H3. PRESSURE INDUCED FERROMAGNETIC SPIN GLASS TRANSITION IN THE GEOMETRICALLY FRUSTRATED PYROCHLORE $(Tb_{1-x}La_x)_2Mo_2O_7$

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In the pyrochlore compounds $R_2Mo_2O_7$, both rare earth R^{3+} and M^{4+} transition metal ions form a three-dimensional network of corner sharing tetrahedra. The pyrochlore lattice is geometrically frustrated both for antiferromagnetic (AF) and ferromagnetic (F) nearest-neighbour exchange interactions, leading to intriguing magnetic states such as spin liquids, spin ices or chemically ordered spin glasses. Pyrochlores are extensively studied since their electrical and magnetic properties strongly depend on the rare earth ionic radius r. Compounds with small ionic radius Y, Dy and Tb are spin glass (SG) insulators, whereas those with Gd, Sm and Nd are ferromagnetic metals. $(R,R')_2Mo_2O_7$ series with different substitutions on the R^{3+} site show a universal dependence of the transition temperature versus r [1], suggesting that Mo-Mo interactions change sign at a critical value r_c, which controls the SG-F threshold. Band structure calculations and photoemission experiments [2] point out that the concomitant changes of the transport and magnetic properties come from strong electron correlations in the Mo t_{2g} band nearby the Fermi level. Up to now, there has been no microscopic investigation of the SG/F threshold, so as to follow the changes in the magnetic correlations and spin fluctuations. To understand the role of interatomic distances in this transition, the most direct way is to combine applied pressure and chemical pressure. We studied the $(Tb_{1-x}La_x)_2Mo_2O_7$ system, allowing us to cross the critical threshold by both chemical and applied pressure. By using three microscopic probes, namely neutron diffraction, μSR and synchrotron X ray diffraction, this study provides the first and complete characterization of the SG-F threshold [3].

Magnetic diffraction patterns were recorded on the powder diffractometers G61 and G41 of the Laboratoire Léon Brillouin (LLB) at ambient pressure, and under pressure on G61. Starting from the spin glass $Tb_2Mo_2O_7$, the dilution by *non magnetic* La ion expands the lattice, inducing long range magnetic order (LRO), which is further destroyed under pressure (Fig.1). Clearly, negative chemical pressure and applied pressure have reversed effects on the magnetic order. The magnetic structure (Fig.2) was solved by a systematic search, using the program BasIreps and symmetry-representation analysis combined with Fullprof. We searched for a solution in the in the space group I41/amd, the highest subgroup of the Fd-3m space group allowing F and AF components simultaneously. In the ordered structure with **k**=0 propagation vector, the four tetrahedra of the cubic unit cell are equivalent, for both Tb and Mo lattices. In a given Tb tetrahedron, the Tb^{3+} moments orient in the local spin ice (2in-2out)

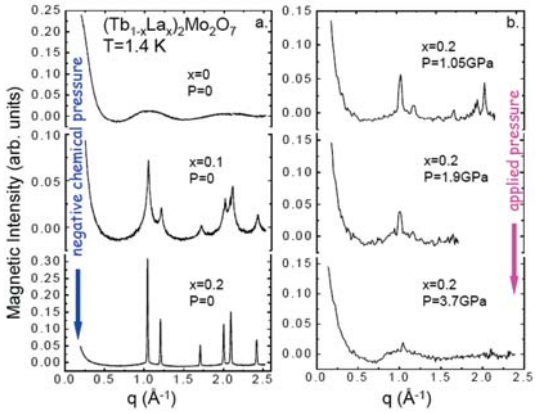

Figure 1. Magnetic intensity of $(Tb_{1-x}Lax)_2Mo_2O_7$ at 1.4 K versus the scattering vector q=4psinθ/λ. The neutron wavelength is λ=4.741 Å. A spectrum in the paramagnetic phase (70 K) was subtracted and the magnetic intensity was scaled to the (222) nuclear peak intensity.

structure, with a small angle qt with the local <111> anisotropy axes. Their F component orders along a [001] axis. The Mo moments align close to a [001] axis, with a slight tilting θ_m towards the local <111> axis (inset Fig. 2). Mo and Tb moments are F coupled.

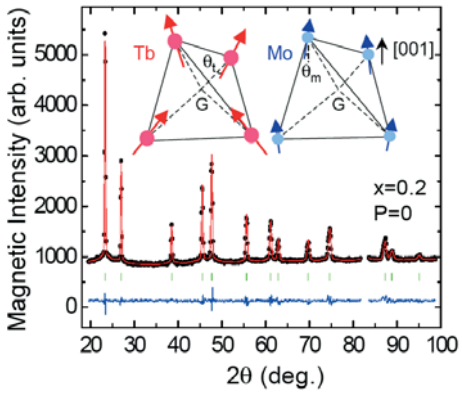

Figure 2. Magnetic intensity for x=0.2 at 1.5 K versus the scattering angle 2q, λ=2.426 Å. A 70 K spectrum was subtracted. Solid lines show the best refinement and the difference spectrum (bottom). In inset: magnetic structure of the Tb- and Mo- tetrahedra.

