$Pb_9Cu(PO4)_6O$ is a charge-transfer semiconductor - Supplementary Materials

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I. EFFECT OF THE STRUCTURAL RELAXATION ON THE BAND GAP

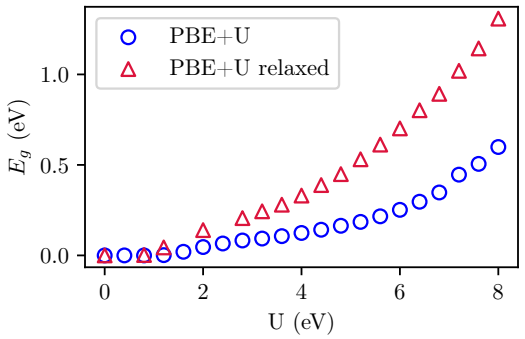

FIG. 1: Band gap as a function of U. Comparison between fixed and relaxed structure calculations.

II. SUBSTITUTION AT THE PB2 SITE

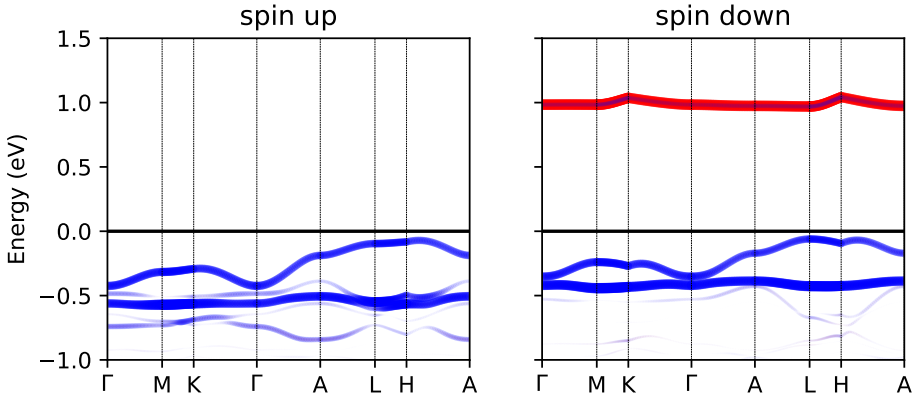

FIG. 2: Band structure for the spin up and down channels as calculated with VASP ncl using $U = 5.5$ eV and $J = 0.8$ eV and Cu at the Pb2 site. The system is insulating with $E_{gap} = 1.03$ eV.

III. ELECTRONIC SYMMETRY BREAKING ANALYSIS

Calculation performed with $U = 5.5$ eV and $J = 0.8$ eV.

$$O^{std} = \begin{pmatrix} 0.8694 & 0.0227 & -0.0000 & -0.1016 & -0.0000 \\ 0.0227 & 0.8636 & -0.0000 & 0.0000 & -0.1016 \\ -0.0000 & -0.0000 & 0.9665 & 0.0000 & 0.0000 \\ -0.1016 & 0.0000 & 0.0000 & 0.8636 & -0.0227 \\ -0.0000 & -0.1016 & 0.0000 & -0.0227 & 0.8694 \end{pmatrix} \tag{1}$$

$$O^{ncl} = \begin{pmatrix} 0.827 + 0.000i & 0.019 - 0.151i & 0.000 + 0.000i & -0.146 - 0.018i & -0.000 - 0.153i \\ 0.019 + 0.151i & 0.827 + 0.000i & 0.000 + 0.000i & 0.000 + 0.152i & -0.146 + 0.018i \\ 0.000 + 0.000i & 0.000 + 0.000i & 0.971 + 0.000i & -0.000 + 0.000i & -0.000 + 0.000i \\ -0.146 + 0.018i & -0.000 - 0.152i & 0.000 + 0.000i & 0.827 + 0.000i & -0.019 - 0.151i \\ 0.000 + 0.153i & -0.146 - 0.018i & 0.000 + 0.000i & -0.019 + 0.151i & 0.827 + 0.000i \end{pmatrix} \tag{2}$$

