

# Hybrid-functional calculations of structural, electronic, magnetic, mechanical and thermodynamic properties of $\alpha$ -Cu<sub>2</sub>P<sub>2</sub>O<sub>7</sub>

**Xiaoyong Yang<sup>1,2</sup>, Ping Zhang<sup>3</sup>, Pavel A. Korzhavyi<sup>1\*</sup>**

<sup>1</sup> Department of Materials Science and Engineering, KTH Royal Institute of Technology,  
Stockholm, SE-100 44, Sweden

<sup>2</sup> State Key Laboratory of Environment-friendly Energy Materials, Southwest University of Science  
and Technology, Mianyang 621010, China

<sup>3</sup> LCP, Institute of Applied Physics and Computational Mathematics, Beijing 100088, China

\* Corresponding author: pavelk@kth.se

## **Formalism based on Voigt-Reuss-Hill (VRH) approximation for the evaluation of direction-averaged bulk modulus ( $B$ ) and shear modulus ( $G$ )**

(1) Under Voigt [1] and Reuss [2] approximation, the bulk modules and shear modulus of a tetragonal crystal can be expressed as:

$$B_V = \frac{2(C_{11} + C_{12}) + 4C_{13} + C_{33}}{9}, \quad (1)$$

$$G_V = \frac{M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}}{30} \quad (2)$$

$$B_R = C^2 / M, \quad (3)$$

$$G_R = \frac{15}{18B_V / C^2 + 6/(C_{11} - C_{12}) + 6/C_{44} + 3/C_{66}} \quad (4)$$

$$M = C_{11} + C_{12} + 2C_{33} - 4C_{13}, \quad (5)$$

$$C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2, \quad (6)$$

The bulk modules and shear moduli of an orthorhombic crystal can be expressed as:

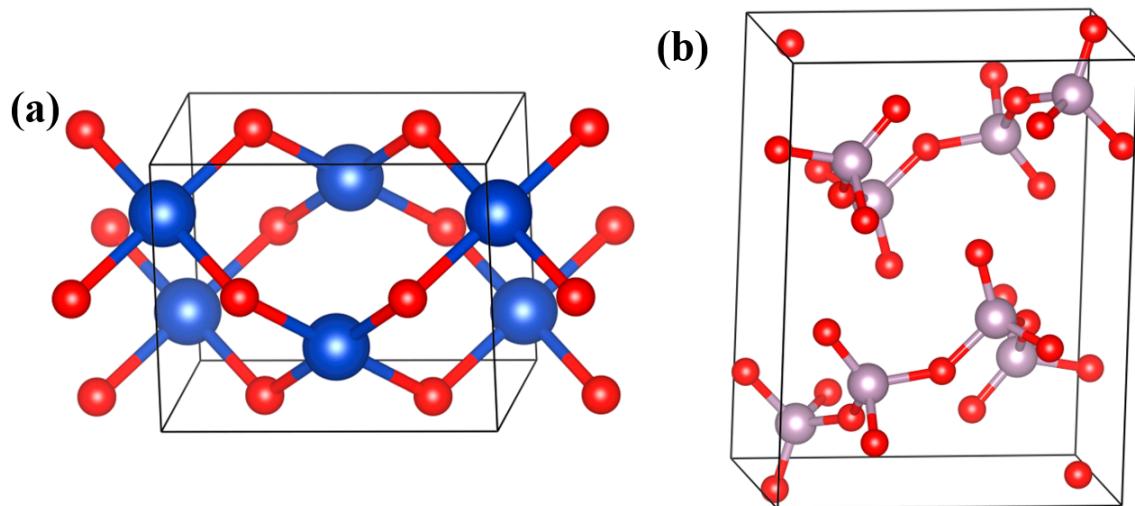
$$B_V = \frac{C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})}{9} \quad (7)$$

$$G_V = \frac{C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})}{15} \quad (8)$$

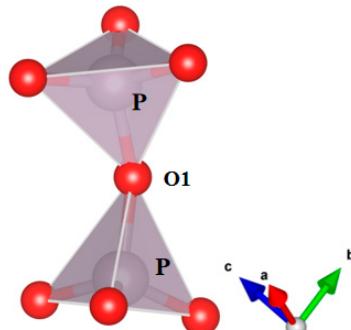
$$B_R = \Delta [C_{11}(C_{22} + C_{33} - 2C_{23}) + C_{22}(C_{33} - 2C_{13}) - 2C_{33}C_{12} + C_{12}(2C_{23} - C_{12}) + C_{13}(2C_{12} - C_{13}) + C_{23}(2C_{13} - C_{23})]^{-1} \quad (9)$$

$$G_R = 15\{4[C_{11}(C_{22} + C_{33} + C_{23}) + C_{22}(C_{33} + C_{13}) + C_{33}C_{12} - C_{12}(C_{23} + C_{12})] - C_{13}(C_{12} + C_{13}) - C_{23}(C_{13} + C_{23})]/\Delta + 3[(1/C_{44}) + (1/C_{55}) + (1/C_{66})]\}^{-1} \quad (10)$$

