Muon spin-rotation studies of the highly-frustrated quantum-spin system Zn-paratacamite

M.A. de Vries
Centre for Science at Extreme Conditions, The University of Edinburgh, UK
in collaboration with
A. Olariu, F. Bert, P. Mendels$^{(1)}$, A. Amato and C. Baines$^{(2)}$
(1) Lab. de Physique des Solides, Orsay France,
(2) Paul-Scherrer Intitute, Villingen Switserland.

January 16, 2006

1 Introduction

Last summer M.P.Shores *et.al.* reported on a structurally perfect $S = 1/2$ kagomé antiferromagnet [1] Zn-paratacamite. The $S = 1/2$ kagomé antiferromagnet has been of intense theoretical interest over the last 15 years [2, 3, 4, 5], and Zn-paratacamite seems to be the best physical realisation known to date. Hence the low-temperature magnetic properties and thermodynamics of this new material scream to be characterised.

For non-frustrated low-dimensional antiferromagnetic quantum-spin systems the energy gap between the classical Neél state and the theoretical quantum-mechanical non-magnetic groundstate seems to vanish in the macroscopic limit [6, 7]. In such cases the quantum effects can be accounted for by a renormalisation of the classical theory [8, 9]. In this respect the kagomé Heisenberg antiferromagnet is unique because even in the classical case no Néel order can exist down to the lowest temperatures. Magnetic moments are therefore expected to exist only as finite-energy excitations on a non-magnetic resonant-valence-bond(RVB) -like groundstate. The system is therefore called to be 'gapped', even though in this case it is expected [3] that this gap is filled with non-magnetic excitations.

In real physical systems all this is easily spoilt by a magnetic anisotropy or too strong dipole-dipole interactions, causing long range order at some finite temperature. Hence one of the first questions which arise is "Does this system show long-range magnetic order at low temperatures or does it remain in a fluctuating state?". Muon spin-rotation spectroscopy is the best way to answer this question.

In Edinburgh we had started synthesising Zn-paratacamite, and variations on it, soon after the above-mentioned work was published, and prof. P.Mendels invited me to join in the first muon characterisation on these samples during beam-time at the Low Temperature Facility (LTF) and the General Purpose Station (GPS) muon stations at the Paul Scherrer Institut (PSI) in Villingen, Switserland.

2 Description of work

Pellets were pressed of the powder samples; $ZnCu_3(OH)_6Cl_2$, $Zn_{0.67}Cu_{3.33}(OH)_6Cl_2$ and also $CdCu_3(OH)_6Cl_2$. All these samples were inserted in GPS in turn, and the forward and backward asymmetry of the muon relaxation was measured as a function of the muon lifetime in the sample, at temperatures between 1.5 and 40K, in zero-field, and with longitudinal and transverse fields of typically 100 Gauss.

Because the $ZnCu_3(OH)_6Cl_2$ sample remains paramagnetic down to 1.5 K, this sample was also measured in LTF, in which with a dilution fridge the temperature can be driven down to 20 mK.

3 Main results

We found that Zn-paratacamite stays perfectly paramagnetic down to 20 mK, which clearly is a remarkable result. We know of no other material with such strong super-exchange coupling (of the order of ≈ 60 K[1]) which is spin-liquid at these temperatures, and we expect that, were dipole-dipole or magnetic anisotropy to play any role, there would be a transition at much higher temperature.

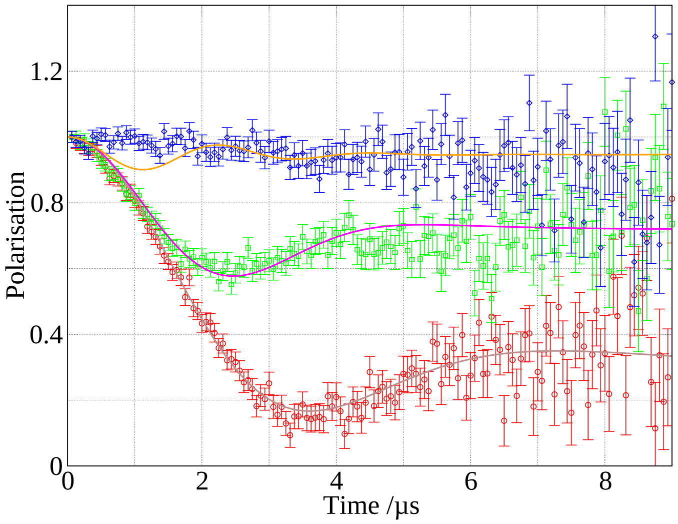

Figure 1: The muon-spin relaxation signal from $ZnCu_3(OH)_6Cl_2$ at 20 mK and in zero field (red circles), 11 ± 2 Gauss (Green squares) and 81 ± 2 Gauss (Blue diamonds). The lines are fits with double Gaussian distributions for increasing longitudinal external fields.

