Progress report for HFM exchange grant:

Neutron studies, the theory and the chemistry of a spin 1/2 kagomé antiferromagnet.

Visitor: Mark de Vries
Host: Prof. Henrik Rønnow, Laboratory for Quantum Magnetism, EPFL

November 8, 2007

1 Purpose of visit

The main subject of this exchange visit to the Laboratory for Quantum Magnetism at the EPFL, hosted by Professor Henrik Rønnow, was the recently discovered $S = 1/2$ kagomé antiferromagnet [1], the $x = 1$ phase of zinc paratacamite of general stoichiometry $Zn_xCu_{4-x}(OH)_6Cl_2$. A six month programme was proposed, to work on a select number of tightly linked topics;

- The improvement of the synthesis of a recently discovered experimental $S = 1/2$ kagomé antiferromagnet.
- Study the influence of high-pressure on the transport and magnetic properties of zinc paratacamite.
- Studies of copper acetate monohydrate (including the synthesis of large crystals) in order to test the balance between direct and kinetic exchange interaction.
- Pursue theoretical ideas developed during the applicants PhD, including a systematic study of the broken and non-broken symmetries in condensed matter systems with increasingly narrow bands.

The $x = 1$ phase of zinc paratacamite is by far the best known physical realisation of the $S = 1/2$ kagomé antiferromagnet. Muon spin relaxation measurements have confirmed that according to theoretical expectations the system does not freeze, even at 50 mK [2], and hence this system is of outstanding theoretical interest. However, the interpretation of experimental data is far from straightforwards, due to antisite disorder between the Cu^{2+} ions on the kagomé lattice and Zn^{2+} ions on the interplane Zn sites. From neutron diffraction, heat capacity and magnetic susceptibility measurements the antisite disorder was found to be between 18 and 30% in Zn^{2+} and 6 to 10% in Cu^{2+} [3, 4, 5].

Zinc paratacamite is most commonly synthesised hydrothermally at 200°C, with a slow cooling-down period. Vastly increased cool-down periods during the synthesis have not been found to reduce the antisite disorder. We now hope to reduce the entropy built into the crystals by reducing the temperature at which the synthesis is carried out. It is well known that zinc paratacamite can be synthesised at temperatures [6] as low as room temperature, but the applicant has found that this leads to a reduced sample quality, even when the reaction time is extended to several months. This is evident from broader peaks on the X-ray powder diffraction patterns.

2 Work carried out and results obtained

2.1 Experimental work

Presently we are investigating the influence of the pressure at which the hydrothermal synthesis is carried out to the sample quality. The vapour pressure of water at 200°C is $\sim$ 15 Bar, which is the pressure realised in the reaction vessel during synthesis. When a small volume of methanol is added to the reaction mixture before the reaction vessel is sealed, the same pressure can be achieved at a temperature of only 150°C. Using this method with an extended reaction time of two weeks has yielded phase-pure zinc paratacamite of high quality, as confirmed by X-ray powder diffraction and DC-SQUID magnetometry both within the host institute. However, the magnetic susceptibility of zinc paratacamite synthesised using this method also indicates that lower temperatures are required to obtain a significant reduction in the antisite disorder.

To be able to carry out the synthesis at pressures up to 16 Bar but at temperatures well below 150°C, we have developed a reaction vessel which can be pressurised using an external pump. Here we greatly benefited from the help of Henri Jotterand of the "Laboratoire de physique des couches minces" and from the infrastructure already present at the "Institute Physique Materie Condensée" (IPMC) at the EPFL. Different methods for pressurising the reaction vessel have been tested, and the simplest solution was found to be to connect the vessel to a bottle of pressurised nitrogen via a pressure reducing valve. Currently we are still working to improve the air-tightness of the set-up after prolonged periods of heating to up to 100°C, but expect to start the synthesis using this system in the first week of November.

Copper acetate mono hydrate (CAMH) crystals can be grown by cooling down a solution of copper acetate saturated at 60°C. Using this method we have obtained single crystals up to $3 \times 4 \times 2$ mm^3, but we are exploring several ways to achieve a slow and controlled crystallisation from solutions onto a single seed crystal at room temperature, under a constant nitrogen flow. A closely controlled environment has been set up where presently 4, and soon 8 crystal growths can be carried out and controlled independently. We hope to find a reproducible recipe for the growth of large crystals by monitoring the nitrogen flow, temperature evolution, air humidity and evaporation rate. Currently we have succeeded in growing exceptionally large crystals of around 1 cm^3 (2 g), and it is clear that we will soon be in a position to start the synthesis of high-purity deuterated single crystals for neutron spectroscopy measurements.

