

Supplementary Information: Order from disorder phenomena in BaCoS₂

Benjamin Lenz^{1*}, Michele Fabrizio² and Michele Casula¹

¹IMPMC, Sorbonne Université, CNRS, MNHN, 4 place Jussieu, Paris, F-75005, France.

²International School for Advanced Studies (SISSA), Via Bonomea 265, Trieste, I-34136, Italy.

*Corresponding author(s). E-mail(s):

benjamin.lenz@sorbonne-universite.fr;

Contributing authors: fabrizio@sissa.it;

michele.casula@sorbonne-universite.fr;

Supplementary Note 1: Pressure-driven metal-insulator transition

The insulator-metal transition in BaCoS₂ can either be controlled by chemical doping, for instance with Ni atoms [1], or by applying pressure [2]. We focus here on the latter case, where a critical pressure of $p_{cr} \sim 1.3$ GPa [3–6] was found in experiments to be sufficient to render the system metallic. Close to p_{cr} the transition from AFM insulator to PM metal occurs via the formation of an intermediate antiferromagnetic metal phase. As we will show in the following, the orbital ordered solution discussed in the main text is crucial to account for this pressure-driven metal-insulator transition within DFT+U.

Based on the structural changes under pressure reported in Ref. [5], we performed DFT+U calculations for the low-energy solutions identified in the main text. In Ref. [5] the structural parameters show a rather continuous evolution upon pressure within the metallic and insulating regimes. At the phase transition, however, the structural changes are large. Nevertheless, one can parametrise the distinct low- and high-pressure regimes separately, whose structural parameters vary as a function of pressure. In order to be consistent with the rest of the paper, we used the relative structural changes of the lattice constants under pressure reported in Ref. [5] and

applied them to the ambient pressure data of Ref. [7].

Here, we focus on the low-pressure parametrisation and compare the energy gap of the two C-AFS-a competing solutions $C(xyxx)$ and $C(yyyy)$ as a function of pressure. In Supplementary Figure 1(a) we plot the density of states (DOS) of both configurations as function of pressure. We note that, while $C(xyxx)$ remains insulating at all pressures, the gap of the $C(yyyy)$ configuration closes around $p \simeq 8$ kbar. Such behaviour is robust either choosing the atomic positions of Ref. [5] or those of Ref. [7]. On the contrary, the relative energies of the $C(xyxx)$ and $C(yyyy)$ configurations, which are extremely sensitive to the distance between Co and apical S atoms, do depend on that choice, since Ref. [5] and Ref. [7] report significantly different Co-apical S distances. Indeed, the insulating $C(xyxx)$ configuration remains the lowest energy state at all investigated pressures using the atomic positions of Ref. [7], see Supplementary Figure 1(b). Conversely, the reduced Co-apical S distance of the crystal structure reported in Ref. [5] predicts a first order transition at $p \sim 12$ kbar between an insulating $C(xyxx)$ and a metallic $C(yyyy)$, consistent with the metal-insulator transition reported experimentally, see bottom panel. Should the latter scenario be representative of BaCoS_2 under pressure, it would imply that the metal-insulator transition is also accompanied by the recovery of the non-symmorphic symmetry.

Supplementary Note 2: Exchange constants estimated from density functional theory calculations

Extracting the magnetic exchange couplings from DFT+U data is known to be complicated since it often depends, e.g., on the precise value of on-site Coulomb interaction U . Here, the situation is even more complicated since the orbital degrees of freedom enter the game and lead to an even larger amount of arbitrariness.

