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Local magnetic susceptibility of the positive muon in the quasi-1D $S = 1/2$ antiferromagnet $KCuF_3$

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Abstract

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 $KCuF_3$. Signals from two distinct sites are resolved which have a temperature-dependent frequency shift which is different than the magnetic susceptibility. This difference is attributed to a muon-induced perturbation of the spin 1/2 chain.

Keywords: Magnetism; 1D spin chains; Kondo problem; Impurities

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Novel magnetic effects are predicted for a non-magnetic impurity in a one-dimensional (1D) 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 (1D) spin 1/2 chains have no long-range ordering above $T = 0$, real materials always exhibit 3D Néel ordering due the finite interchain coupling, $J_\perp$. Nevertheless, the 1D properties can be studied down to low temperatures ($T \ll J$) in quasi-(1D) systems where $J_\perp \ll J_\parallel$.

A μSR experiment is an ideal way to test such ideas since the muon acts as both the impurity and

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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 muon spin rotation measurements on a single crystal of $KCuF_3$, which is a well-known quasi-1D Heisenberg $S = 1/2$ antiferromagnet [4,5]. We find evidence for two magnetically inequivalent FμF centers in which the muon is hydrogen bonded to two neighboring F^- ions implying a large lattice distortion. The raw frequency shifts are opposite for the two sites and they display temperature dependence which is distinctly different than the bulk magnetic susceptibility (χ). These effects are attributed to a muon-induced perturbation of the local spin susceptibility.

$KCuF_3$ has a tetragonal crystal structure with lattice parameters $c = 3.914$ Å and $a = 4.126$ Å at 10 K (see inset in Fig. 1). The structure is similar to a perovskite. However, a Jahn–Teller distortion in the *a–b* plane causes F^- ions in the *a–b* plane to be displaced slightly away from the edge center by 0.31 Å [6]. The magnetic properties of $KCuF_3$ arise from the $S = 1/2$ Cu^{2+} ions which are almost perfectly Heisenberg coupled but with very different coupling strengths for spins along the *c*-axis versus in the *a–b* plane. The ratio between the interchain and intrachain coupling constants $J_\perp/J_\parallel = 0.01$ with $J_\parallel = 190$ K so the system is very 1D. There are two polytypes (a and d) with slightly different arrangements of F^- ions and Néel temperatures of 39.3 and 22.7 K, respectively [5]. The crystal used in this experiment was polytype a as shown in Fig. 1. Recent ZF-μSR results indicate the magnetic transition in polytype a is first order [7].

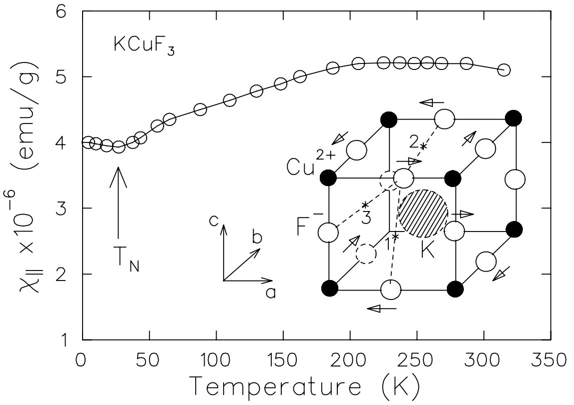

Fig. 1. Magnetic susceptibility of $KCuF_3$ measured in a SQUID magnetometer in the applied magnetic field of 1 T. An inset shows a tetragonal pseudo-unit cell of $KCuF_3$. The displaced F^- ions are indicated by arrows. Possible muon sites are indicated by the numbered $*$ symbol.

All the 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 $H = 1.45$ T was chosen to provide a balance between the magnitude of the frequency shift which increases with field and the amplitude of the μSR 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 [8].

Fig. 2 shows a frequency spectrum at 100 K obtained by fast Fourier transforming the muon

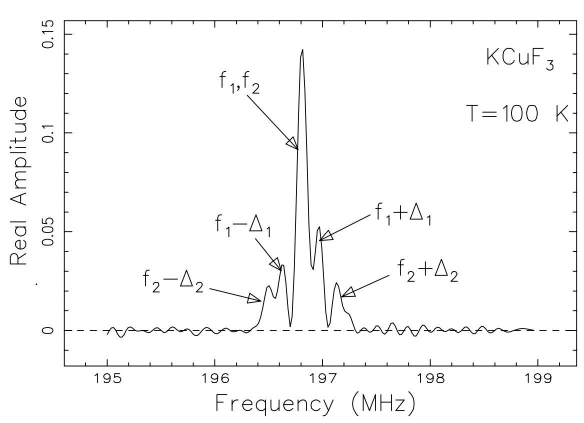

Fig. 2. Fourier transform of the μSR time spectrum measured in a field of 1.45 T applied along the *c*-axis.