As a striking feature, the long range order (LRO) is induced by diluting the Tb lattice with a non magnetic ion. It proves that the main effect of dilution is the lattice expansion. From the variation of the lattice constant, a small La content (x~0.06) is expected to induce the SG-F transition. The SG-F transition is mostly determined by the change in sign of the Mo-Mo exchange interactions and the onset of F interactions like in $Nd_2Mo_2O_7$ [4]. We notice that Tb magnetism should still play a role since $(Y_{1-x}La_x)_2Mo_2O_7$ compounds do not show LRO. The non collinear structure for both Tb^{3+} and Mo4+ comes from the uniaxial anisotropy of the Tb^{3+} ion, which brings spin ice frustration in the ferromagnetic region. The ground state moments are strongly reduced with respect to the free ion values.

Under pressure, the ordered moments (x=0.2) decrease and reorient. At 1.05 GPa, LRO and SRO phases coexist. The ordering temperature decreases under pressure. At 3.7 GPa the Bragg peaks disappear (see Fig. 3a). When fitting the 3.7 GPa data with a SRO model [5] involving correlation parameters up to the fourth neighbours, we find short range F Tb-Tb spin correlations and AF Tb-Mo spin correlations. So the Tb-Mo correlations change sign at the threshold. The strong intensity at small angles, not taken into account by the SRO model was fitted by a Lorentzian, yielding a mesoscopic correlation length between Tb moments of 18(7) _. All parameters are close to the values in $Tb_2Mo_2O_7$ spin glass.

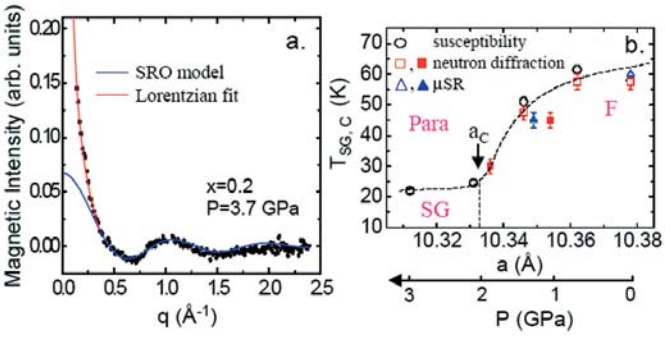

Figure 3. a. Magnetic intensity for x=0.2 sample at 1.4 K and 3.7 GPa. Lines are fits using SRO model and Lorentzian fit respectively. b. Phase diagram for $(Tb_{1-x}La_x)_2Mo_2O_7$ in the threshold region: ambient pressure (open symbols) and under pressure (full symbols).

μSR measurements (Fig. 4) shed a new light on the magnetic order by probing the spin fluctuations and the static local field below T_C. We measured the x=0.2 sample at ambient pressure on GPS and GPD at the Paul Scherrer Institute (PSI) and at 1.3 GPa on GPD. Data analysis allows us to separate the dynamic term λ_Z and static terms $<B_{loc}>$ and λ_T (see [3] for a complete description). The longitudinal relaxation rate λ_Z which reflects the spin fluctuations shows a critical peak at TC then a broad maximum at a lower temperature T*. The static terms reflecting the static local field "seen" by the muon spin, scale with the Tb moment measured by neutrons. The dynamical anomaly at T*, akin to that observed in $Sm_2Mo_2O_7$ and re-entrant spin glasses, suggest a freezing of short range correlated moments. It occurs without any anomaly in the static terms, which means that it does not break the LRO.

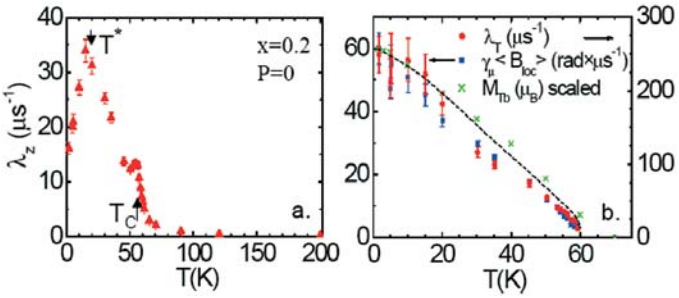

Figure 4. μSR ambient pressure results for x=0.2. Temperature dependence of: a. λ_Z. b. $<B_{loc}>$, λT and M_{Tb} (scaled).

The phase diagram (Fig. 3b) shows the transition temperatures determined by all probes versus the lattice constant. The equation of state a(P) measured by X ray synchrotron diffraction at ID31 (ESRF) allowed us to combine ambient pressure data on compounds with different x, with high pressure data for x=0.2. The critical lattice constant agrees with previous determinations [1].

The fact that high pressure and ambient pressure data merge in a single curve supports a dominant mechanism induced by a change in the Mo-Mo interactions. But our microscopic study also shows important features not taken into account by current theories: i) the role of rare earth magnetism at the threshold should be taken into account. ii) the mechanism by which Mo-Mo interactions change sign should be different under chemical pressure and applied pressure. In the fist case, it reflects the aperture of a Mott-Hubbard gap, yielding an insulating spin glass. In the second case, it is likely connected with the increase of the Mo bandwidth, yielding a metallic spin glass. iii) the role of Tb anisotropy in the spin correlations and fluctuations is clarified thanks to a comparative study in $Gd_2MO_2O_7$. In $Gd_2Mo_2O_7$, with isotropic Gd ion, the ferromagnetic ground state is collinear and the transition at T* is strongly suppressed [6]. The rare earth anisotropy also plays a role on the conductivity, leading to a giant abnormal Hall effect in the ferromagnetic region.

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