Field-induced staggered magnetization near impurities in the $S=\frac{1}{2}$ one-dimensional Heisenberg antiferromagnet Sr_2CuO_3

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We report an impurity effect in the spin-$\frac{1}{2}$ one-dimensional Heisenberg antiferromagnet Sr_2CuO_3. The ^{63}Cu NMR spectra develop a broad background with sharp edges at low temperatures. The anisotropy and the temperature dependence of this structure indicate that the external magnetic field induces local staggered magnetization near impurities, whose spatial extent grows with decreasing temperature. The results are in good agreement with the theoretical prediction by Eggert and Affleck for a semi-infinite spin chain with an open end. [S0163-1829(97)08017-X]

Impurity effects in quantum spin chains with a singlet ground state have attracted recent interest, since even a nonmagnetic defect may disturb the correlated ground state of the bulk in a subtle manner and locally restore magnetic behavior. A good example is the extra spin-1/2 degree of freedom localized near an open end of an integer-spin Heisenberg chain, which has an excitation gap (Haldane gap) in the bulk.[1] Also it has been observed that only a few percent of nonmagnetic impurities in the spin-Peierls material $CuGeO_3$ induce long-range magnetic order.[2,3]

The case of half-integer-spin Heisenberg chains has been considered by Eggert and Affleck.[4–6] From field-theoretical and Monte Carlo calculations, they found that the local susceptibility near an open end of a semi-infinite chain has a large alternating component. This means that a uniform magnetic field will induce local staggered magnetization near the end. The staggered moment has a maximum at a finite distance from the end, which increases as $1/T$ with decreasing temperature.[5] Such a long-range disturbance near a chain end is a manifestation of the critical nature of half-integer-spin chains whose correlation length diverges at $T=0$, yet there is no long-range order. An analogy to other impurity problems such as the Kondo effect and the tunneling in one-dimensional wires has been also pointed out.[4,6] Thus experimental confirmation of such an exotic impurity effect in a quantum many-body system should be important. In this paper we report observation of the field-induced staggered magnetization near impurities in Sr_2CuO_3 by ^{63}Cu nuclear magnetic resonance (NMR) experiments.

Recent studies have shown that the static[7–10] and dynamic[11,12] properties of Sr_2CuO_3 are well described by a spin-1/2 one-dimensional (1D) Heisenberg model. The ratio of the intrachain exchange $J=2200\pm200$ K, obtained from susceptibility data,[10] to the 3D ordering temperature $T_N=5$ K, determined by muon[7] and neutron experiments,[13] is larger than any other material.[14] Single crystals of Sr_2CuO_3 were grown by the traveling-solvent-floating-zone method. The susceptibility of as-grown crystals shows a low-temperature Curie term corresponding to about 0.1% spin-1/2 impurities, which are reduced by subsequent annealing in an Ar atmosphere down to 130–200 ppm.[10] This indicates that the dominant source of impurities in this material is the interstitial excess oxygen. The NMR spectra reported here were obtained on an Ar-annealed crystal by integrating the spin-echo signal with a boxcar averager at a fixed frequency while sweeping the magnetic field. The same crystal was used in the previous measurements of nuclear relaxation rates.[11] Intentional impurity doping has not been successful so far. In the following, we first describe the theoretical prediction for the NMR spectra and then present the experimental results.

The inset of Fig. 1 shows the Monte Carlo result for the local spin susceptibility $\chi(l)$ in units of $(g\mu_B)^2/J$ at $T=J/15$ as a function of distance l from the open end obtained by Eggert and Affleck.[5] Using a field-theoretical technique valid at low temperatures ($T\ll J$), they also obtained a simple analytic expression for $\chi(l)$, which consists of the uniform and alternating parts[5]