spin-precession signal, which is analogous to the free induction decay in an NMR experiment. All the frequency shift measurements were taken with the external magnetic field applied along the *c*-axis. 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. Below room temperature the line broadens and develops clear splittings as shown in Fig. 2. Such splittings are attributed to the large ^{19}F nuclear moments and provide important information on the muons site and the symmetry of the perturbation that the muon induces. The observed splittings are characteristic of a static FμF center in which the positive muon forms a collinear ionic bond between two F^- ions [9]. The presence of the FμF center was also confirmed with measurements in zero applied field. Fig. 3 shows the characteristic muon oscillation in zero applied field for FμF in $KCuF_3$. The curve is a fit to the polarization signal generated from the spin Hamiltonian for FμF with a muon-^{19}F nuclear dipolar coupling $\nu_d = \gamma_\mu \gamma_F / r^3 = 0.216$ MHz where r is muon-^{19}F distance. This value of ν_d is typical of that seen in many compounds containing fluorine and implies a F–F separation of 2.38 Å which is about twice the ionic radius of the F^- ion [9]. Similar ZF spectra have recently been reported in polycrystalline $KCuF_3$ [7]. In a high transverse magnetic field one expects that each FμF center will give rise to a triplet of lines with an amplitude ratio of 1:2:1 and corresponding frequencies:

$$\begin{aligned} \nu^- &= \gamma_\mu B - \nu_d(1 - 3\cos^2\theta), \\ \nu^0 &= \gamma_\mu B, \\ \nu^+ &= \gamma_\mu B + \nu_d(1 - 3\cos^2\theta), \end{aligned} \qquad (1)$$

where B is the local magnetic field at the muon with no contribution from the ^{19}F nuclear moments, and θ is the angle between the magnetic field and the FμF bond axis. Note from the spectrum at 100 K in Fig. 2 that four satellite lines are well resolved, implying two magnetically inequivalent FμF centers with two distinct values of θ. The central lines are unaffected by the nuclear dipolar coupling and therefore are not resolved in the spectrum.

Good fits to all the data between 50 and 200 K were obtained with the above model assuming two static FμF centers with satellite splittings of $\Delta_1 = 0.30(1)$ MHz and $\Delta_2 = 0.17(1)$ MHz for sites 1 and 2, respectively. These splittings are slightly less than one would expect from the face center positions (sites 1 and 2 in Fig. 1) assuming that the angle between the *c*-axis and the F–F direction is unchanged by the muon. In this case we would expect dipolar splittings of approximately $1.9\nu_d$ and ν_d; whereas, the observed splittings are $1.4\nu_d$ and $0.8\nu_d$, respectively. Diagonal sites (site 3) are possible but the splittings for these sites should be about $0.5\nu_d$ and ν_d. We are led to the conclusion that F–F internuclear direction rotates slightly by the presence of the muon. In retrospect this is reasonable considering that the Jahn–Teller distortion displaces the F^- ions in the *a–b* plane so that the Cu–F bonds are not of equal strength. Therefore, we attribute the two signals to muons at sites 1 and 2 in Fig. 1. The large contraction of the F–F distance is typical of FμF centers seen in other F-containing compounds [9]. However, $KCuF_3$ is unusual in that the muon also produces a small rotation of the F–F internuclear direction. Such a large lattice distortion should produce a significant perturbation of the exchange coupling between the nearest-neighbor Cu^{2+} spins.

Measurements of the precession frequency signal in the sample and a reference material (Ag) were taken simultaneously. This eliminates many systematic effects, such as field drift, which

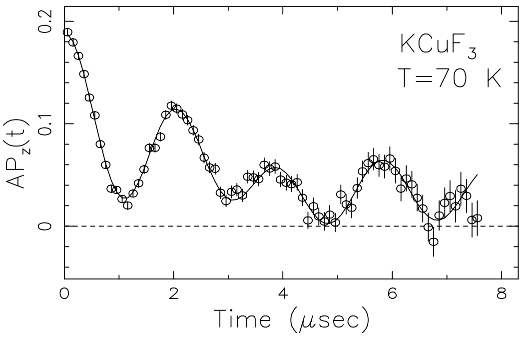

Fig. 3. Time evolution of the muon polarization in a zero applied magnetic field. The signal is characteristic of the muon-^{19}F nuclear dipolar interaction in an FμF center.

are important when the frequency shifts are small. After correcting for the temperature independent Knight shift in Ag (+94 ppm) [10] and the small difference in field between the reference and sample (22 ppm) we obtain the frequency shifts for the two sites shown in Fig. 4.

