Local Magnetic Susceptibility of the Positive Muon in the Quasi-One-Dimensional $S = 1/2$ Antiferromagnet Dichlorobis (Pyridine) Copper (II)

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We report muon spin rotation measurements of the local magnetic susceptibility around a positive muon in the paramagnetic state of the quasi-one-dimensional spin 1/2 antiferromagnet dichlorobis (pyridine) copper (II). Signals from three distinct sites are resolved and have a temperature dependent frequency shift which is significantly different than the magnetic susceptibility. This difference is attributed to a muon induced perturbation of the spin 1/2 chain. The obtained frequency shifts are compared with transfer matrix density–matrix renormalization-group numerical simulations.

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Novel magnetic effects are predicted for a nonmagnetic impurity in a one-dimensional spin 1/2 antiferromagnetic chain [1–3]. In particular, at low temperatures the magnetic susceptibility in the region of a perturbed link is expected to differ dramatically from the uniform bulk susceptibility. Furthermore, the effects of such a perturbation propagate far along the chain and differ depending on whether the perturbation is link or site symmetric. The effect is closely related to Kondo screening of a magnetic impurity in a metal, and arises in part because of the gapless spectrum of excitations which characterizes a Heisenberg spin 1/2 chain. Although truly one-dimensional spin 1/2 chains have no long range ordering above $T = 0$, real materials always exhibit 3D Néel ordering due to the finite interchain coupling, $J_{\perp}$. Nevertheless the one-dimensional properties can be studied down to low temperatures ($T \ll J$) in quasi-one-dimensional systems where $J_{\perp} \ll J_{\parallel}$.

A $\mu$SR experiment is an ideal way to test such ideas since the muon acts as both the impurity and the probe of the local magnetic susceptibility. We anticipate that the positively charged muon will distort the crystal lattice, thereby altering the exchange coupling between the magnetic ions in the vicinity of the muon. The resulting modification of the local susceptibility will be reflected in the muon frequency shift.

In this paper we report the first muon spin rotation measurements on a powdered sample of dichlorobis (pyridine) copper (II) ($\text{CuCl}_2 \cdot 2\text{NC}_5\text{H}_5$) or CPC, which is a well-known quasi-1D Heisenberg $S = 1/2$ antiferromagnetic salt [4,5]. We find evidence of three magnetically inequivalent muon sites where the muon localizes upon thermalization. In particular the local spin susceptibility as measured by the muon frequency shift for two sites displays temperature dependence which is distinctly different from the bulk magnetic susceptibility. This
effect is attributed to a muon induced perturbation of the local spin susceptibility.

CPC has a monoclinic crystal structure ($P2_1/n$ space group) and consists of coplanar units assembled into polymeric chains in which each Cu$^{2+}$ ion is surrounded by four chlorine anions and two nitrogen atoms (see Fig. 1). Each Cu$^{2+}$ ion has two Cl$^-$ (1) ions (2.28 Å) located in the $a$-$b$ plane and two more distant Cl$^-$ (2) ions (3.05 Å) located on adjacent planes in the chain as illustrated in Fig. 1. The angle between the copper-chlorine and the copper-nitrogen bonds is close to 90°. The in-chain copper ions are separated by a distance of 3.57 Å, compared to the interchain nearest-neighbor separation of $b = 8.59$ Å [4]. This large interchain separation assures a high degree of one dimensionality. Note that despite the complex crystal structure the effective exchange coupling can be assumed to be isotropic as indicated by ESR and magnetic specific heat measurements [5,6].

In order to verify the effect of the $\mu^+$ perturbation and to test the theory we first measured the bulk susceptibility $\chi$ in fields of 0.5 T without the perturbing influence of the muon. The data were fit to the theory of Eggert, Affleck, and Takahashi [7] and precise values for the interchain coupling $J$ and $g$ factor were obtained. The excellent agreement with data is evident from Fig. 1, which shows the dc susceptibility of CPC along with the best fit curve. The theoretical fit to the experimental data is shown in Fig. 1. The angle between the copper-chlorine and the copper-nitrogen bonds is close to 90°. The in-chain copper ions are separated by a distance of 3.57 Å, compared to the interchain nearest-neighbor separation of $b = 8.59$ Å [4]. This large interchain separation assures a high degree of one dimensionality. Note that despite the complex crystal structure the effective exchange coupling can be assumed to be isotropic as indicated by ESR and magnetic specific heat measurements [5,6].