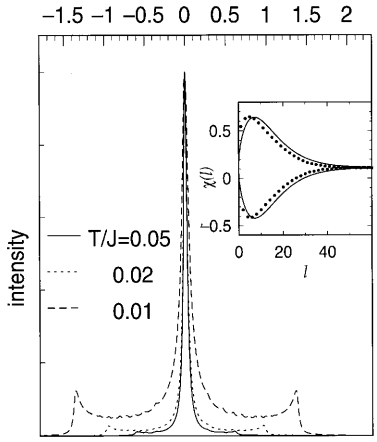

FIG. 1. Distribution function, Eq. (5), of the local susceptibility $\chi(l)$ which is equivalent to the NMR spectrum. The uniform part of $\chi(l)$ is omitted. In the inset is plotted $\chi(l)$ as a function of the distance l from the chain end at $T=J/15$. Dots and lines are the Monte Carlo (Ref. 5) and the analytic results [Eq. (2) with $a=0.58$], respectively.

$$\chi(l)=\chi_u(l)+(-1)^l\chi_{\rm alt}(l). \quad (1)$$

While $\chi_u(l)$ is nearly constant with a value close to the bulk susceptibility, the alternating part is given by

$$\chi_{\rm alt}(l)=\frac{aJ}{v}\frac{l}{\sqrt{(v/\pi T)\sinh(2\pi Tl/v)}}, \quad (2)$$

where $v=\pi J/2$ is the spin-wave velocity. This result, shown by the solid line in the inset of Fig. 1 for $T=J/15$, agrees with the Monte Carlo result if the constant a is chosen to be 0.58, except for a shift of a few sites. A distinct feature is that $\chi_{\rm alt}(l)$ shows a maximum

$$\chi_{\rm alt,\,max}=0.137\sqrt{J/T} \quad (3)$$

at $l=0.48J/T$ and decreases exponentially for larger l.

Such alternating (staggered) magnetization can be detected by broadening of NMR spectra. The hyperfine interaction

$$\mathcal{H}=\sum_{\alpha,i,l}A_\alpha^{i-l}I_{i\alpha}S_{l\alpha}(\alpha=x,\ y,\ \text{or}\ z), \quad (4)$$

between a nuclear spin at the ith site and an electron spin at the lth site, causes a shift of the resonance field,

$$K_i=(\gamma_e/\gamma_n)\sum_l A_z^{i-l}\chi(l)/J$$

$$\approx(\gamma_e/\gamma_n)[A_z(0)\chi_u+A_z(\pi)\chi_{\rm alt}(i)]/J, \quad (5)$$

where γ_n (γ_e) is the nuclear (electron) gyromagnetic ratio, $A(q)=\sum_l A^l e^{iql}$ is the Fourier component of the hyperfine coupling constant, and z is the direction of the magnetic field. Since the range of A^{i-j} in magnetic insulators is unlikely to go beyond the first neighbors and much shorter than the distance over which significant changes occur in $\chi_{\rm alt}(l)$ at low temperatures, we used the approximation $\chi(l)\approx\chi_u+\exp(i\pi l)\chi_{\rm alt}(i)$ in Eq. (5). The NMR spectrum represents the distribution function of K_i, which is equivalent to $\chi_{\rm alt}$ apart from the uniform shift. Figure 1 shows the calculated distribution function

$$g(x)=\sum_l f\{x-(-1)^l\chi_{\rm alt}(l)\}, \quad (6)$$

using Eq. (2), where f is chosen to be a Lorentzian with small width (0.05) to make $g(x)$ a smooth curve and the summation is taken up to $l=450$. It shows a distinct shape with a sharp center peak on top of a broad background. Notice that the maximum in $\chi_{\rm alt}$ gives rise to peaks at the edges of the background, whose separation varies as $1/\sqrt{T}$.

We now turn to the experimental results. Figure 2 shows the NMR spectra at different temperatures with the magnetic field along the a axis (see the crystal structure in the inset). Only the center lines of the quadrupolar split spectra are shown. A sharp single peak observed at 200 K gets broadened at lower temperatures. In addition to this central peak, a broad background with sharp edges becomes clearly visible at low temperatures. Both the intensity and the width, denoted as ΔH in Fig. 2, of the background grow with decreasing temperature. The spectrum at 30 K shows two distinct features in addition to this background: the splitting of the central peak (δH) and the shoulders on both side of the peak (DH).[15] Similar spectra were obtained for $H\|b$.