Note that the raw frequency shifts of f_1 and f_2 are similar but have opposite sign. This difference in sign is attributed to site-dependent dipolar field from the polarized Cu^{2+} moments. For example, if one subtracts a calculated dipolar field from all Cu^{2+} moments except the four nearest-neighbor Cu^{2+} assuming these more distant moments are polarized according to the bulk χ shown in Fig. 1, then one obtains the corrected frequency shifts shown in Fig. 4b. As may be inferred from Figs. 4a and 4b this correction is large and negative for site 1 and almost zero at site 2. The corrected frequency shifts in Fig. 4b are then both positive and originate from the local dipolar field from the four nearest-neighbor Cu moments plus the contact interaction. Note that the temperature dependence of the raw and corrected shifts are somewhat different, which is due to the fact that the size of the corrections are different and scale with the bulk susceptibility in Fig. 1. Clearly, the dipolar corrections to the frequency shift depend on the site. However, given the large deviations between the raw frequency shifts and the bulk χ (Fig. 1) the local χ must also be very different. In particular, the bulk χ in a spin 1/2 chain peaks at around J and decreases at lower temperatures due to short-range AF correlations. This is clearly not the case for f_2 where the magnitude of the shift increases dramatically below 200 K. The temperature dependence of f_1 on the other hand is somewhat weaker, but still quite different from the pure susceptibility. This behavior is in agreement with the theoretical predictions [1–3,11,12]. The solid lines in Fig. 4b show a quantitative comparison with the theoretical calculations [1–3,11,12] assuming a completely broken link (location 1) and two completely broken links (location 2), 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. The overall agreement is rather convincing, but some deviations should be expected since we assumed earlier that all Cu-atoms away from the muon have the same dipole moment, which is a simplification since an impurity in a 1D system will affect many magnetic sites in the chain [1–3,11,12].

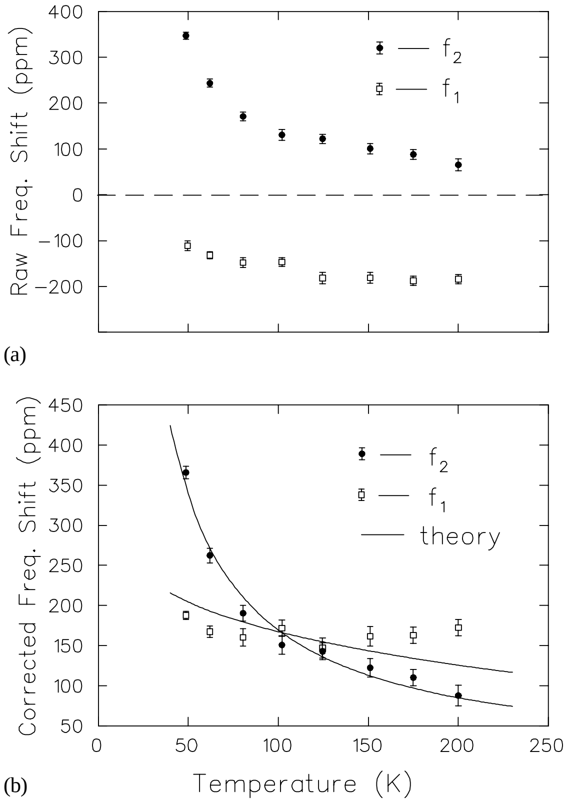

Fig. 4. (a) Temperature dependence of the raw muon frequency shifts at two interstitial sites in a magnetic field $H = 1.45$ T. (b) Frequency shifts for sites 1 and 2 subtracting the dipolar fields from all Cu^{2+} moments other than the four nearest neighbors.

In summary, the local magnetic susceptibility around the muon in quasi-1D $S = 1/2$ antiferromagnetic chain compound $KCuF_3$ has been investigated using μSR. Signals from two distinct sites are identified and shown to have the local magnetic susceptibilities which are different from each other and also different from the bulk χ. The theoretical fits capture the effect of muon perturbation rather well. These results confirm the high sensitivity of 1D spin 1/2 chain compounds to impurities.

Acknowledgements

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