First-Principles Magnetic Exchange in Multiferroic $CoCr_2O_4$: The Role of the Hubbard *U*

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$CoCr_2O_4$ is a type-II multiferroic in which ferroelectricity emerges from a ferrimagnetic spin spiral, but its magnetic Hamiltonian is still not well established [1–3]. We compute the exchange couplings from DFT+*U* with Hubbard parameters obtained *ab initio* from density-functional perturbation theory. The magnetic force theorem [4–6], formulated in reciprocal space on maximally localized Wannier functions, gives access to many neighbor shells at once. It shows that the Hamiltonian is dominated by the three nearest-neighbor couplings ($J_{Cr–Cr}$, $J_{Co–Cr}$, $J_{Co–Co}$), with negligible farther-neighbor interactions. These couplings have the correct signs and orders of magnitude, but $J_{Cr–Cr}$ is strongly underestimated relative to inelastic neutron scattering. We trace this to overestimated *U*, which suppresses direct Cr–Cr exchange and overestimates the 3*d*–O-2*p* hybridization compared to XPS [7]. Restricting to the three dominant couplings, we then scan the Hubbard parameters with four-state energy mapping [8–10]. A single pair of Hubbard parameters reproduces all three experimental couplings while improving agreement with XPS spectra.

[1] D. H. Lyons, T. A. Kaplan, K. Dwight, and N. Menyuk, Phys. Rev. **126**, 540 (1962).

[2] C. Ederer and M. Komelj, Phys. Rev. B **76**, 064409 (2007).

[3] A. Sundaresan and N. V. Ter-Oganessian, J. Appl. Phys. **129**, 060901 (2021).

[4] A. I. Liechtenstein, M. I. Katsnelson, V. P. Antropov, and V. A. Gubanov, J. Magn. Magn. Mater. **67**, 65 (1987).

[5] M. I. Katsnelson and A. I. Lichtenstein, Phys. Rev. B **61**, 8906 (2000).

[6] A. Szilva *et al.*, Rev. Mod. Phys. **95**, 035004 (2023).

[7] P. Mohanty *et al.*, Nanotechnology **31**, 285708 (2020).

[8] H. J. Xiang, E. J. Kan, S.-H. Wei, M.-H. Whangbo, and X. G. Gong, Phys. Rev. B **84**, 224429 (2011).

[9] H. J. Xiang, C. Lee, H.-J. Koo, X. G. Gong, and M.-H. Whangbo, Dalton Trans. **42**, 823 (2013).

[10] D. Šabani, C. Bacaksiz, and M. V. Milošević, Phys. Rev. B **102**, 014457 (2020).