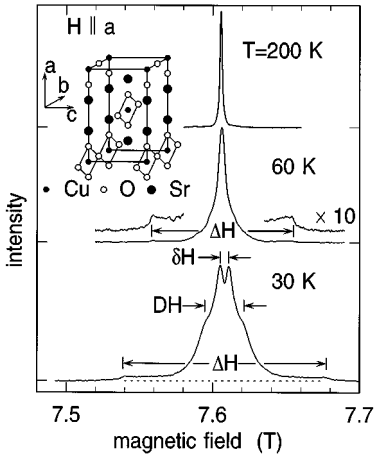

FIG. 2. The ^{63}Cu NMR spectra for $H\|a$ at 86 MHz. The inset shows the crystal structure of Sr_2CuO_3.

Figure 3 shows the spectra for $H\|c$. All three quadrupolar split lines are shown. Common features with the spectra for $H\|a$ such as the broadening of the central peaks, the background with clear edges, and the shoulder structure are observed. By taking spectra for several field directions in the ac plane, we confirmed that the positions of the edges and shoulders move smoothly and that both ΔH and DH show a simple $\cos^2\theta$ angular dependence. However, the spectrum at 30 K shows a very sharp peak (a few mT wide) on top of the broadened central peak, in contrast to the splitting observed for $H\|a$ and b. The intensity of this sharp peak, however, is only about 0.1% of the total integrated intensity.

Since the spectra in an infinite periodic spin chain should be a single line, whose width is determined by the dynamic relaxation rates ($1/T_1$ and $1/T_2$) and is of the order of mT in this material,[11] any broadening or additional structure at low temperatures must be due to spatial variation of $\chi(l)$ near impurities including chain ends.[17] Indeed the shape of the observed background resembles the spectra in Fig. 1 calcu-

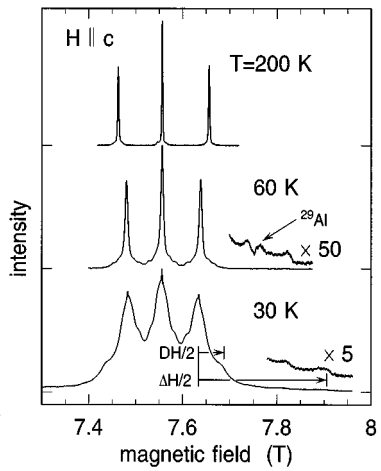

FIG. 3. The ^{63}Cu NMR spectra for $H\|c$ at 86 MHz. The peak at 7.76 T in the 60 K spectrum is due to Al_2O_3 contained in the NMR probe.

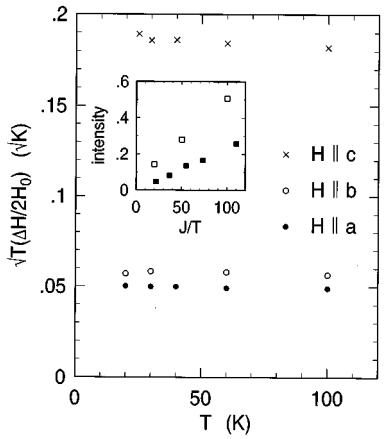

FIG. 4. Temperature dependence of the normalized background width multiplied by $\sqrt{T}$ (H_0 is the field at the central peak). In the inset is plotted the integrated intensity of the background normalized by the total intensity as a function of J/T. The solid squares show the experimental results for $H\|a$ and the open squares show the results obtained from the calculated spectra in Fig. 1.

lated for a chain end. We first focus on this broad background, in particular on its anisotropy and temperature dependence.

From the spectra for three different field directions, the anisotropy of ΔH is obtained as

$$\Delta H_a:\Delta H_b:\Delta H_c = 1:1.16\pm 0.03:3.73\pm 0.05, \qquad (7)$$

which is independent of temperature (see Fig. 4). This result is nearly identical to the anisotropy of the hyperfine coupling to the staggered magnetization $A_\alpha(\pi)$, which has been determined by the anisotropy of the nuclear spin-lattice relaxation rates $1/T_1$,[11,16]

$$|A_a(\pi)|:|A_b(\pi)|:|A_c(\pi)| = 1:1.12\pm 0.03:3.34\pm 0.04. \qquad (8)$$

This fact indicates that *the broad background is due to hyperfine coupling to local staggered magnetization* as expressed by Eq. (5). Even the small discrepancy between Eqs. (7) and (8) is consistent with approximately 10% anisotropy of the g value of Cu ions expected from crystal field effects.[18] Direct dipolar coupling to possible dilute impurity spins should be more isotropic.

