ESRF	**Experiment title:** Local charge and orbital ordering distortions in vanadium spinels	**Experiment number**: HC-2310
Beamline: ID22	**Date of experiment**: from:4/5/16 to: 9/5/16	**Date of report**: 7/9/16
Shifts: 15	**Local contact(s)**: Mauro Coduri	*Received at ESRF:*

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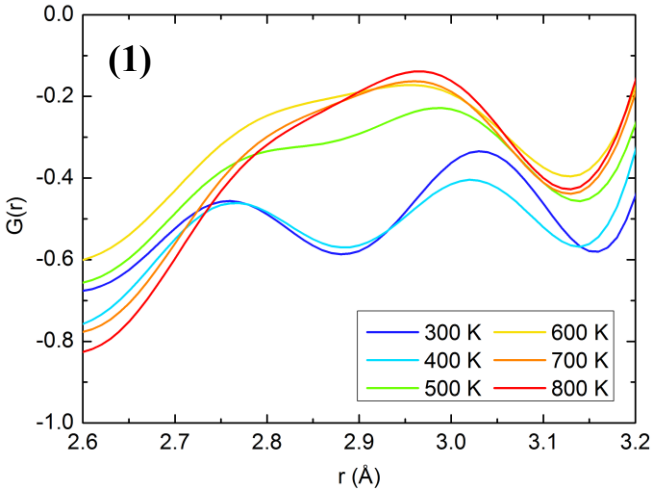
Report:

The aim of this experiment was to investigate local structural distortions in vanadium spinels (AlV_2O_4, GaV_2O_4, LiV_2O_4) that would result from the formation of an orbital molecule ground state. [1] This was achieved by generating and analysing X-ray pair distribution functions (PDFs). Orbital molecule formation results in metal-metal distances being shorter (or longer) than in an undistorted spinel structure, which is evident in a PDF, most noteably by a splitting of the metal-metal nearest neighbour peak.

AlV_2O_4 and GaV_2O_4 undergo long range orbital and charge ordering, accompanied by a structural distortion, to form V_7 'heptamer' orbital molecules (T_C = 700 K and 470 K respectively). [2] A hot air blower was used to heat capillaries during measurement (300-1100 K), which could change temperature rapidly and gave time for data collection at a large number of temperature steps. Capillary loading was carried out in an N_2-filled glovebag, which succesfully prevented oxidation at elevated temperature. The scattering patterns collected were high quality and we have accessed Q_{max} = 25.8 Å, which has allowed high resolution PDFs to be generated. In the ordered phases of the two materials a clear splitting of the first V-V peak, corresponding to heptamer formation, can be seen (**Figure 1**). Significantly, this splitting is still evident above the ordering temperature, implying that orbital molecules still exist locally even when the average structure is disordered. Such behaviour has previously been observed for orbital molecule dimers, but not larger clusters. Fitting using PDFgui is being used for full analysis (**Figure 2**).

LiV_2O_4 is noteable for its unusual heavy fermion ground state. [3] Charge and orbital correlations, which could manifest as local structural distortions, are implicated in its formation. As the effective mass enhancement only occurs below 30 K an He cryostat was required, and data were collected over the range 5-300 K. The PDFs generated are also of good quality, and analysis is in hand at the initial stage. Our only technical problem during this experiment came towards the end of the cryostat experiment, when an ice bloackage prevented the last measurments from being carried out (though a sufficient number had been collected already).

Observing orbital molecule ordering on a local scale is an important development in understanding orbitally ordered ground states. We are grateful for the assitance provided by the beamline staff, particularly Mauro Coduri, at all stages of this experiment.



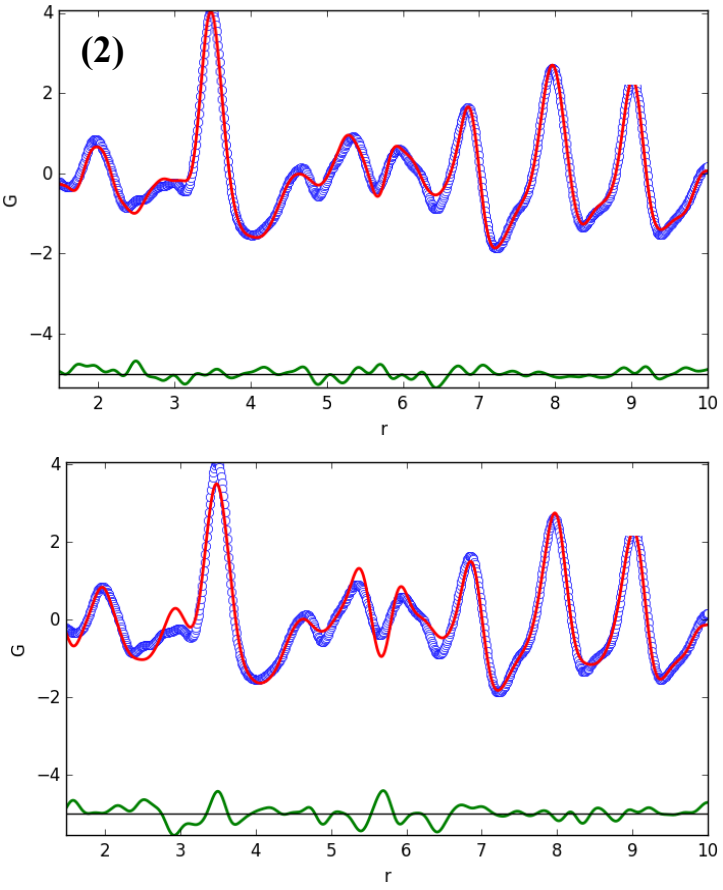


Figure 1: Splitting of the first V-V peak of GaV_2O_4 is caused by orbital molecule formation. **Figure 2**: The PDF of GaV_2O_4 at 500 K is much better fit by the heptamer structural model (upper) than an undistorted cubic spinel model (lower), despite being above T_C.

References:

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[2] Y. Horibe, M. Shingu, K. Kurushima, H. Ishibashi, N. Ikeda, K. Kato, Y. Motome, N. Furukawa, S. Mori, and T. Katsufuji, Phys. Rev. Lett. **96**, 086406 (2006).

[3] S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, Y. J. Uemura, O. Chmaissem, and J. D. Jorgensen, Phys. Rev. Lett. **78**, 3729 (1997).