Figure 2 shows frequency spectra at 200 and 8.6 K which were obtained by fast Fourier transforming (FFT) the muon spin precession signal, which is analogous to the free induction decay in an NMR experiment. Near room temperature one observes a single narrow line, which is attributed to fast muon diffusion whereby the dipolar interactions with nuclear magnetic moments are motionally averaged. As the temperature decreases, the line becomes noticeably broadened and eventually splits into three frequency lines as the temperature drops below 25 K (see Fig. 2). At 8.6 K the best least-square fits show that there are two fast exponentially relaxing $\mu$SR signals (labeled as S1 and S2) with relaxation rates $\lambda_{S1} = 0.89(1) \mu$sec$^{-1}$ and $\lambda_{S2} = 0.57(2) \mu$sec$^{-1}$ and small amplitudes $A_{S1} = 0.06(4)$ and $A_{S2} = 0.04(2)$ and one slower relaxing signal (S3) with $\lambda_{S3} = 0.21(4) \mu$sec$^{-1}$ and a large amplitude $A_{S3} = 0.12(1)$. From this observation, it is clear that muons occupy more than one magnetically inequivalent site. Note from the spectrum at 8.6 K in Fig. 2 that three satellite lines are well resolved, implying three magnetically inequivalent muon sites. At low temperatures, signals S1 and S2 become very broad which is attributed to the spread of frequency shifts arising from the dipolar interaction in a powder. Above 30 K the lines merge due to the decreasing local spin susceptibility.

Because the measurements of the muon precession frequency signal in the CPC sample and a reference material (silver) were taken simultaneously, many systematic effects are eliminated. After correcting for the temperature independent Knight shift in Ag (+ 94 ppm) [9] and the small difference in field between the reference...
and sample (22 ppm), we obtain the frequency shifts for the three sites shown in Fig. 3.

A few important observations are in order. First, since the experiment was performed on a powdered CPC sample, the dipolar interaction contributes only to the linewidth and thus the magnitude of the frequency shift should depend only on the contact interaction [10]. The contact hyperfine interaction in CPC is attributed to either direct overlap of the wave function tails of the magnetic electrons with the $\mu^+$ or to the supertransferred hyperfine field arising from the covalency effects. Considering the localized nature of the Cu$^{2+}d$ orbital, the latter effect is more likely. In this picture, the implanted muon can be viewed as competing for bonding to the Cl$^-$ ions with some degree of spin density transfer onto the $\mu^+$ [11].

The three distinct signals indicate that there are at least three inequivalent sites where the muon may localize. We suggest that the two fast signals S1 and S2 correspond to sites where the muons are effectively locked between chloride ions, forming a strongly interacting complex (i.e., Cl$^-$-$\mu^+$--Cl$^-$) close to a Cu$^{2+}$ ion. Although from our measurements we cannot identify the exact muon locations in the crystal structure a similar complex has been identified in a variety of ionic solids containing fluorine [12] including another well-known $S = 1/2$ antiferromagnetic chain KCuF$_3$ [13].

This picture is consistent with the strong temperature dependence of the S1 and S2 signals which indicates a

FIG. 2. The evolution of the FFT transforms with temperature in CPC.

FIG. 3 (color online). Temperature dependence of the frequency shifts of the S1, S2, and S3 relaxing signals in CPC compared to the numerical calculations assuming two weak links of $J' = 0.34J$ for S1 and $J' = 0.36J$ for S2. For S3 a single weak link with $J' = 0.95J$ has been assumed.
strong perturbation of the local coupling parameters. A diverging Curie-like frequency shift has also been observed in another low-dimensional antiferromagnet, namely, the spin 1/2 ladder compound KCuCl₃ where the measured frequency shift does not scale with the bulk susceptibility at all [14]. In the present case, however, the divergence appears to be more logarithmic in temperature in agreement with the theoretical prediction for a site symmetric perturbation on two neighboring exchange couplings [1,15]. In fact the signals are quantitatively consistent with the local susceptibility of the closest Cu²⁺ ion from numerical transfer matrix simulations from Refs. [15,16] assuming two weak links of $J' = 0.34J$ for S1 and $J' = 0.36J$ for S2 as shown in Fig. 3. Although there is a clear deviation between the experiment and theory this is reasonable considering the simplified assumption that the muon affects only the closest exchange coupling $J'$ in the chain, which is the only adjustable parameter in the fit apart from the overall strength of the hyperfine coupling. The hyperfine coupling appears to have the opposite sign for the two signals S1 and S2, which is attributed to a site dependent hyperfine field induced by the polarized Cu²⁺ moments.

The signal S3 has a much weaker temperature dependence and resembles the bulk magnetic susceptibility displaying a minimum around 14 K, which is in the vicinity of the former characteristic peak seen in the dc susceptibility (see Fig. 1). Considering the large interchain distances in CPC (8.59 Å), it is likely that the S3 signal is associated with the muons thermalized in the interchain space, far from the super-exchange path. In this case, the signal can be compared to the numerical simulations of the nearest Cu²⁺ ions of a single weak link in the chain with $J' = 0.95J$.

In summary, the local magnetic susceptibility around the muon in quasi-one-dimensional $S = 1/2$ antiferromagnetic chain compound dichlorobis (pyridine) copper (II) has been investigated using the $\mu$SR technique. Signals from three distinct sites are identified and shown to have the local magnetic susceptibilities which are different from each other and for two locations are also significantly different from the bulk susceptibility $\chi$. The theoretical fits capture the effect of muon perturbation rather well. These results confirm the predicted high sensitivity of one-dimensional spin 1/2 chain compounds to impurity effect.

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