In Fig. 4 is plotted the normalized width of the background $\Delta H_\alpha/2H_0$ (H_0 is the field at the central peak) multiplied by $\sqrt{T}$ as a function of temperature. It is independent of temperature, which is consistent with the theoretical prediction of Eq. (3). We emphasize that the $1/\sqrt{T}$ dependence of ΔH is unique and distinguished from conventional Curie behavior, which is expected for broadening due to isolated impurity spins. The integrated intensity of the background normalized by the total intensity represents the ratio of the spatial extent of the staggered magnetization to the average half chain length. As shown by the dots in the inset of Fig. 4, it varies as $1/T$, consistent with the result (open circles) for the spectra in Fig. 1 calculated for the half chain length of 450. Since the slope of this plot for the calculated spectra is about twice as large as that for the experimental data, we estimate the average chain length to be 1800 ± 500. It is not surprising that the chain length is much shorter than the average distance between impurity spins (5000–7000) estimated from the Curie term of the susceptibility, since χ_u near an end is not Curie like but close to the bulk susceptibility,[5,6] unlike spin-1 chains whose ends have extra free spin degrees of freedom.[1] Curie susceptibility arises from finite segments with odd numbers of spins only at low enough temperatures such that the whole segment is frozen into the ground state with total spin 1/2. Thus there will be a certain correlation between the Curie term and the density of defects that creates chain ends.

To make a quantitative comparison with the theory, the values of $|A_\alpha(\pi)|$ are calculated from the relation $\Delta H_\alpha/2H_0 = |K_{\mathrm{alt,max}}| = (\gamma_e/\gamma_n)0.137\sqrt{J/T}|A_\alpha(\pi)|/J$ [obtained from Eqs. (3) and (5)] with $J = 2200$ K and the data in Fig. 4. We obtained $|A_\alpha(\pi)|/(2\hbar\gamma_n) = 6.2$, 7.3, and 22.0 (T) for $\alpha = a$, b, and c, respectively. These values may be compared with the results for high-T_c cuprates having the similar local structure. The values of the anisotropic on-site coupling A^0 and the isotropic nearest-neighbor coupling A^1 in $YBa_2Cu_3O_{6+x}$ have been determined as $A_c^0/(2\hbar\gamma_n) = -16.4$, $A_{ab}^0/(2\hbar\gamma_n) = 3.2$, and $A^1 = 4.1$ T.[19] Since $A(q) = A^0 + 2A^1\cos q$ for a linear CuO_3 chain, these values give $|A_\alpha(\pi)|/(2\hbar\gamma_n) = 5.0$, 5.0, and 24.6 T for $\alpha = a$, b, and c, in good agreement with the above values. It should be noted that the strong q dependence of the anisotropy of $A(q)$ makes our result firm evidence for the staggered magnetization.

Although the background spectra show good agreement with the theoretical prediction for chain ends, we do not have direct evidence that the observed phenomena are due to chain ends. However, the following supportive argument can be made. As mentioned earlier, the excess oxygen is the most likely source of impurities. As in high-T_c cuprates, these oxygens will dope holes into the CuO_3 chains. The doped hole state will be the bonding combination of the four oxygen p_σ orbitals neighboring to one Cu site. The spin of a doped hole and the central Cu ion will then form a Zhang-Rice singlet[20] with a large binding energy of several eV and effectively decouple both sides of the chain. Furthermore, renormalization group analysis[4,6] shows that many other impurity models are reduced to decoupled chains with the open boundary condition at $T = 0$. Thus the results in Eqs. (1) and (2) are expected to be qualitatively valid for such impurities as well.