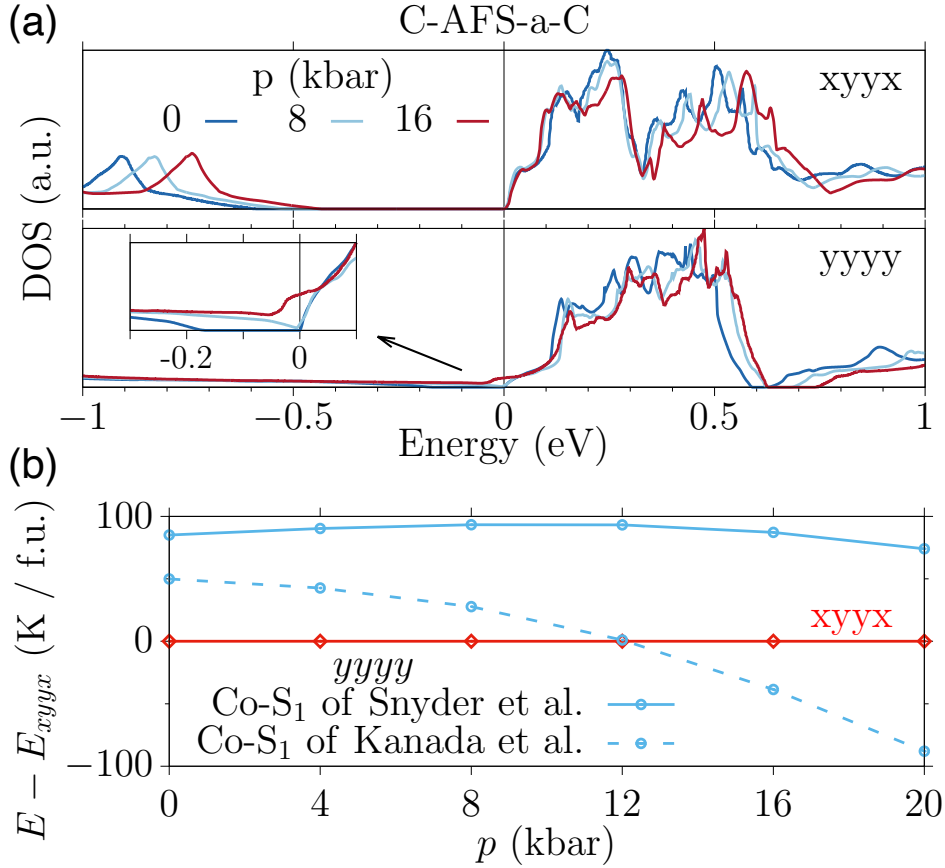
In the orthorhombic phase of BaCoS_2 , we will show in the following an estimation of the exchange couplings by freezing the orbital configuration into the lowest energy one for the $C - AFS - a$ magnetic configuration, $(xyxx - xyxx)$. Hereafter, we define $J_{ax} = J_a(1 - \delta_a)$ and $J_{ay} = J_a(1 + \delta_a)$, with $a = 1, 3$. Besides the states included in Table 3 of the manuscript, we also considered the spin configurations $C(G) - FM$, ferromagnetic planes stacked ferromagnetically (antiferromagnetically), as well as $C(G) - AF$ of antiferromagnetic planes. We also assumed that the DFT+U energy differences can be interpreted as energy differences between classical spin-3/2 configurations. In that way, taking the energy per formula unit, we obtain

$$\begin{aligned}
 J_1 &= (E_{G-FM} - E_{C-AF})/(4S^2) = 3.83\text{meV}, \\
 J_2 &= (E_{C-FM} + E_{C-AF} - E_{G-AFS-b} - E_{G-AFS-b})/(8S^2) = 12.69\text{meV}, \\
 J_3 &= (E_{C-FM} - E_{G-FM})/(4S^2) = 0.09\text{meV}, \\
 J_3 \delta_3 &= (E_{G-AFS-a} - E_{C-AFS-a})/(4S^2) = 0.02\text{meV}, \\
 J_1 \delta_1 &= (E_{G-AFS-b} - E_{C-AFS-a})/(4S^2) = 0.21\text{meV}.
 \end{aligned}$$

We can also use our J_1 - J_2 - J_3 model to fit the inelastic neutron scattering data of Ref. 17. In this case, we estimated in the main text

$$J_2 = 9.3\text{meV}, \quad J_1 + J_3 = -2.34\text{meV}, \quad J_1 \delta_1 + J_3 \delta_3 = 0.53\text{meV},$$

as well as $0 < 4J_1 \delta_1 J_3 \delta_3 < 0.08\text{meV}^2$, where the upper bound is due to experimental resolution. We observe that the main difference between the DFT+U and neutron data estimates is the sign of $J_1 + J_3$, as well as of $\delta_{1(3)}$. Even though both signs stabilise the same $C - AFS - a$ ground state configuration, the origin of the disagreement is unclear to us. Taking for granted the validity of the neutron scattering data, we have preferred to use the latter in the main text to estimate the model parameters.