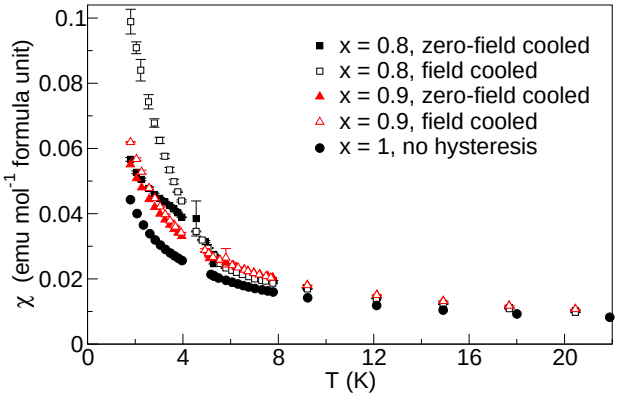

Figure 1: The zero-field cooled and field cooled magnetic susceptibility for zinc paratacamite with $x = 0.8$ and $x = 0.9$ compared with the susceptibility for $x = 1$ which has a negligible hysteresis.

2.2 Computational work

The magnetic susceptibility showing a magnetic hysteresis for samples with $x < 1$, as shown in figure 1 suggests that the antisite disorder for these phases might induce a symmetry-broken state in which a mean-field approximation can be applied. To test this idea we have carried out classical Monte Carlo simulations of zinc paratacamite with $x = 0.5$, $x = 0.7$ and $x = 1$, including the antisite disorder as present in the real material. These calculations have been carried out on lattices of up to $8 \times 8 \times 4$ crystallographic unit cells using a program developed by the applicant [7]. It was found that no freezing occurs even at $x = 0.5$, when in addition to the strong exchange interaction J_1 between the Cu^{2+} ions on the kagomé lattice a weaker exchange ($J_2 = 0.005J_1 \ldots 0.9J_1$) between the Cu^{2+} spins on the kagomé lattice and Cu^{2+} spins on Zn sites (antisite spins) was included. This confirms that the problem of the anisotropic and diluted pyrochlore lattice is closely related to that of the isotropic diluted pyrochlore antiferromagnet [8]. It was also found that the geometric frustration in the kagomé layers is only lifted to a very small degree, with the experimentally observed levels of antisite disorder. We conclude that in addition to J_1 and J_2 as defined above, there must be an exchange pathway between neighbouring antisite spins (J_3), which is most likely ferromagnetic, to explain the "freezing" which occurs for lower x. Currently we are adapting the Monte Carlo software so that simulations can be made with a small ferromagnetic value for J_3. These results will provide the basis for numerical solutions of the mean field-hamiltonian on the same lattices.

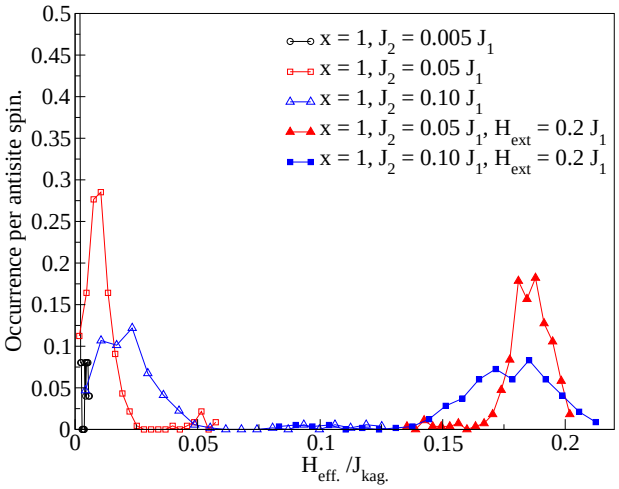

Figure 2: The distribution of effective fields from the kagomé layers as *seen* by the antisite spins in the $x = 1$ zinc paratacamite structure with 30% antisite disorder in Zn, for different J_2.

For each ground state configuration generated by the Monte Carlo simulation, a histogram was made[1] of the effective fields $H_{i,\mathrm{eff}} = \sum_j J_{ij}\langle S_j\rangle + H_{\mathrm{ext}}$ as "seen" by the antisite spins. It was found that for $J_2 < 0.01J_1$ the effective field from the kagomé layers vanished as $T \to 0$, while for a larger J_2 distributions as shown in figure 2 were found. Both the distribution of fields as well as the dependence of the effective field on an external field for $J_2 = 0.05J_1$ are in good agreement with the level splittings found in the heat capacity [3] and neutron spectroscopy data [4] for $x = 1$. Heat capacity data suggests that for $x < 1$ the level splitting increases from 1.7 eV to 2.1 eV for

[1] Thanks to Gøran Nilsen for this suggestion

$x = 0.8$, while at the same time a magnetic hysteresis develops (figure 1) and the spin fluctuations slow down [2]. In the calculations an only a very small increase of the effective field is observed for $x = 0.7$. Again this points to the importance of direct interactions between the antisite spins. We have also considered the scenario where $J_2 < 0.01J_1$ and only direct interactions between the antisite spins J_3 are taken into account. However, since an 70% - 80% diluted triangular lattice is not frustrated the distribution of effective fields was in this case found to be discrete, for each antisite depending mainly on the number of its nearest neighbours. We are still working on comparison with experimental results, to decide whether this scenario can be ruled out or not.

