

The manuscript presents a study of wolframite $A\text{ReO}_4$ compounds ($A = \text{Mg}, \text{Zn}$) using neutron diffraction and muon spin spectroscopy. These compounds consist of one-dimensional zigzag chains of edge-sharing ReO_6 octahedra, with Re^{6+} ions in a $5d^1$ electronic configuration. While MgReO_4 was previously reported by the authors, here both compounds are synthesized under high pressure and characterized in polycrystalline form. Neutron and x-ray diffraction indicate the presence of unidentified impurities. The authors use muon spin spectroscopy to elucidate magnetic long-range order yet find no magnetic Bragg peaks in neutron diffraction. They perform muon stopping site calculations to estimate reduced magnetic moments and propose possible magnetic structures, attributing the absence of magnetic reflections in neutron diffraction to the reduced moment. Bond valence sum analysis supports the assignment of the Re oxidation state as $6+$.

The study presents interesting new materials and includes a thorough muon spin spectroscopy analysis, as well as muon stopping site and bond valence sum calculations. However, I find that the conclusions regarding the ground states of ZnReO_4 and MgReO_4 are not fully convincing. Additionally, the possible presence of multipolar order—highly relevant in strongly spin-orbit-coupled d^1 or d^2 systems—is not discussed. Therefore, I do not recommend this manuscript for publication in SciPost Physics. It may become suitable for SciPost Physics Core after revision. My concerns and suggestions are detailed below.

1. Characterisation of ZnReO_4

It would be recommended to include DC magnetic susceptibility and specific heat to substantiate the claim of long-range magnetic order in ZnReO_4 . However, it would appear the air-sensitivity of this material poses significant experimental challenges. The authors report AC-susceptibility shown in Appendix A, Figure 4, but don't show the temperature range below approx. 35 K. They ascribe the upturn at 100 K is a ferromagnetic impurity similar to what was observed in MgReO_4 (E. Nocerino *et al.*, *J. Phys.: Conf. Ser.* **2462**, 012037 (2023), Figure 2 (a)). However, in the case of MgReO_4 the upturn at low temperatures is attributed to a paramagnetic tail originating from orphan spins, as discussed in the previous publication. For ZnReO_4 , the magnitude of the low-temperature AC susceptibility signal and its interpretation as a ferromagnetic impurity remain unclear and require clarification.

2. Neutron powder diffraction data

The refined neutron powder diffraction patterns in Fig. 1(a) and (b) display several unindexed peaks, and the fits to peak shapes and intensities for the indexed reflections are not ideal. This raises questions about the structural model, sample quality, and potential presence of secondary phases. While it is appreciated the challenges due to high-pressure synthesis and air-sensitivity, these factors may undermine the reliability of the analysis and conclusions. In the high-temperature–low-temperature difference pattern, the inset for ZnReO_4 shows some possible reflections ($q=0?$), but these are not clearly visible and may be artifacts from thermal shifts.

The authors suggest that the absence of magnetic reflections is due to the reduced moment inferred from muon calculations. However, only 0.5 g of sample was used for neutron powder diffraction. In contrast, G. J. Nilsen *et al.*, *Phys. Rev. B* **103**, 104430 (2021), reported observable magnetic Bragg peaks in Ba_2YReO_6 (Re^{5+} , $5d^2$), using 10 g of sample hosting comparable dipole moments (although with *polarized* neutron diffraction experiment). Therefore, one of the reasons for absence of magnetic

reflections could be small amount of sample. The authors should discuss in more detail why magnetic reflections are absent and should provide simulated patterns showing the expected signal for their computed moments and proposed magnetic structures.

3. Muon spin spectroscopy and calculations

The muon spin spectroscopy analysis and simulations are comprehensive, and I have no major concerns about this aspect. Nevertheless, it would strengthen the manuscript to present muon spin spectra of MgReO_4 near the 280 K transition and to discuss expected neutron diffraction peaks based on the proposed magnetic structures. Finally, as mentioned above, it would be recommended to include other experimental results (specific heat, magnetic susceptibility, neutron diffraction with larger sample) to support the obtained magnetic ground states.

4. Context of multipoles

There is a significant amount of literature on multipole physics of $5d$ transition metal compounds with d^1 and d^2 configuration (e.g. G. Chen *et al.*, *PRB* 2010, J. Romhányi *et al.*, *PRL* 2017, H. Ishikawa *et al.*, *PRB* 2019...). In d^1 systems, the spin-orbit-entangled $J_{\text{eff}} = 3/2$ state with g -factor = 0 gives suppressed dipole moment and higher-order multipoles are expected to dominate. Multipolar order is observable with few experimental probes and hence is called “hidden order”.

While the ReO_6 in the wolframite compounds in this study are distorted, unquenched orbital moments may persist. For instance, the authors' previous work (E. Nocerino *et al.*, *J. Phys.: Conf. Ser.* **2462**, 012037 (2023), Figure 2 (d)) reports a specific heat anomaly at 280 K in MgReO_4 , which is discussed to be structural in origin; could this correspond instead to multipolar order? The possibility is not addressed in the present manuscript, nor is the broader relevance of multipolar physics to the ground states of MgReO_4 and ZnReO_4 .

The authors mention only briefly that the nominal $J_{\text{eff}} = 3/2$ state could explain the reduced moment of Re^{6+} , but do not fully discuss ground state interpretations or relate their findings to the literature on multipolar physics. I believe this context is important and should be addressed.

5. Other remarks

- a. Please provide error bars for the refined values in Tables 1 and 6.
- b. Could the authors explain why the χ^2 values in Table 1 are less than 1?
- c. Extracting crystal structure parameters from data on degraded samples (as in Fig. 5) is questionable—the reported oxygen positions appear unreasonable and may be artefactual. I advise caution in interpreting or reporting results from these refinements.
- d. Given the moderate refinement quality of the neutron powder diffraction data, the validity of the bond valence sum analysis may be questionable. The authors should comment on the limitations and potential uncertainties introduced by using such data for this analysis.