Supplementary Figure 1. Pressure-driven insulator-metal transition. (a) Density of states as a function of pressure in the C-AFS-a-C phases with orbital nematic ($yyyy$) and anti-ferro orbital order ($xyyx$). The energy gap of the $yyyy$ phase is closing at $p \gtrsim 8$ kbar. (b) Relative energy of these two phases within the structure taken from Ref. [7] as well as with the reduced apical sulfur distance Co-S_1 of Ref. [5].

Supplementary References

- [1] Martinson, L.S., Schweitzer, J.W., Baenziger, N.C.: Metal-insulator transitions in $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_{2-y}$. *Phys. Rev. Lett.* **71**, 125–128 (1993) <https://doi.org/10.1103/PhysRevLett.71.125>
- [2] Kodama, K., Shamoto, S.-i., Harashina, H., Takeda, J., Sato, M., Kakurai, K., Nishi, M.: Electronic Structure of the Quasi Two-Dimensional Mott System $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$. *Journal of the Physical Society of Japan* **65**(6), 1782–1786 (1996) <https://doi.org/10.1143/JPSJ.65.1782> <https://doi.org/10.1143/JPSJ.65.1782>
- [3] Sato, M., Sasaki, H., Harashina, H., Yasui, Y., Takeda, J., Kodama, K., Shamoto, S., Kakurai, K., Nishi, M.: Metal-Insulator Transition of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ Induced by Pressure and Carrier Number Control. *The Review of High Pressure Science and Technology* **7**, 447–452 (1998) <https://doi.org/10.4131/jshpreview.7.447>
- [4] Yasui, Y., Sasaki, H., Sato, M., Ohashi, M., Sekine, Y., Murayama, C., Mōri, N.: Studies of Pressure-Induced Mott Metal-Insulator Transition of BaCoS_2 . *Journal of the Physical Society of Japan* **68**(4), 1313–1320 (1999) <https://doi.org/10.1143/JPSJ.68.1313> <https://doi.org/10.1143/JPSJ.68.1313>
- [5] Kanada, M., Harashina, H., Sasaki, H., Kodama, K., Sato, M., Kakurai, K., Nishi, M., Nishibori, E., Sakata, M., Takata, M., Adachi, T.: High-pressure neutron and X-ray studies on the Mott transition of BaCoS_2 . *Journal of Physics and Chemistry of Solids* **60**(8), 1181–1183 (1999) [https://doi.org/10.1016/S0022-3697\(99\)00078-5](https://doi.org/10.1016/S0022-3697(99)00078-5)
- [6] Guguchia, Z., Frandsen, B.A., Santos-Cottin, D., Cheung, S.C., Gong, Z., Sheng, Q., Yamakawa, K., Hallas, A.M., Wilson, M.N., Cai, Y., Beare, J., Khasanov, R., De Renzi, R., Luke, G.M., Shamoto, S., Gauzzi, A., Klein, Y., Uemura, Y.J.: Probing the quantum phase transition in Mott insulator BaCoS_2 tuned by pressure and Ni substitution. *Phys. Rev. Materials* **3**, 045001 (2019) <https://doi.org/10.1103/PhysRevMaterials.3.045001>
- [7] Snyder, G.J., Gelabert, M.C., DiSalvo, F.J.: Refined Structure and Properties of the Layered Mott Insulator BaCoS_2 . *Journal of Solid State Chemistry* **113**(2), 355–361 (1994) <https://doi.org/10.1006/jssc.1994.1380>