We also observed a good correlation between the impurity content and the intensity of the background. We have investigated an as-grown crystal showing a Curie term corresponding to 0.25% spin-1/2 impurities, which is an order of magnitude larger than the value for the Ar-annealed crystal, indicating a larger impurity concentration. Similar spectra were obtained. In particular, the positions of the edges and the shoulders (ΔH and DH) remain unchanged in both samples. However, the as-grown crystal shows a background intensity about 4 times larger than the Ar-annealed crystal. Unfortunately, we have been unable to estimate the impurity concentration quantitatively, since the susceptibility of a finite segment of arbitrary length is not known and possible contribution to the Curie term from other sources such as surface contamination, which would not affect the NMR spectrum of the bulk, cannot be excluded.

In contrast to the background spectrum, the central peak shows peculiar features, which are not seen in the calculated spectra and not understood yet. The separation between the shoulders (DH) has the same anisotropy as ΔH. Therefore, it should be also due to the staggered magnetization. However, DH follows approximately a Curie temperature dependence rather than $1/\sqrt{T}$. Deviations from the ideal open end boundary condition may change $\chi_{\mathrm{alt}}(l)$. However, Monte Calro results for more realistic impurity models do not show such a distinguishable structure.[21] Since the shoulder structure is not much enhanced for the less pure sample, it may not be a single-impurity effect.

The splitting or sharpening of the central peak is even more puzzling. The splitting δH observed for $H\|a$ and b suggests a tiny staggered magnetization spread over the whole crystal. We found that δH increases more rapidly than $1/T$ with lowering T and is larger for the as-grown crystal. Also δH varies only weakly with the field and extrapolates to a finite value at zero field, while both ΔH and DH are proportional to the field. These facts suggest that the splitting is not a single-impurity effect but caused by interaction among impurities. A plausible explanation for the sharp peak for $H\|c$ is the short even segments frozen into the singlet ground state. In fact, if the chain ends are distributed randomly, a few hundred ppm of the Cu sites should belong to segments much shorter than the antiferromagnetic correlation length at $T=30$ K. However, why such a sharp peak is not observed for other field directions remains to be explained.

In conclusion, we have observed the development of a broad background in the NMR spectrum in Sr_2CuO_3 due to field-induced local staggered magnetization near impurities, in quantitative agreement with the theoretical prediction for chains with an open end. However, the spectra show additional structure in the central peak, which remains to be explained.

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[1] M. Hagiwara *et al.*, Phys. Rev. Lett. **65**, 3181 (1990).
[2] M. Hase *et al.*, Phys. Rev. Lett. **71**, 4059 (1993).
[3] L. P. Regnault *et al.*, Europhys. Lett. **32**, 579 (1995).
[4] S. Eggert and I Affleck, Phys. Rev. B **46**, 10 866 (1992).
[5] S. Eggert and I. Affleck, Phys. Rev. Lett. **75**, 934 (1995).
[6] S. Eggert, Ph.D. thesis, University of British Columbia, Vancouver, 1994.
[7] A. Kerren *et al.*, Phys. Rev. B **48**, 12 926 (1993).
[8] T. Ami *et al.*, Phys. Rev. B **51**, 5994 (1995).
[9] S. Eggert, Phys. Rev. B **53**, 5116 (1996).
[10] N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. **76**, 3212 (1996).
[11] M. Takigawa, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. **76**, 4612 (1996).
[12] H. Suzuura *et al.*, Phys. Rev. Lett. **76**, 2579 (1996).
[13] K. Kojima *et al.*, Czech. J. Phys. **46**, 1945 (1996).
[14] The estimated value of J in the literature ranges from 1700 K (Ref. 9) to 3000 K (Ref. 12).
[15] The central peaks mentioned here should not be confused with the center line of the quadrupolar split spectrum. In fact all features mentioned in this paragraph are observed in the quadrupolar satellite lines as well.
[16] Since the spin fluctuations with the wave vector near $q=\pi$ are responsible for nuclear relaxation, $(1/T_1)_z \propto \{A_x(\pi)\}^2 + \{A_y(\pi)\}^2$.
[17] There is only one Cu site in a unit cell and no structural or magnetic transition has been observed above 5 K.
[18] R. E. Walstedt *et al.*, Phys. Rev. B **45**, 8074 (1992).
[19] H. Monien, D. Pines, and M. Takigawa, Phys. Rev. B **43**, 258 (1990).
[20] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[21] S. Eggert (private communication).