Experimental report

09/05/2022

Proposal: 5-32-897 **Council:** 10/2019

Title: Unravelling Structural, Orbital and Magnetic Complexity in the Frustrated Spinel ZnV2O4

Research area: Physics

This proposal is a new proposal

Main proposer: Lucy CLARK

Experimental team: Andrew WILDES
Jennifer GRAHAM
Lucy CLARK
John Ross STEWART

Local contacts: Andrew WILDES

Samples: ZnV2O4

Instrument	Requested days	Allocated days	From	To
D7	3	3	21/09/2020	24/09/2020

Abstract:

ZnV2O4 is a frustrated spinel oxide in which antiferromagnetically coupled V3+ S = 1 ions dress a pyrochlore network of corner-sharing tetrahedra. Previous studies of polycrystalline samples of ZnV2O4 have revealed a series of magnetic and structural transitions stemming from a complex interplay between structural, orbital and magnetic orders. Single crystal samples of ZnV2O4, on the other hand, do not undergo the same series of transitions and instead retain cubic symmetry and magnetic disorder to low temperatures. We have recently developed a rapid microwave-assisted preparation of polycrystalline ZnV2O4, for which magnetic susceptibility data indicate an absence of long-range magnetic order and the onset of a spin glass-like state at 10 K. Here, we seek to identify the short-range magnetic correlations that stabilise this state by measurement and analysis of the diffuse magnetic scattering from our samples of ZnV2O4.

5-32-897 - D7 Experimental Report

May 9, 2022

Diffuse neutron scattering data were collected on the polarised D7 diffractometer using the xyz-polarisation technique. In Fig. 1a) an example of the nuclear-coherent (NC) and nuclear-spin-incoherent (NSI) cross-sections collected at 1.5 K are shown. There was no variation with either the NC or NSI cross-sections with temperature. The flat nature of the NSI indicates that the separation has worked very well. The background of the NC measurement is also flat, which shows there is no detectable chemical short-range order within the sample.

The magnetic diffuse scattering data are presented in Fig. 1b) and have been vertically shifted by 0.15 b/ster./f.u. for clarity. The diffuse magnetic signal at all temperatures is weak, and is not indicative of a long-range ordered magnetic structure. At 1.5 K, there is a feature emerging at $Q = 1.1$ Å^{-1} which is asymmetric. Most of the intensity of this feature is lost by 25 K and there are subtle differences as the

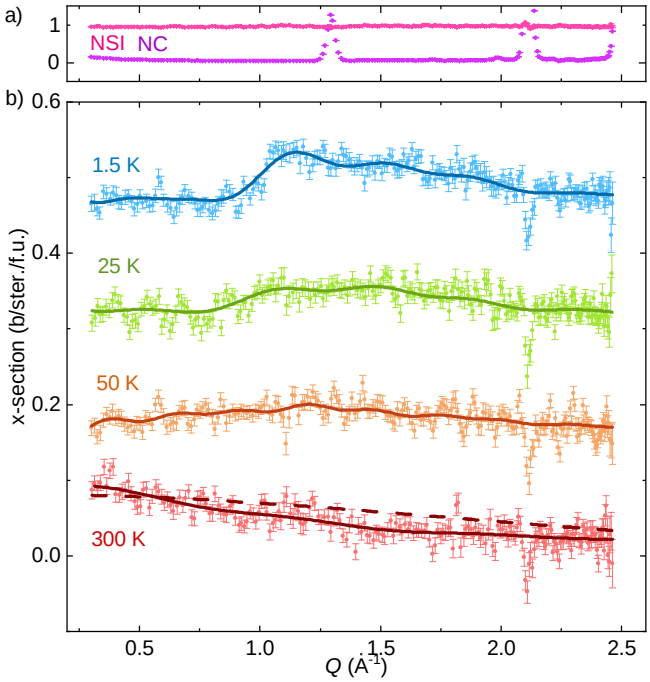

Figure 1: Experimental powder neutron scattering data of the sintered sample from D7. a) Nuclear-coherent (NC) and nuclear-spin-incoherent (NSI) cross-sections measured at 1.5 K. b) Magnetic diffuse scattering contributions. Data have been vertically shifted by 0.15 b/ster./f.u. for clarity. Fits produced from a RMC `SPINVERT` refinement are shown by the solid lines and a fit of the paramagntic form factor of V^{3+} ions is shown by the dashed line.

temperature increases to 50 K. These data were fit using SPINVERT (solid lines) and agree with the data well. At each temperature, a dip can be seen at $Q = 2.15$ Å^{-1}, this is an error in the separation of the data, as a large nuclear Bragg peak is at the same position. For the SPINVERT analysis, this region was excluded from the data in order to not skew the results. A box size of $6 \times 6 \times 6$ unit cells was constructed in the cubic $Fd\bar{3}m$ setting, with moments allowed complete rotational degrees of freedom and weight = 10. The choice to use the cubic as oppose to the tetragonal structure is based off the results of the Rietveld refinement which showed only a slight distortion along the c-axis, and so the structure at 1.5 K can be well approximated by a cube. This also removes some ambiguity in the spin correlation calculations later on. The derived magnetic moment from SPINVERT at 1.5 K is $\mu_{\text{eff}} = 0.62\ \mu_{\text{B}}$ per V^{3+} ion, which is significantly reduced from the expected moment of $\mu_{\text{eff}} = 2\ \mu_{\text{B}}$ per V^{3+} ion. However, this experimental effective moment is in line with previous neutron scattering measurements of $\mu_{\text{eff}} = 0.65\ \mu_{\text{B}}$ by Lee *et al.*. We verified the absolute normalisation of our data was correct to within a 10% error by comparing the SPINVERT scale of 1.509 with the absolute FULLPROF scale of 1.643. This gives us confidence that the spin contributions to our effective moment are correct. Some possible explanations for this underestimate of the effective moment could be significant spin-orbit couplings, a low spin state on the V^{3+} ions or a dimerised state.

At 300 K, the diffuse structure to the scattering has collapsed and the data have the appearance of a paramagnetic form factor. Data at 300 K have been modelled two ways; firstly using an analytical approximation of a magnetic V^{3+} form factor (dashed line), and secondly using SPINVERT (solid line). The analytical approximation agrees with the data reasonably well, however after $Q = 1.4$ Å^{-1} there is a dip in the data leading to an overestimate in the magnetic intensity by the form factor. Additionally, at low Q (< 0.5 Å^{-1}) the magnetic scattering begins a strong upturn, which is often associated with ferromagnetic correlations. Given these issues, and the difficulties in modelling the susceptibility data with a Curie-Weiss law at 300 K the sample may not be within its paramagnetic regime and therefore an analytical approximation is invalid. The SPINVERT fit was performed in the same way as before but with a smaller box size of $2 \times 2 \times 2$ unit cells. The effective moment is slightly reduced to $\mu_{\text{eff}} = 0.52\ \mu_{\text{B}}$ per V^{3+} ion, which is significantly reduced from the moment derived from the Curie-Weiss fit of the susceptibility data, $\mu_{\text{eff}} = 2.30\ \mu_{\text{B}}$ per V^{3+}.