# Magnetic Anisotropy in Layered Vanadyl Phosphates: Insights from DFT+U and X-Ray Charge Density Studies

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2D Layered Vanadyl Phoshates and their metal-intercalants have garnered attention through the decades due to their catalytic, optical and magnetic properties [1]. When intercalated by 3d transition metals, they provide a platform to study geometrical frustration, low-dimensional magnetism and anisotropy, owing to their dimensionality. This study examines two isostructural tetragonal compounds, $Ni(VO)_2(PO_4)_2*4H_2O$ and $Co(VO)_2(PO_4)_2*4H_2O$, space group *I4/m*. Their structure consists of V4+ square pyramids interconnected via four phosphate tetrahedra to form layers in the ab crystallographic plane, linked along the c-axis through V=O-M-O=V (M = $Ni^{2+}$, $Co^{2+}$) linear trimer units, with M in an $MO_2(OH_2)_4$ octahedral coordination (Figure 1). This introduces an interesting through-space magnetic exchange interaction among $V^{4+}$ ions in the plane whilst M interact through the oxygen ligand by magnetic superexchange.

Previous studies suggest bulk ferromagnetic coupling based on an isotropic linear trimer spin Hamiltonian model, with assumed overlap of orthogonal $e_g$ d-orbitals [2]. However, inverse susceptibility plots indicate antiferromagnetic interactions. To clarify this, we combined oriented magnetic measurements on single crystals, *DFT+U* calculations, and X-ray charge density analysis.

Oriented susceptibility measurements reveal a low-dimensional, anisotropic behaviour: ferromagnetic along c, antiferromagnetic in the *ab*-plane due to a partial moment cancellation. Long-range ordering occurs at $T_C = 4$ K, confirmed by Heat Capacity ($C_p$) measurements. DFT+U electronic structure calculations using *CP2K* code [3] indicate significant d-orbital overlap beyond the assumed orthogonality. X-ray charge density analysis at 100 K, employing Multipole Modelling (WINXD2024 [4]) corroborates these findings, aligning with theoretical orbital populations.

Our results suggest dominant short-range spin-spin correlations, low-dimensional interactions within the *ab*-plane, preceding long-range ordering of trimers.

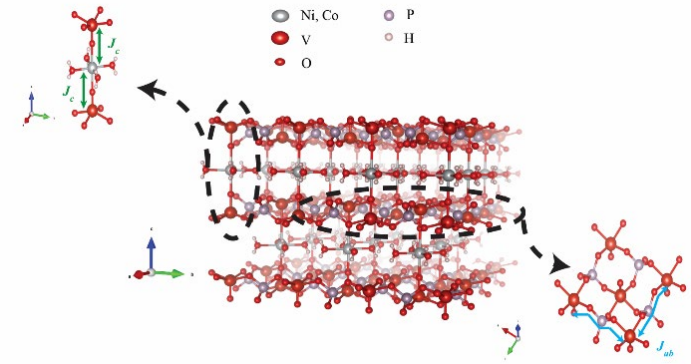


**Figure 1**. Layered structure of $M(VO)_2(PO_4)_2*4H_2O$ compounds, showing trimer linker motifs (upper right) and Vanadyl phosphate layers (lower right), with magnetic super-exchange interaction pathways (green and blue arrows indicating interplane and intraplane pathways respectively)

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