Figure 1 shows the zero- and longitudinal-field muon decay at 20mk. These muon relaxation signals can be fitted to the Kubo-Toyabe function, if we accept there are two main muon sites in the unit-cell. At the main site, accounting for $\approx 86\%$ of the muons, the local field is around 5 Gauss. At the second site which makes up the remaining 14% the field must be around 1 Gauss. When the nuclear dipoles are decoupled, there remains a slow relaxation resulting from fast paramagnetic fluctuations of $S = 1/2$ copper spins.

Another remarkable aspect of this system is that it can be doped from $ZnCu_3(OH)_6Cl_2$ all the way to $Cu_2(OH)_3Cl$. The latter is known as clinoatacamite, and it has a pyrochlore structure. This

---

[1] as obtained from a fit of the susceptibility data to the theoretically expected susceptibility using a Padé expansion[10].

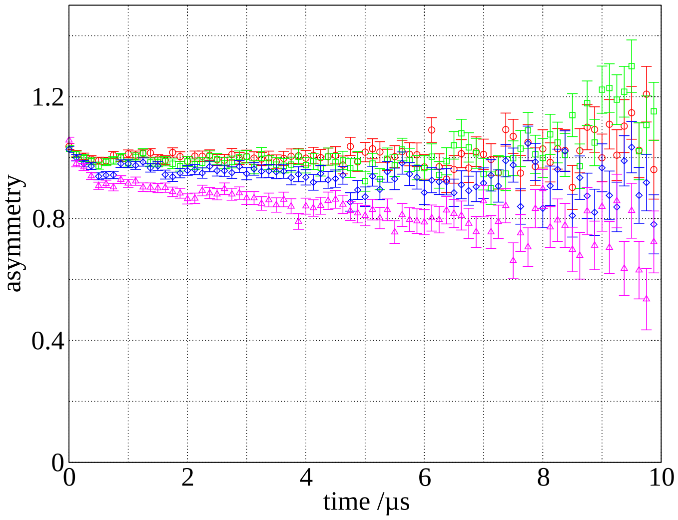

Figure 2: Muon-spin relaxation signal from $Zn_{0.67}Cu_{3.33}(OH)_6$ in a longitudinal field of 100 Gauss, at 10K (red), 5K (green), 3K (blue) and 2K (magenta).

material shows a currently ill understood sequence of phase transitions below 18K [11], and we hope that creating and studying the intermediate compounds will help us understanding both extremes. Hence measurements were carried out on $Zn_{0.67}Cu_{3.33}(OH)_6Cl_2$ and, $Zn_{0.33}Cu_{3.67}(OH)_6Cl_2$. The former remains fluctuating down to 20mK despite a progressive slowing down of the spins fluctuations below 1.1K. In the latter a glassy transition similar to the one of the pure Cu4 compound was observed.

$CdCu_3(OH)_6Cl_2$ has a similar structure to Zn-paratacamite, albeit with some problems of crystallinity, and there are more impurity phases contaminating this sample. More work is needed for a conclusive characterisation. From a muon perspective this material was worth studying. A slow, continuous freezing transition was observed to a glassy ground-state.

We are still working on a more detailed analysis of this data, as well as on ac-susceptibility- and specific heat data.

