

Experimental report

06/07/2017

Proposal: 7-01-450

Council: 4/2016

Title: Orbital molecule fluctuations in vanadate spinels

Research area: Materials

This proposal is a new proposal

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Samples: GaV2O4

Instrument	Requested days	Allocated days	From	To
IN6	3	3	27/06/2016	30/06/2016

Abstract:

In certain materials, notably with the spinel structure, orbital ordering can result in the formation of a ground state with electrons delocalising between small numbers of adjacent cations, called orbital molecules. AlV_2O_4 is notable as it undergoes a long range structural and charge ordering transition to form V7 clusters, the largest known orbital molecules, below 700 K. We have recently synthesised a new analogue GaV_2O_4 which has the same rhombohedral spinel superstructure. Variable temperature PND study showed that long range orbital molecule order persists up to $T_{\text{CO}} = 470$ K. Magnetic susceptibility data provide strong evidence that the V7 clusters persist above T_{CO} where the average crystal structure is cubic spinel with no long range orbital molecule distortions, so the clusters must be present in a glassy or liquid-like disordered state. The high incoherent scattering cross-section of V, makes this material ideal for INS. QENS from IN6 will be particularly useful as it enables the V self-self correlation function to be extracted, giving the timescale for the cluster fluctuations and hence showing whether the high temperature state is an cluster liquid or glass.

Orbital molecule fluctuations in vanadate spinels

This experiment was conducted at beamline IN6, 27th-30th June 2016.

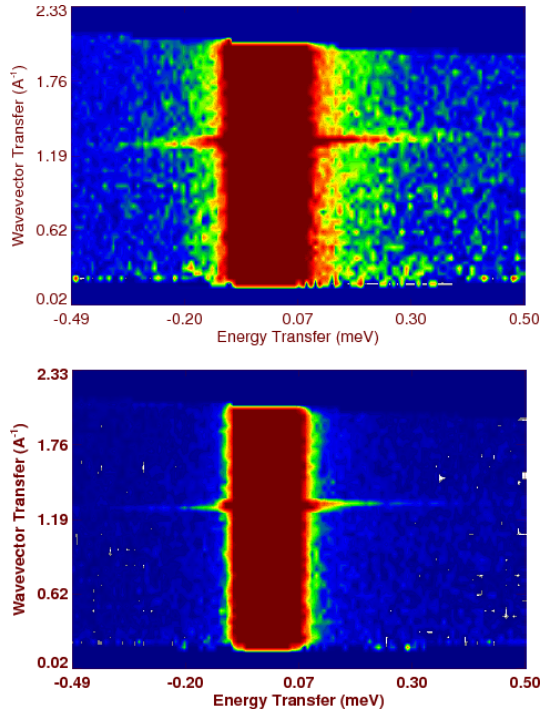
Our aim was to investigate the quasi-elastic neutron scattering (QENS) of the vanadate spinel GaV_2O_4 . Below an orbital-/charge-ordering transition at $T_{\text{CO}} = 470$ K, a long-range structural distortion forms clusters of vanadium cations. Prior to this experiment, we investigated the local structure of this material using X-ray total scattering and found that these clusters persist into a disordered state above T_{CO} . We therefore sought to use incoherent inelastic neutron scattering to extract the vanadium self-self correlation function, and hence determine the timescale of the cluster fluctuations in the disordered state.

Measurements were carried out on a 3g sample in a standard furnace sample environment. Neutrons with incident $\lambda = 5.12$ Å were used. QENS spectra of GaV_2O_4 were collected at nine temperature steps from 400 K to 1100 K, with ample time for good counting statistics. Empty can background and vanadium normalisation measurements were also made, and scattering functions $S(|Q|, E)$ generated (Fig. 1).

Each $S(|Q|, E)$ was integrated over the full measured Q -range, to determine how the width of the elastic line and any QENS contributions to this vary with temperature. However, over the whole measured temperature range we observe little change other than a decreasing peak intensity consistent with Debye-Waller effects (Fig. 2). The peak FWHM (~ 350 μeV) is constant for all temperatures. Although this is above the instrumental resolution (70 μeV), the lack of temperature-dependent broadening shows that any dynamic fluctuations of the vanadium clusters are slower than the $\sim 10^{-11}$ s timescale of the QENS experiment.

This demonstrates that the disordered clusters found at high temperatures in GaV_2O_4 are well defined. This is an important insight, and these results have been included in a manuscript submitted for publication in July 2017.

(1)



(2)

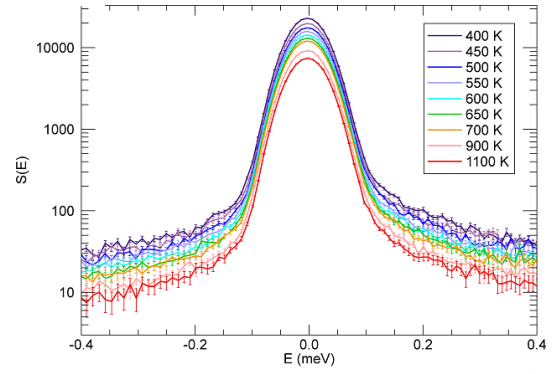


Fig.1: $S(|Q|, E)$ of GaV_2O_4 at 400 K (top) and 1100 K (bottom). The cubic-111 Bragg peak is evident at $|Q| = 1.30 \text{ \AA}^{-1}$. The intensity scale is the same for both temperatures.

Fig. 2: Scattering as a function of energy transfer. Little change other than thermal effects are seen between 400 and 1100 K.