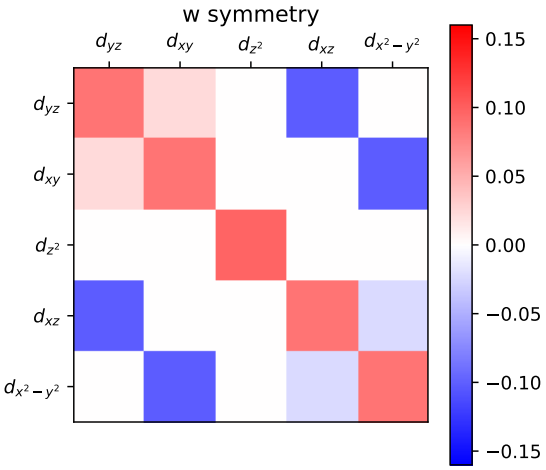

FIG. 3: Graphical representation of the occupation matrices O^{std} calculated with VASP `std`. The diagonal elements have been scaled by a factor 0.1 to improve the visibility of the off-diagonal terms.

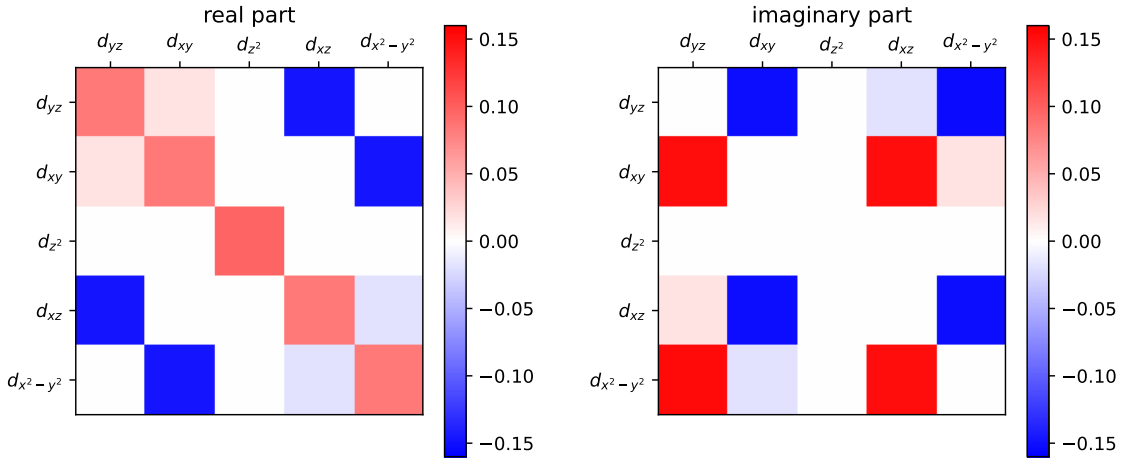

FIG. 4: Graphical representation of the occupation matrices O^{ncl} calculated with VASP `ncl`. The real and imaginary part are respectively given in the right and left panel. The diagonal elements have been scaled by a factor 0.1 to improve the visibility of the off-diagonal terms.