4 Conclusion

In this experiment we have confirmed that as predicted the perfect $S = 1/2$ kagomé antiferromagnet does not have a Néel ground state, at least down to 20mK. We believe that if dipole-dipole or magnetic anisotropy play a significant role in this system, they would cause a phase transition to a long range ordered Néel state at much higher temperature. Theoretical work [3] predicts that the spin-gap for this system lies at about $J/20$, which comes out at $\approx$ 3K in this case. This means we will be able to report on the first quantum paramagnet known, and we aim to submit a publication to a high ranked journal soon. The people involved from Edinburgh, Paris-sud and PSI aim to keep working closely together; Beam-time has been accepted for a further muon experiment at ISIS, and more susceptibility measurements might be carried out in Paris. In Edinburgh we are also trying to grow larger single crystals of Zn-paratacamite, for NMR experiments which will be carried out in prof. P.Mendels group in Paris-sud. We also aim to map-out the entire phase diagram between Zn-paratacamite and Clinoatacamite, and if chemically possible Zn-diluted Zn-paratacamite.

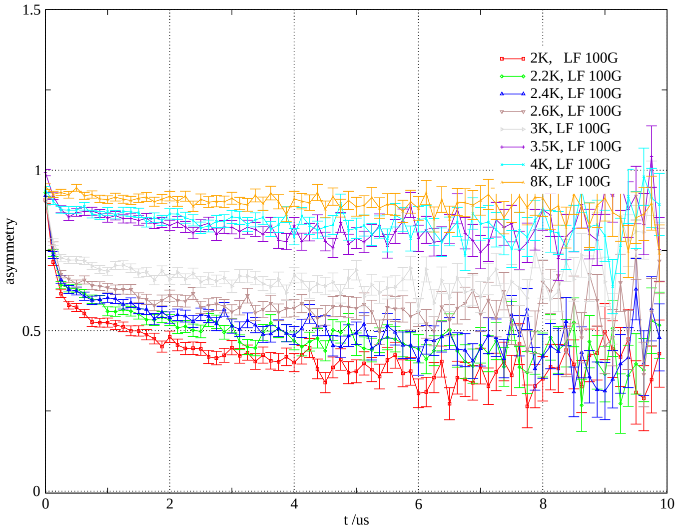

Figure 3: Muon spin-relaxation signal from $CdCu_3(OH)_6Cl_2$ in a longitudinal field of 100 Gauss and a temperature of 2K (red), 2.2K (green), 2.4K (blue), 2.6K (brown), 3K (grey), 3.5K (purple), 4K (cyan) and 8K (orange). Showing a slow glassy freezing transition.

References

[1] M.P.Shores *et.al.*, *A structurally perfect S = 1/2 kagomé antiferromagnet*, J. AM. Chem. Soc. **127** (2005), 13462-13463.

[2] A.Chubukov, *Order from disorder in a kagomé antiferromagnet*, Phys. Rev. Lett. **69** (1992), 832.

[3] Ch.Waldtmann *et.al.*, *First excitations of the spin 1/2 Heisenberg antiferromagnet on the kagomé lattice*, Eur. Phys. J. B **2** (1998), 501-507.

[4] B.H.Bernhard, B.Canals, C.Lacroix, *Green's function approach to the magnetic properties of the kagomé antiferromagnet*, Phys. Rev. B **66** (2002), 10442.

[5] G.Misguich, B.Bernu, *Specific heat of the S=1/2 Heisenberg model on the kagomé lattice: High-temperature series expansion analysis*, Phys. Rev. B **71** (2005), 014417.

[6] P.Fazekas, *Lecture notes on electron correlation and magnetism*, World Scientific, Singapore 1999.

[7] C.Lhuillier, *Frustrated quantum magnets*, arXiv:cond-mat **0502464** (2005).

[8] H.M.Ronnow, D.F.McMorrow, A.Harrison, *High-temperature magnetic correlation in the 2D S=1/2 antiferromagnet copper formate tetradeuterate*, Phys. Rev. Lett. **82** (1999) 3152-3155.

[9] O.P.Vajk *et.al.*, *Quantum impurities in the two dimensional spin one-half heisenberg antiferromagnet*, Science **295** (2002), 1691-1695.

[10] A.B.Harris, C.Kallin, A.J.Berlinsky, *Possible Néel orderings of the kagomé antiferromagnet*, Phys. Rev. B **45** (1992), 2899.

[11] X.G.Zheng *et.al.*, *Coexistence of long-range order and spin fluctuation in geometrically frustrated clinoatacamite* $Cu_2Cl(OH)_3$, Phys. Rev. Lett. **95** (2005) 057201.