ESRF	**Experiment title: ZnV2O4: On the Border of Disorder**	**Experiment number**: HC-4782
Beamline: ID22	**Date of experiment**: from: 25/02/22 to: 27/02/22	**Date of report**: 09/03/22
Shifts: 6	**Local contact(s)**: Giorgia Confalonieri	*Received at ESRF:*

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Report: Geometric magnetic frustration arises when the magnetic moments in a crystalline material are unable to align in the most energetically favourable way, leading to unconventional magnetic ground states [1]. In three dimensions, a model system in which to explore geometric frustration is the pyrochlore antiferromagnet, whose structure is comprised of a network of corner sharing tetrahedra. This network is realised within cubic spinels, such as ZnV_2O_4 [2], where the antiferromagnetically coupled S = 1 V^{3+} ions form a frustrated pyrochlore sublattice. However, the chemical and magnetic (dis)orders of ZnV_2O_4 are deeply intertwined, and as such, a consensus over the nature of the structural and magnetic ground states are currently lacking.

Previous characterisation shows that in polycrystalline samples there are commonly two phase transitions; structural (cubic to tetragonal distortion), T_S = 50 K and ordered antiferromagnetic, T_N = 40 K [3,4]. For single crystal samples, the reported structure remains cubic, and only a single transition is observed in magnetic susceptibility data at 11K, which is attributed to the formation of a frustrated spin glass phase [5]. Crushing these single crystals led to the two transitions returning, albeit at much lower temperatures than reported for powder samples. More recently, reports in the literature demonstrate that doping powder samples of ZnV_2O_4 with non-magnetic ions, such as Ga^{3+} [4], and magnetic ions, such as Ni^{2+} [5], eventually suppresses the structural transition, leaving only a single glass transition, like in the single crystal. This has been explained due to the orbital disorder caused as a result of doping. We believe that this idea could be extended to explain the origin of the apparent sample dependence of ZnV_2O_4, with subtle variations in the structure, stemming from the preparation method, strongly affecting the magnetic ground state.

We have prepared two polycrystalline samples of ZnV_2O_4, one through a conventional sintering method (as used in previous studies) and the other via a novel rapid microwave assisted route [6]. To investigate the average chemical structure, we previously performed a high-resolution diffraction measurement (λ = 0.35 Å) on both samples on ID22 (Experiment HC-4575). The room temperature diffraction patterns of both samples were well described using the cubic $Fd\bar{3}m$ space group. However, on lowering the temperature, the sintered sample underwent the expected cubic-tetragonal phase transition, as indicated by the peak splitting below 35 K, while

the "microwave" sample remained in the cubic spinel phase down to 4 K. Additionaly, underneath the well-ordered chemical Bragg peaks, we observed significant diffuse scattering in both of our samples, which given the eventual evolution of the chemical ground states were remarkably similiar. Attempts at fitting the sintered sample with the experimentally accepted low-temperature $I4_1/amd$ structure also failed to capture all the features of the data, including the diffuse tails.

Our previous experiment therefore suggested that the local structure plays a role in the chemical ground state selection of ZnV_2O_4 and so in our current experiment we explored this using PDF analysis. Initial findings from our experiment show that the PDFs of the data are quite similar to eachother, both at base and room temperature, and the theoretical PDF from our earlier refinement. However, on closer inspection, we see subtle differences do exist, some of which are highlighted in Fig. 1. These observations indicate that across the average and local structures, the defects are small, but despite this lead to significantly different chemical ground states. Future analysis should tell us if these features are relevant to determining if a phase transition occurs or not. Our first refinements using PDFGUI show good agreement with the average model, with most deviations at 300 K occuring at features assosciated with the V-O bonds. Furthermore, in the sintered sample, at low temperaures, the tetragonal $I4_1/amd$ fits better than the high-temperature cubic model, confirming a phase transition does occur in this sample.

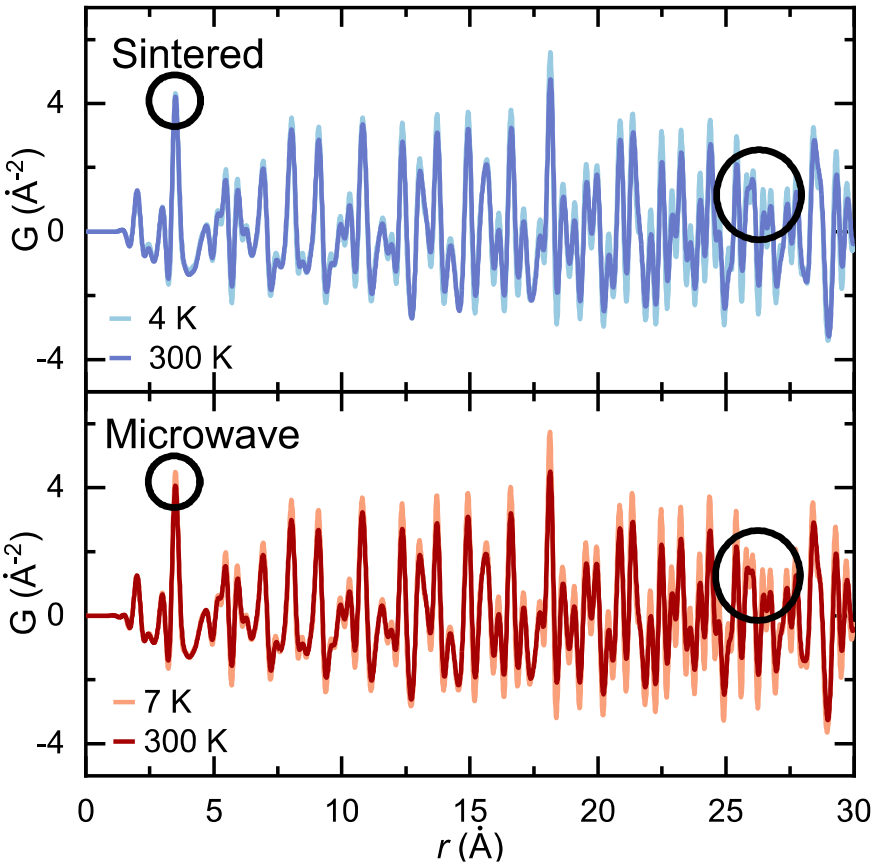

Fig. 1. PDFs of the sintered (top) and microwave (bottom) samples at 300 K (dark) and base (light) temperatures. PDFs were created over a momentum transfer of $1 < Q < 20$ Å^{-1}. Some subtle differences, which may be key to understanding the phase transition, are highlighted by the black circles, such as a change in the intensity ratios of two peaks at r = 26 Å.

References: **[1]** L. Balents Nature **464**, 199 (2010), **[2]** P. G. Radaelli New J. Phys. **7**, 54 (2005), **[3]** Y. Yamashita and K. Ueda, Phys. Rev. Lett. **85**, 4960 (2000), **[4]** A. J. Browne and J. P. Attfield Phys. Rev. B **101**, 024112 (2020), **[5]** M. Singha et al. Physica B. Condens. Matter **563**, 101 (2019), **[6]** E. E Levin *et al.* Chem Mater. **31** 18, 7151 – 7159 (2019).