Charge and orbital correlations in single crystalline $Y_2Mo_2O_7$

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The cubic pyrochlore structure ($A_2B_2O_7$) can be thought of as two interpenetrating networks of corner sharing tetrahedra (with A and B sublattices). This family of oxides has been well studied with ground states ranging from the canonical spin ices $C_2D_2O_7$ (C = Ho, Dy) [1], to the dynamic spin ice $Pr_2Sn_2O_7$ [2], to potential spin liquids $Yb_2Ti_2O_7$ [3], $Tb_2Ti_2O_7$ [4] and $Er_2Sn_2O_7$ [5], to a host of spin glasses [6-8]. $Y_2Mo_2O_7$ is perhaps one of the most frequently studied pyrochlores, the first of which dates back over three decades [9]. Powder $Y_2Mo_2O_7$ displays all the experimental signatures of spin glass behaviour including a FC-ZFC split in the susceptibility, linear temperature dependence in the heat capacity, a strong frequency dependence in both the real and imaginary parts of the AC susceptibility, a sharp increase in the time-scale of the spin-fluctuations below T_g, and finally, the absence of magnetic Bragg peaks in neutron diffraction. However, no bulk structural disorder, thought to be a prerequisite for spin glass behaviour, has ever been reported. Although recent NMR, EXAFS, and nPDF experiments have shown signs of local disorder, whether or not this is enough to elucidate the spin glass state is debatable [10-12]. Furthermore, signs of local magnetic ordering have been seen with neutrons at the NCNR (NIST) near the glassy transition temperature T_g = 22.5 K [13]. The gap in our understanding of the underlying physics may be due to the powder nature of these samples. Until now, no single crystal has ever been synthesized due to the rapid oxidation of Mo^{4+} to non-magnetic Mo^{6+} at growth temperatures. But we have made, to our knowledge, the world's first single crystalline sample of $Y_2Mo_2O_7$ using the floating zone technique with an inert or slightly reducing atmosphere.

Initial characterization of this compound yielded similar behaviour to the powder samples except with respect to the heat capacity measurements: a T^2 relationship was observed below 10 K which is still unexplained (Figure 1). Neutron diffraction experiments confirmed previous findings of a broad peak in the diffuse scattering centered at Q = 0.44 A^{-1} appearing below T_f = 22.5 K. However, we have determined that the diffuse scattering is completely isotropic and can be seen in the inelastic channel above T_f at temperatures as high as 300 K (Figure 2). New to this study is the presence of elastic diffuse scattering in regions as far out as Q = 8.5 A^{-1} persisting at least until temperatures 100 K, higher than the Weiss temperature θ = -200 K (Figure 3). An experiment was carried out on the C5 triple axis spectrometer to further study this diffuse scattering. We used a vertically focusing PG002 monochromator, flat PG002 analyzer with fixed final energy E_f = 3.52 THz, a single filter and a [none, 0.8°, 0.85°, 2.4°] collimation setting. A series of line scans were made along the <HH0> direction and reorganized into a mesh scan (Figure 3). The butterfly pattern of diffuse scattering seen on the CNCS is completely reproducible using the triple axis instrument. Charge or orbital disorder must be the origin for such high-T, high-Q diffuse scattering and most probably plays a role in the glassy nature of the ground state.

All of this data can be explained via a freezing mechanism from an orbital liquid state. Fluctuating Mo-O and Y-O distances change the spin state of each Mo^{4+} to create a broad continuum. The isotropic inelastic ring of scattering is due to these fluctuations. As the Mo^{4+} spins freeze out below T_f, the orbitals freeze in random orientations. The inelastic ring should move to the elastic channel. Orbital disorder would be seen at high-

Q in the form of diffuse scattering. In this way, the underlying orbital disorder nucleates the spin-glass state at low temperatures. X-ray synchrotron or polarized neutron scattering is needed to confirm that the high-Q diffuse scattering is not due to spin.

References

[1] T. Fennel, O.A. Petrenko, B. Fåk, J.S. Gardner, S.T. Bramwell and B. Ouladdiaf, Phys. Rev. B 72, 224411 (2005).