3 Future collaborations with the host institution

The applicant is anticipated to stay at the EPFL another three months. This time will be needed to take benefit of the experimental progress which has been made over the first three months of the exchange. First of all, we expect it will yield zinc paratacamite with a lower degree of antisite disorder. This material would be an important testing stone for the interpretations of the presently available experimental data. The resulting samples will be characterised using neutron diffraction at the Paul Scherrer Institute (PSI) and the ILL in Grenoble, DC-SQUID magnetometry in the Laboratory for Quantum Magnetism, and heat capacity measurements at PSI.

It is furthermore expected that the first high-pressure transport measurements will be carried out early November in collaboration with Anna Kusmartseva of the Laboratory of Nanostructures and Novel Electronic Materials. In case the sample becomes (semi-)conducting at the pressures achieved in this set up (30 kbar), then further high-pressure experiments will be carried out, in particular using neutrons, to study the relationship between the conductivity and the magnetic properties.

We will also prepare a deuterated sample of $x = 0.8$ zinc paratacamite, on which neutron diffraction will be carried out. Our analysis of the heat capacity data of this phase [3] indicates that most Cu^{2+} added to the structure as compared to the $x = 1$ phase will replace a Zn^{2+} ion on the kagomé lattice. In the heat capacity this is observed relatively indirectly. Neutron diffraction will provide a more direct evidence in case the $x = 0.8$ phase is, from a structural point of view, an equally good, or an even better physical realisation of the $S = 1/2$ kagomé antiferromagnet than $x = 1$ zinc paratacamite.

On the CAMH sub project a number of large deuterated crystals shall soon be available. Beamtime for initial studies is being arranged at IN4, ILL Grenoble.

The theoretical interactions with theory experts at the host institution, most importantly Andreas Läuchli, are just starting to take off, and the next three months will see the implementation of mean-field calculations of the magnetic properties in zinc paratacamite over the entire range of stoichiometries. We will also investigate the effect of a Dzyaloshinsky Moriya interaction in the zinc paratacamite structure using classical Monte Carlo simulations.

4 Present and anticipated publications

The financial support from the ESF has so far helped towards towards the following publications.

- P. Mendels, F. Bert, M. A. de Vries, A. Olariu, A. Harrison, F. Duc, J. C. Trombe, J. S. Lord, A. Amato, and C. Baines. Quantum magnetism in the paratacamite family: Towards an ideal kagomé lattice. *Phys. Rev. Lett.*, vol. 98, no. 7, p. 077204, 2007.

- M. A. de Vries. Spinner, a classical spin-lattice simulation program, using markov-chain monte carlo. http://www.ccp5.ac.uk/librar.shtml#Internal, August 8, (2007).

- M. A. de Vries, K. V. Kamenev, W. A. Kockelmann, J. Sanchez-Benitez, and A. Harrison. Antisite disorder and the magnetic groundstate of an experimental $S = 1/2$ kagomé antiferromagnet. Resubmitted to *Phys. Rev. Lett.*, See also arXiv.org:0705.0654 (2007).

In addition the following publications are anticipated.

- M. A. de Vries, T. K. Johal, A. Mirone, P. Bencok, G. Nilsen, G. van der Laan and A. Harrison. An X-ray spectroscopy study on the geometrically frustrated antiferromagnet iron jarosite; an explanation for the zero-field splitting of $3d^5$ $S = 5/2$ spins. (Manuscript in preparation)
- M. A. de Vries, R. J. Stewart, P. Deen and A. Harrison, Neutron spectroscopy studies on the $S = 1/2$ kagomé antiferromagnet $ZnCu_3(OH)_6Cl_2$.

5 Acknowledgements

The author thanks Claudine Lacroix for providing the opportunity to give a talk at the CNRS in Grenoble, and Philippe Mendels, Virginie Simonet, Gøran Nilsen and Andreas Läuchli for helpfull discussions. Henri Jotterand is acknowledged for lending his technical expertise which greatly helped towards the high-pressure low-temperature synthesis set-up. Special thanks to Henrik Rønnow for his help, and the many ideas and suggestions he has offered.

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