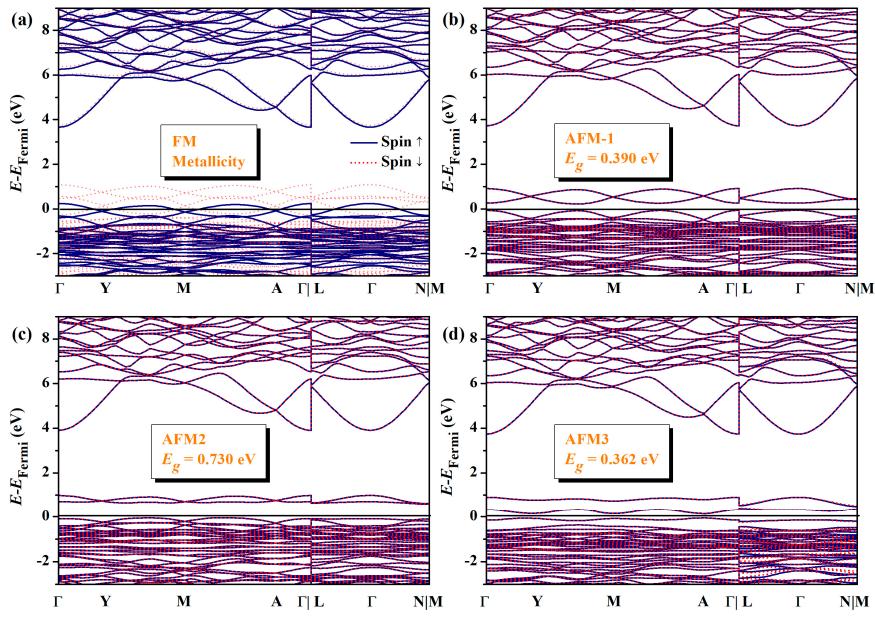
$$\Delta = C_{13}(C_{12}C_{23} - C_{13}C_{22}) + C_{23}(C_{12}C_{13} - C_{23}C_{11}) + C_{33}(C_{11}C_{22} - C_{12}^2) \quad (11)$$



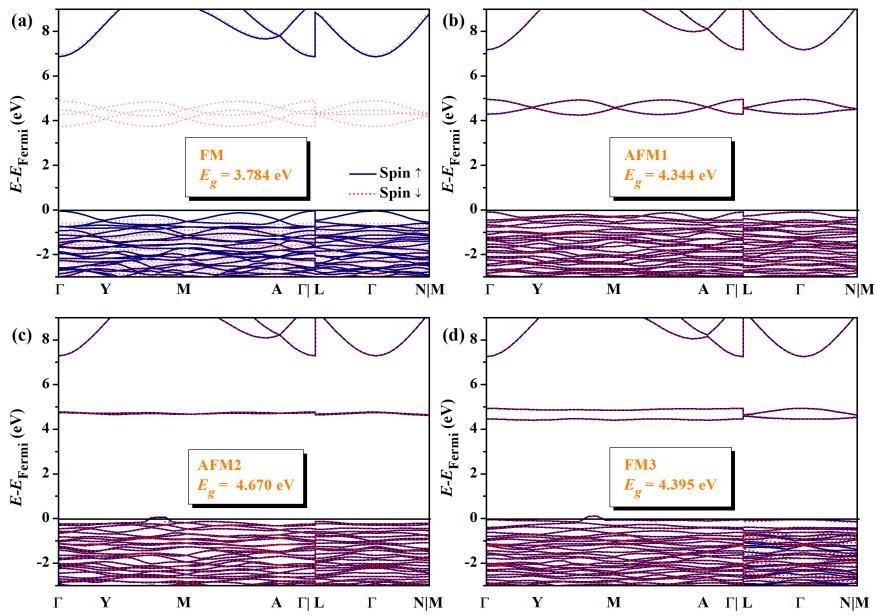
**Figure S1** Optimized crystal structures of (a) CuO and (b) P<sub>2</sub>O<sub>5</sub>.



