Local Magnetic Susceptibility of the Positive Muon in the Quasi 1D S=1/2 Antiferromagnet dichlorobis (pyridine) copper (II)

J.A. Chakhalian, R.F. Kiefl, R. Miller and J. Brewer
Department of Physics and Astronomy, UBC, Vancouver, BC V6T 1Z1, Canada

S.R. Dunsiger and G. Morris
Los Alamos National Lab, MST-10, MS K764, Los Alamos, NM 87545, USA

W.A. MacFarlane
Chemistry Department, University of British Columbia, Vancouver, Canada

J.E. Sonier
Department of Physics, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

S. Eggert
Institute of Theoretical Physics, Chalmers University of Technology and Göteborg University, S412 96 Göteborg, Sweden

I. Affleck
Physics Department, Boston University, 590 Commonwealth Ave., Boston, MA02215, USA

A. Keren
Physics Department, Technion, Israel Institute of Technology, Haifa 32000, Israel

M. Verdaguer
Laboratoire de Chimie Inorganique et Materiaux Moleculaires, Unite CNRS 7071, Universite Pierre et Marie Curie, 75252 Paris, France
(Dated: March 22, 2022)

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 DMRG numerical simulations.

PACS numbers: 71.10.Hf, 71.27.+a,76.75.+i,75.10.Pq

Novel magnetic effects are predicted for a non-magnetic impurity in a one dimensional spin 1/2 anti-ferromagnetic chain [1, 2, 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) (CuCl$_2$2NC$_5$H$_5$) or CPC, which is a well known quasi 1-D Heisenberg $S=1/2$ antiferromagnetic salt [4, 5]. We find evidence for three magnetically inequivalent muon sites where the muon localizes upon thermalization. In particular the local spin susceptibility

*Also at Department of Physics and Astronomy, The University of British Columbia, Vancouver BC, V6T 1Z1, Canada
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. This large interchain separation assures a high degree of one-dimensionality.

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 and precise values for the interchain coupling $J$ and $g$–factor were obtained. The excellent agreement with data is evident from Fig. 1. Note, although the theoretical procedure was developed to deal with the impurity problem, the unperturbed case is also an important test of the theory. Figure 1 shows the d.c. susceptibility of CPC along with the best fit curve according to the theoretical calculation. Within experimental limits the measured susceptibility $\chi(T)$ is close to that reported earlier but more accurate. The measured bulk susceptibility follows a Curie law at high temperatures, goes through a maximum around $T = 17.8$ K and then the slope starts increasing again. As seen in Fig. 1, the theoretical fit to the experimental data is excellent over the entire temperature range with deviations of less than 1%. The best fit yields a value of the intrachain Heisenberg coupling $J$ of 27.32(30) K and a $g$–factor of 2.08(1). This estimate of $J$ is about 2% larger than previously reported. This extremely good fit constitutes strong evidence for the validity of the calculation and manifests a further improvement in theory.

All $\mu$SR measurements were performed at the M20 beamline at TRIUMF which delivers nearly 100% spin polarized positive muons with a mean momentum of 28 MeV/c. The muon spin polarization was rotated perpendicular to the axis of the superconducting solenoid and muon beam direction. The magnitude of the applied magnetic field $H = 0.4$ T was chosen to provide a good balance between the magnitude of the frequency shift which increases with field and the amplitude of the $\mu$SR signal which eventually diminishes with increasing field due to the finite timing resolution of the detectors. The transverse field precession measurements were all performed with a special cryostat insert which allows spectra to be taken on the sample and on a reference material simultaneously.

Figure 2 shows frequency spectra at 200 K and 8.6 K which were obtained by fast Fourier transforming 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). The best least-square fits show that there are two fast relaxing $\mu$SR signals (labeled as S1 and S2) with small amplitudes $A_{S1} = 0.06$ and $A_{S2} = 0.03$ and one slow relaxing signal (S3) with a large amplitude $A_{S3} = 0.15$. From this observation, it is clear that muons occupy more than one magnetically inequivalent sites. Note from the spectrum at 8.6 K in Fig. 2 that three satellite lines are well resolved, implying three magnetically inequivalent muon sites. 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) 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. 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 super-transferred 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 $\mu^+$.