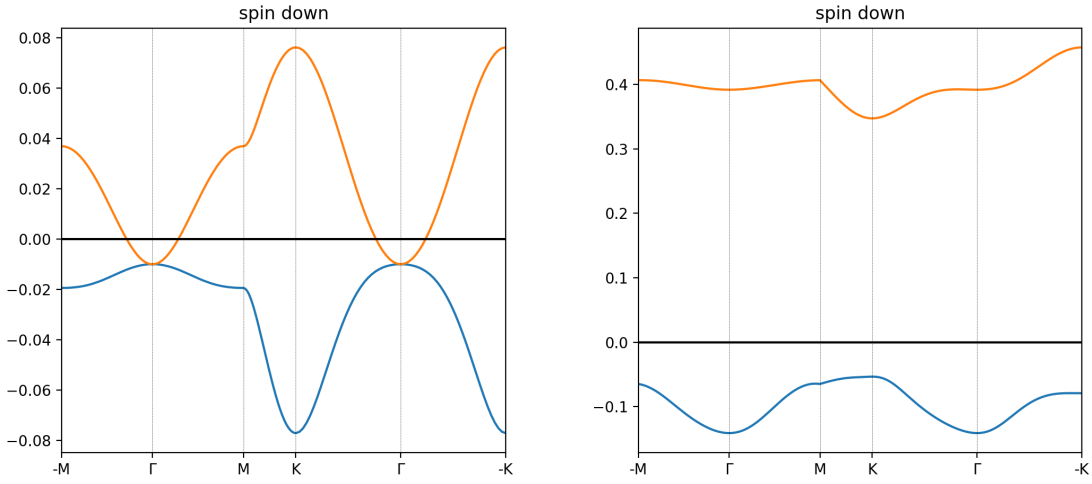

FIG. 5: Comparison between the `std` (right) and `ncl` (left) band structures.

IV. ELECTRONIC STRUCTURE WITH CRPA U AND J VALUES

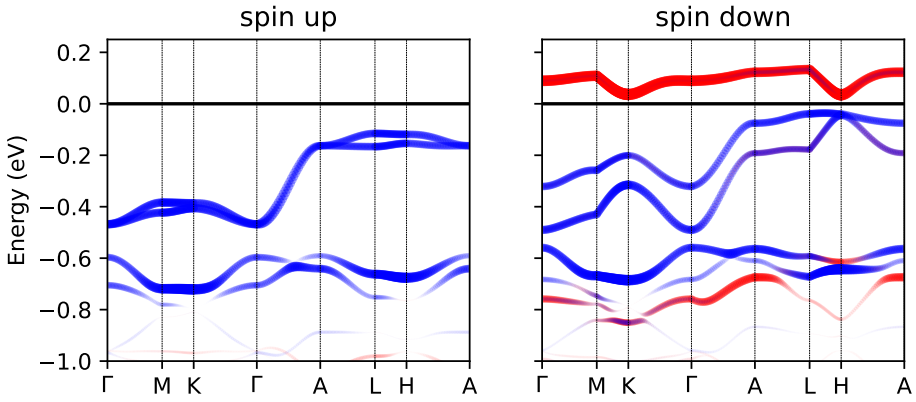

FIG. 6: Band structure for the spin up and down channels as calculated with VASP `ncl` using $U = 3.5$ eV and $J = 0.8$ eV. The latter correspond to the cRPA values obtained within the $d - d$ model (see Tab. 1 of the main text). The system is insulating with $E_{gap} = 0.07$ eV.

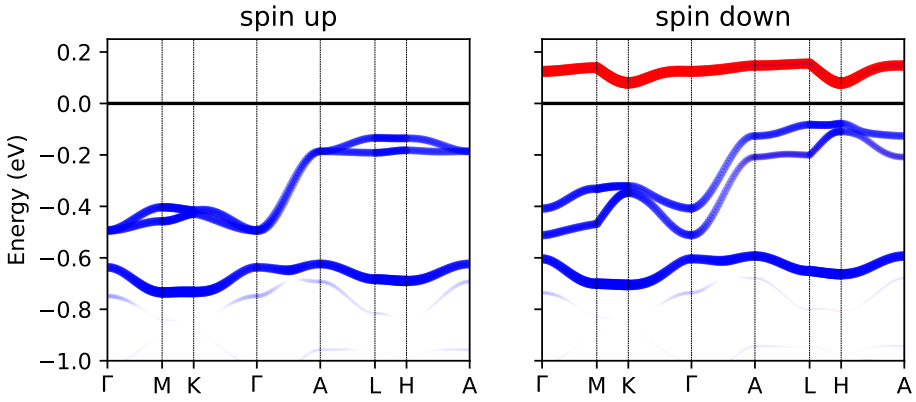

FIG. 7: Band structure for the spin up and down channels as calculated with VASP ncl using $U = 5.5$ eV and $J = 0.8$ eV. The latter correspond to the cRPA values obtained within the $p + d$ model (see Tab. 1 of the main text). The system is insulating with $E_{gap} = 0.16$ eV.