[2] H.D. Zhou, C.R. Wiebe, J.A. Janik, L. Balicas, Y.J. Yo, J.R.D. Copley and J.S. Gardner, Phys. Rev. Lett. 101, 227204 (2008).

[3] K.A. Ross, L. Savary, B.D. Gaulin and L. Balents, Phys. Rev. X 1, 021002 (2011).

[4] J.P.C. Ruff, B.D. Gaulin, J.P Castellan, K.C. Rule, J.P Clancy, J. Roriguez and H.A. Dabkowska, Phys. Rev. Lett. 99, 237202 (2007).

[5] P.M. Sarte, H.J. Silverstein, B.T.K. Van Wyk, J.S. Gardner, Y. Qiu, H.D. Zhou, and C.R. Wiebe, J. Phys. Condens. Mat. 23, 382201 (2011).

[6] J. Yu, A. Huq, C.H. Booth, G. Ehlers, J.E. Greedan and J.S. Gardner, J. Phys. Condens. Mat. 23, 164214 (2011).

[7] H.D. Zhou, C.R. Wiebe, A. Harter, N.S. Dalal and J.S. Gardner, J. Phys. Condens. Mat. 20, 325201 (2008.)

[8] H.D. Zhou, C.R. Wiebe, J.A. Janik, B. Vogt, A. Harter, N.S. Dalal and J.S. Gardner, J. Solid State Chem. 183, 890 (2010).

[9] J.N. Reimers, J.E. Greedan and M. Sato, J. Solid State Chem. 72, 390 (1988).

[10] A. Keren and J.S. Gardner, Phys. Rev. Lett. 87, 177201 (2001).

[11] C.H. Booth, J.S. Gardner, G.H. Kwei, R.H. Heffner, F. Bridges and M.A. Subramanian, Phys. Rev. B 62, R755 (2000).

[12] J.E. Greedan, D. Gout, A.D. Lozano-Gorrin, S. Derahkshan, T. Proffen, H.J. Kin, E. Bozin and S.J.L Billinge, Phys. Rev. B 79, 014427 (2009).

[13] J.S. Gardner, B.D. Gaulin, S.H. Lee, C. Broholm, N.P Raju and J.E. Greedan, Phys. Rev. Lett. 83, 211 (1999).