In CPC one can identify at least three inequivalent sites where the muon may localize. Two of them can be associated with a muon interacting with two chlorine ions (i.e. Cl$^-$–$\mu^+$–Cl$^-$). Note that a similar complex has been identified in a variety of ionic solids containing fluoride including another well known S=1/2 AF chain KCuF$_3$ and then the two fast relaxing signals (S1 and S2) can be attributed to those two sites where muons effectively ‘locked’ between two chloride ions and close to the Cu$^{2+}$ ion. The strong temperature dependence of the frequency shifts of the S1 and S2 signals suggests that the muon perturbation at these lattice sites is strong. In contrast, the frequency shift of the S3 signal is relatively small 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 d.c. suscep-
tibility (see inset in Fig. 1). This indicates that the S3 signal is attributed to the muons whose influence on the chain is weak. Considering the large interchain distances in CPC (8.59 Å), one can speculate that it is likely that the S3 signal is associated with the muons thermalized in the inter-chain space, far from the super-exchange path. Also note that the raw frequency shifts of S1 and S2 signals are similar but have opposite sign. This difference in sign is attributed to site dependent hyperfine field induced by the polarized Cu$^{2+}$ moments.

This overall muon behavior in CPC is also in agreement with the theoretical predictions. The solid lines in Fig. 3 show a quantitative comparison with the theoretical calculations\cite{1, 2, 14, 15}, assuming a completely broken link and two completely broken links, respectively. Here the muon has been assumed to ‘feel’ the local magnetic moment of the nearest copper atoms via a contact interaction of unknown strength. There are no other adjustable parameters in this fit. As seen in Fig. 3 the overall agreement is rather convincing and there is no doubt that the local susceptibility of the nearest neighbor Cu is significantly different from the bulk.

In summary, the local magnetic susceptibility around the muon in quasi 1D S=1/2 antiferromagnetic chain compound dichlorobis (pyridine) copper (II) (CPC) has been investigated using $\mu$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.

**Acknowledgments**

This research was supported by NSERC, CIAR and the Centre for Materials and Molecular Research at TRIUMF. The research of Ian Affleck was supported by the NSF grant DMR-0203159.

\begin{thebibliography}{99}
\bibitem{1} S. Eggert and I. Affleck, Phys. Rev. B \textbf{46}, 10 866 (1992).
\bibitem{2} S. Eggert and I. Affleck, Phys. Rev. Lett. 75, 934 (1995).
\bibitem{3} S. Eggert, UBC Ph.D. Thesis (unpublished), 1994.
\bibitem{4} J. D. Dunitz, Acta Crystallog. \textbf{10}, 307 (1957).
\bibitem{5} S. Eggert, I. Affleck and M. Takahashi, J. Phys. Rev. Lett \textbf{73}, 332 (1994).
\bibitem{6} W. Duffy, Jr. J.E. Venneman, D.L. Strandburg, P.M. Richards, Phys. Rev. \textbf{5}, 2220 (1974).
\bibitem{7} K. Takeda, S. Matsukawa and H. Haseda, J. Phys. Soc. Japan \textbf{30}, 1330 (1971).
\bibitem{8} J. Chakhalian, R.F. Kiefl et al., Hyper. Interact. \textbf{106}, 245 (1997).
\bibitem{9} A. Schenck, Muon Spin Rotation Spectroscopy: Principle and applications in solid state physics 128, (Adam Highler Ltd. Bristol and Boston) (1985).
\bibitem{10} A. Abragam, The Principles of Nuclear Magnetism , Oxford Univ Press, London (1970).
\bibitem{11} G.A. Sawatzky and F. Van Der Woude, J. Phys. (France) \textbf{C6}, 47 (1974).
\bibitem{12} J. H. Brewer, S.R. Kreitzman, D.R. Noakes, E.J. Ansaklo, D.R. Harshman and R. Keitel, Phys. Rev. B \textbf{33}, 7813 (1986).
\bibitem{13} J. Chakhalian, R. F. Kiefl et al., Physica B, in press (2002).
\bibitem{14} S. Eggert and S. Rommer, Phys. Rev. Lett. \textbf{81}, (1998) 1690.
\bibitem{15} S. Rommer and S. Eggert, Phys. Rev. B \textbf{62}, (2000) 4370.
\end{thebibliography}
FIG. 1: Theoretical fit to the SQUID CPC data: The data were taken in an applied magnetic field of 0.5 T. The inset show the chain of Cu$^{2+}$ ions (adopted from ref. [6]).
FIG. 2: The evolution of the FFT transforms with temperature in CPC.
Temperature dependence of the frequency shifts of the S1, S2 and S3 relaxing signals in CPC. In theory simulations, a link-symmetric muon location is assumed for the signals S1 and S2, whereas a site-symmetric location is assumed for the S3 signal.