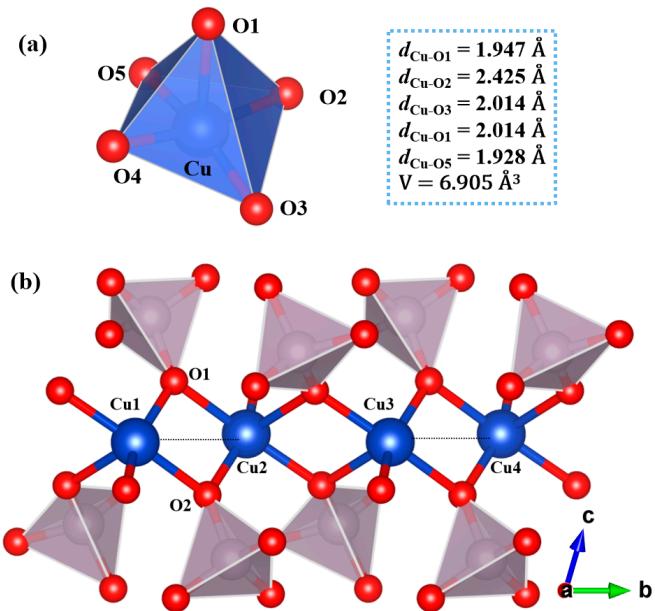
**Figure S2** The local crystal structure of a pyrophosphate group [P<sub>2</sub>O<sub>7</sub>]<sup>4-</sup> in α-Cu<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. (For interpretation of the color code in this figure, the reader is referred to the web version of the main article.)



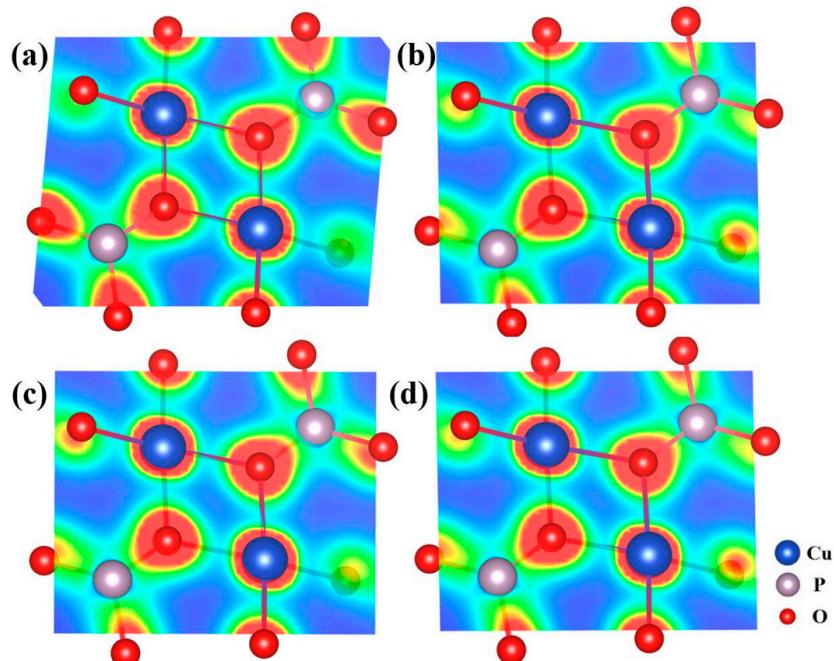
**Figure S3** Electronic energy band structures calculated using PBE functional for  $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$  in (a) FM, (b) AFM-1, (c) AFM-2, and (d) AFM-3 magnetic states.



**Figure S4** Electronic energy band structures calculated using PBE0 functional for  $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$  in (a) FM, (b) AFM-1, (c) AFM-2, and (d) AFM-3 magnetic states.



**Figure S5** Different representations of the Cu local environment: (a) the  $[CuO_5]$  pyramid and (b) the  $[CuO_4]$  distorted plaquette.



**Figure S6** Charge density in the  $(-1.5, 1, -2.5)$  plane with  $[Cu_2O_6]$  layer in  $\alpha$ - $Cu_2P_2O_7$  in four different magnetic states calculated using HSE functional. The isosurface level of the charge density is set at  $0.3 \text{ e}/\text{\AA}^3$ .

[1] Voigt, W. *Lehrbuch der Kristallphysik*; Teubner: Leipzig, Germany, 1928.

[2] Reuss, A. Berechnung der Fließgrenze von Mischkristallen auf Grund der Plastizitätsbedingung für Einkristalle. *Z. Angew. Math. Mech.* **1929**, 9, 49–58.