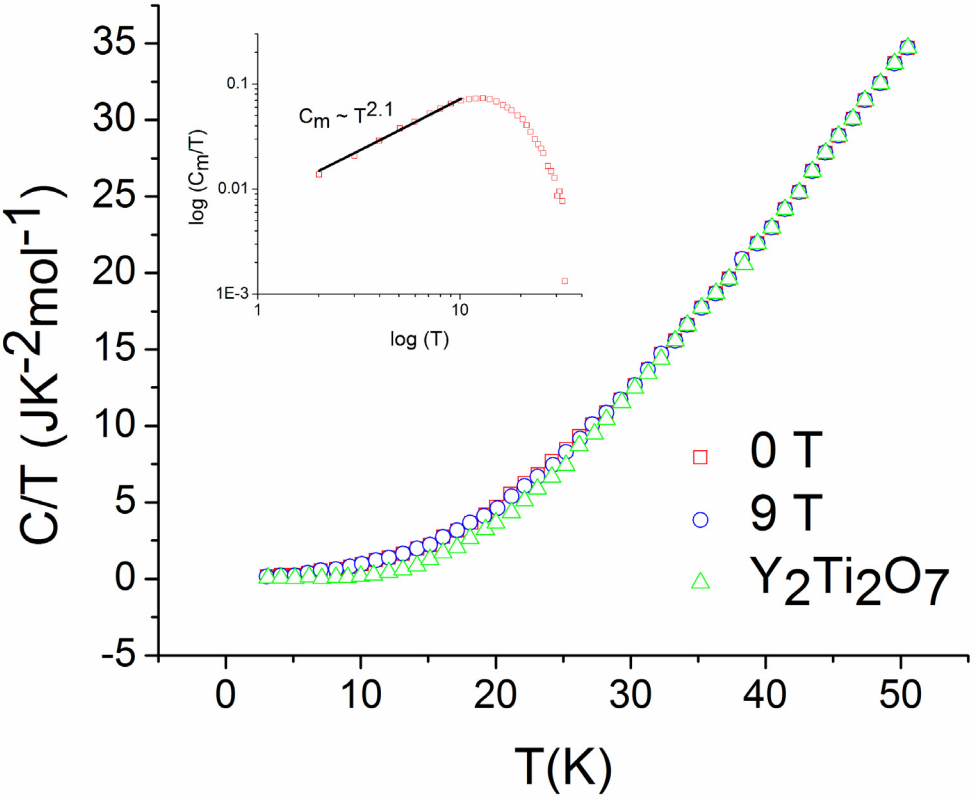

Fig. 1 The ZFC and FC heat capacity of single crystal $Y_2Mo_2O_7$ using an external magnetic field of 9 T. Inset: The magnetic heat capacity was obtained by subtracting the heat capacity from non-magnetic $Y_2Ti_2O_7$ lattice standard at low temperatures.

