should consider the possibility that, in this material, $\xi(T)$ is limited by mobile charge defects, even in the nominally pure samples, a hypothesis already formulated.[8,17] In $Sr_2CuO_2Cl_2$, on the other hand, the substitution of the apical oxygen with chlorine,[1] apparently drastically reduces the concentration of charge defects related to O nonstoichiometry.

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