

# Structural Investigation of Some Molecular Solids Containing Anion Dimers

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Mixed-anion solids are a promising class of materials, often displaying superior properties compared to single-anion systems, such as enhanced ferroelectricity and catalytic activity. A key focus in this field is anion ordering, as seen in various studies on oxynitride, oxyhydride, and oxyhalide perovskites. Among these, MXY compounds (M = transition metals; X = pnictides; Y = chalcogenides) are notable for forming covalent-like anion dimers (XY)<sup>3-</sup>, instead of typical ionic states (X<sup>3-</sup>Y<sup>2-</sup>).

Understanding the ordering of these dimers is important as it directly influences functionalities such as ferroelectricity; a parallel arrangement of XY dimers breaks inversion symmetry, inducing electric polarization. When M is paramagnetic, different anion configurations may also affect magnetic super-exchange interactions. Despite extensive studies on MXY materials, the exact crystal structures, particularly the anion arrangements, often remain unclear. This is primarily due to the similar X-ray scattering factors of the anions, especially within the same periodic group.

For example, the structure of MPS (M = Co, Fe, Ni) remains ambiguous. Early reports on FePS suggested fully ordered PS pairs, but this conclusion, based on X-ray diffraction, is not definitive due to its limitations in distinguishing between anions.

Neutron diffraction, however, can differentiate anions more clearly, with scattering lengths of 5.1 fm for phosphorus and 2.8 fm for sulfur. To resolve the structure of CoPS, we conducted neutron diffraction experiments on two batches of CoPS, synthesized at low and high temperatures, using the HERMES diffractometer at JRR-3 with a neutron wavelength of  $\sim 2.2$  Å. The synthesis temperature was chosen due to its known impact on ion ordering in crystalline solids.

Our neutron powder diffraction (NPD) data showed no significant differences between the two batches, indicating that the anion arrangement in CoPS, at least in the long range, is robust and unaffected by synthesis temperature. The data were best fitted using an anion-disordered model (Fig. 1), suggesting no long-range anion ordering.

This raises further questions about the local arrangement of anion dimers, which may involve P-P, S-S, or P-S pairs. While this is beyond the scope of NPD, it could be explored using local probes such as NMR or neutron pair distribution function analysis. We plan to apply these methods to examine the local anion arrangements and are also investigating other MXY materials with different pnictide and chalcogenide combinations.

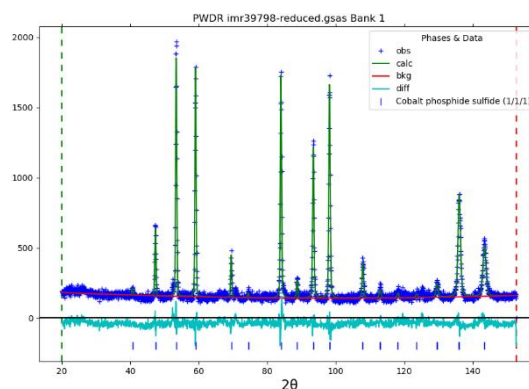


Fig. 1. Refinement against neutron diffraction data collected from CoPS at 300 K with an anion-disordered high-symmetry model.