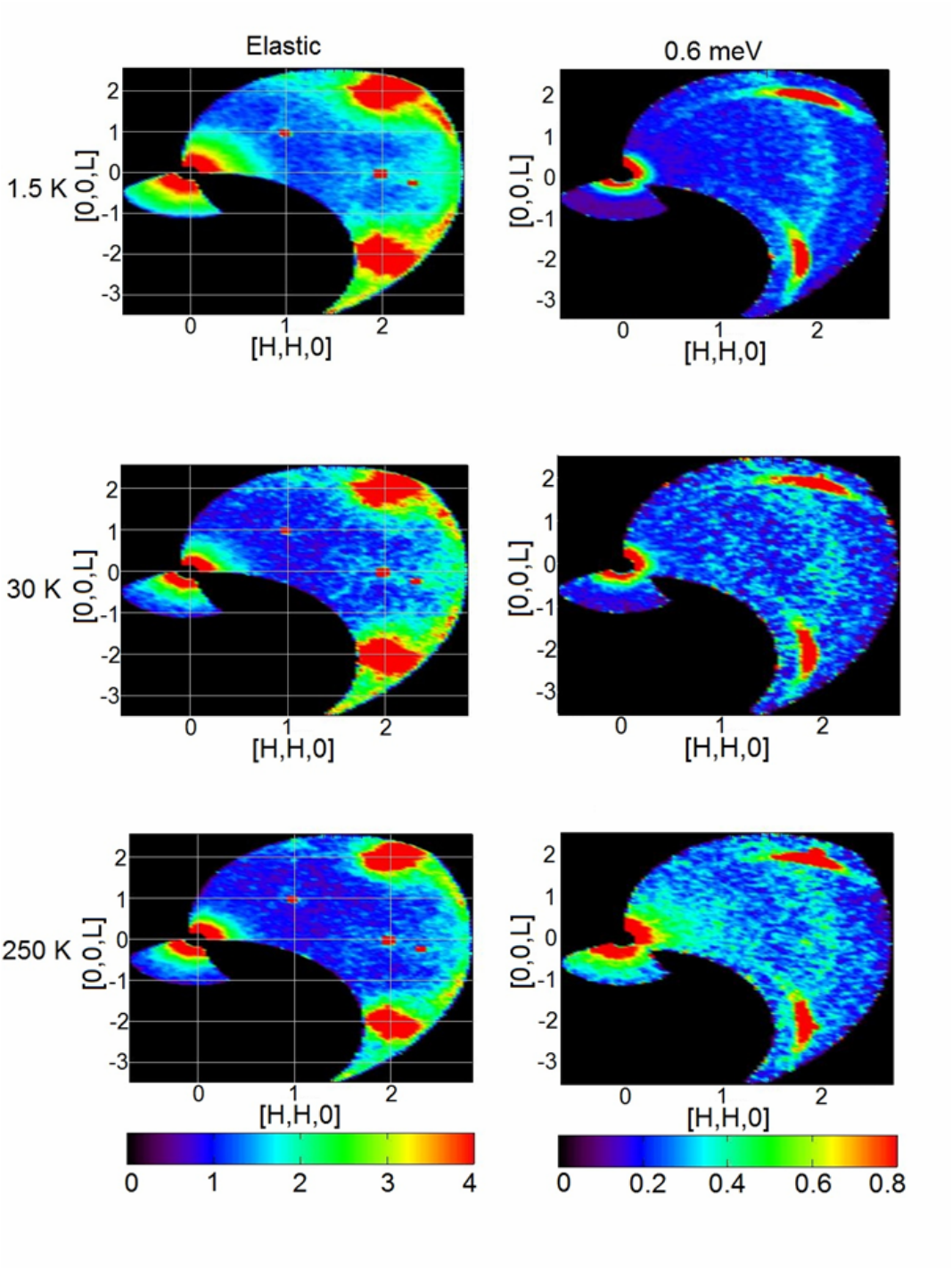

Fig. 2 Elastic (left column) and inelastic (0.6 meV, right column) scans taken at 1.5 K (top), 30 K (middle) and 250 K (bottom) from the Disc Chopper Spectrometer at the NCNR (NIST). The ring transitions from the inelastic channel at high temperatures to the elastic channel at temperatures below the spin glass transition consistent with results from J.S. Gardner *et al.* Phys. Rev. Lett. 83, 211 (2011).

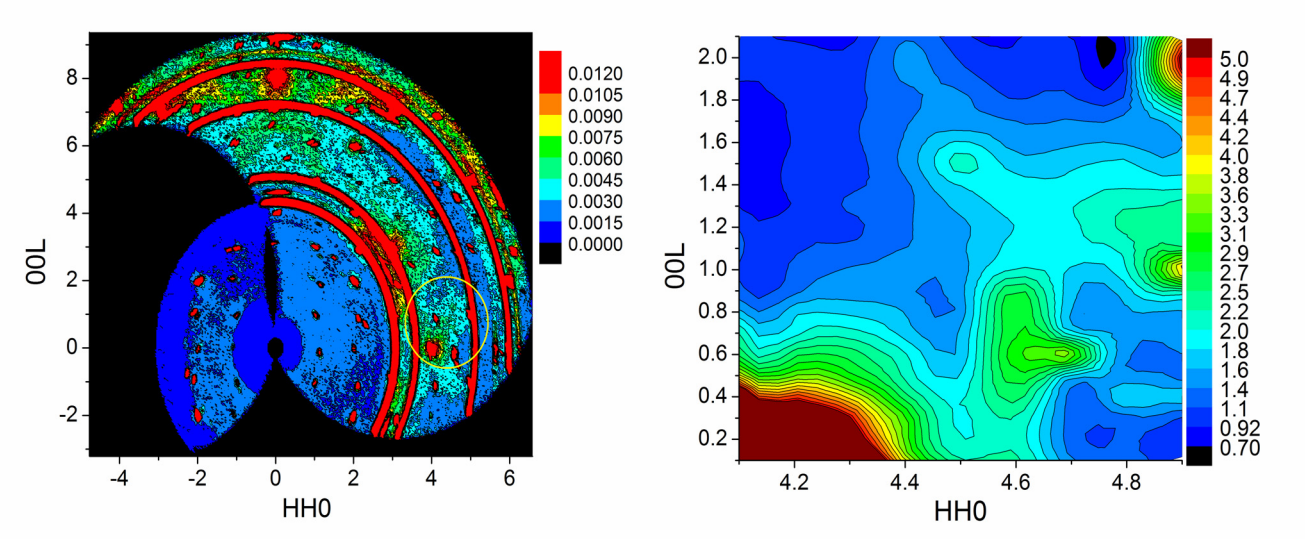

Fig. 3 The butterfly pattern can is easily seen in data from the Cold Neutron Chopper Spectrometer (Oak Ridge, left) and C5 triple axis spectrometer (right) taken at 3 K. Similar patterns exist at 300 K (not shown). Due to time constraints, only the top half of the butterfly pattern (yellow circle, left) was measured using the C5.