Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplemental Material for

Metallic to half-metallic transition driven by pressure and anion composition in niobium oxyfluoride

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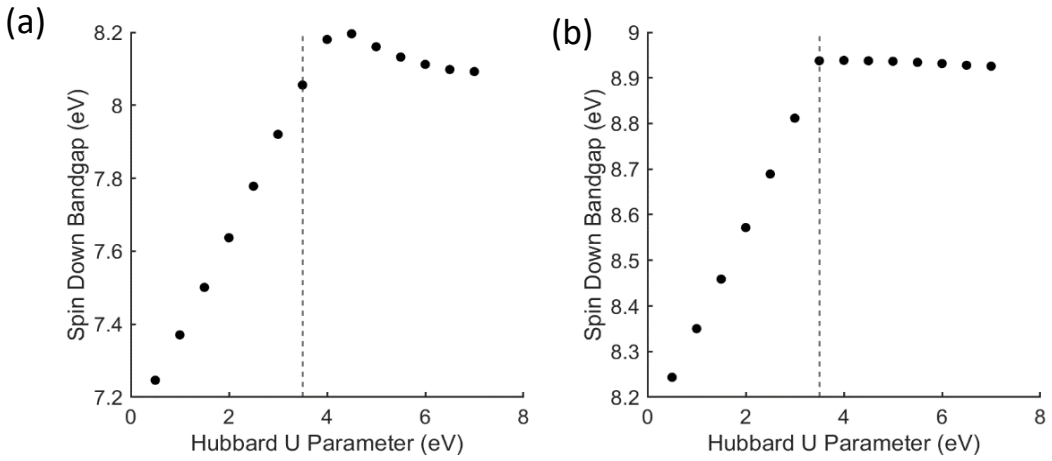

FIG. S1. Variation in calculated spin down band gap for cubic NbF_3 with Hubbard U parameter for (a) optimised geometry and (b) experimental geometry (ICSD #280539).

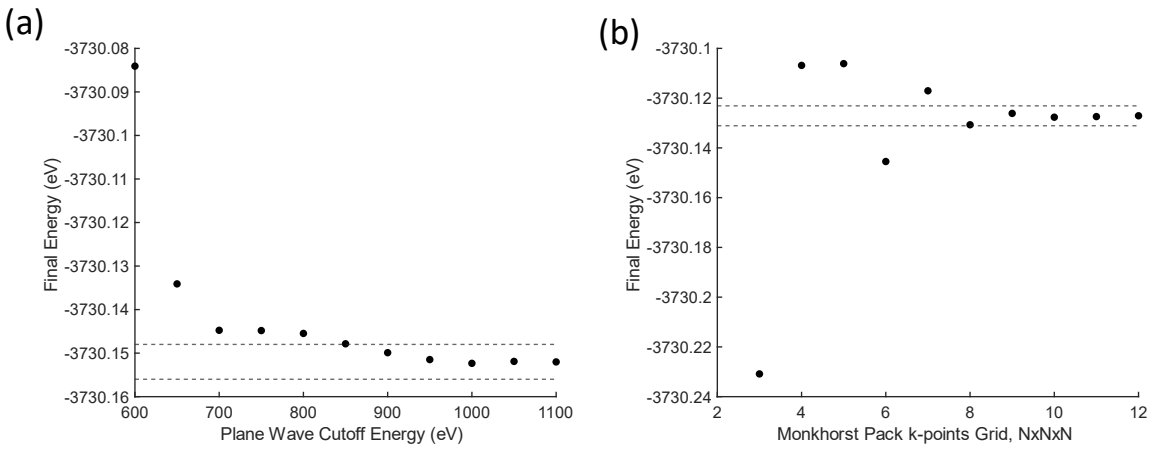

FIG. S2. Convergence testing for DFT calculations on cubic NbF_3 to optimise (a) plane wave cutoff energy and (b) k-point grid spacing to within a tolerance of +/- 0.004 eV shown by dashed lines.

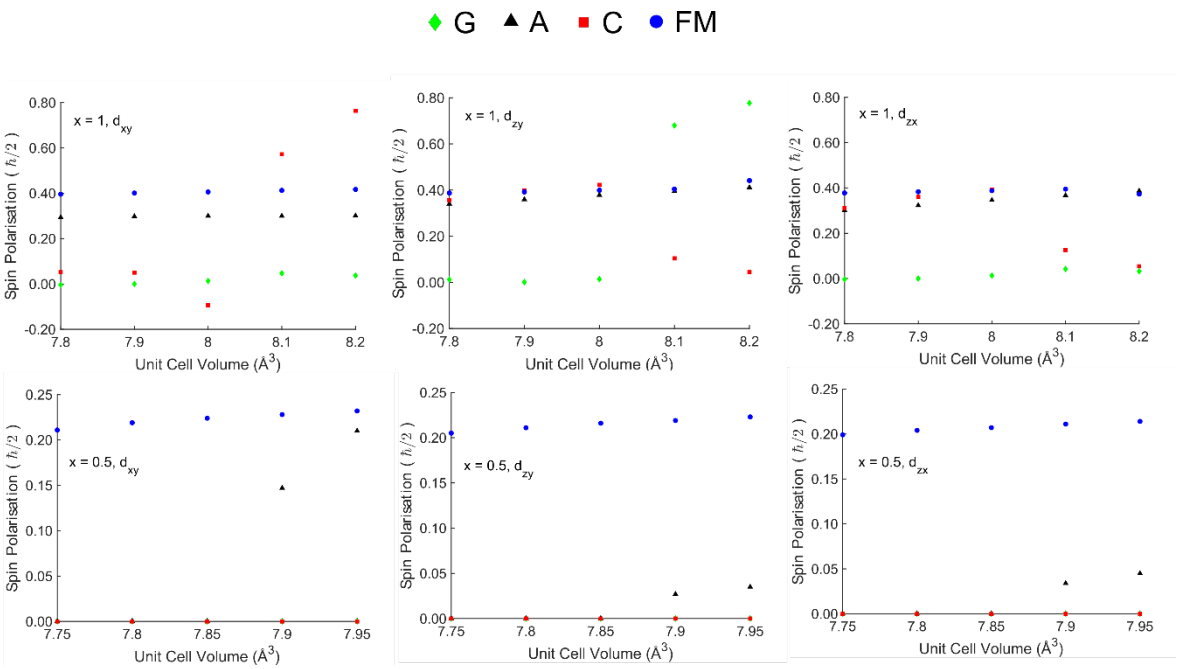

FIG. S3. Calculated atomic orbital spin polarisations for the $NbO_{2-x}F_{1+x}$ t_{2g} orbitals calculated using the LCAO projection approach within CASTEP.

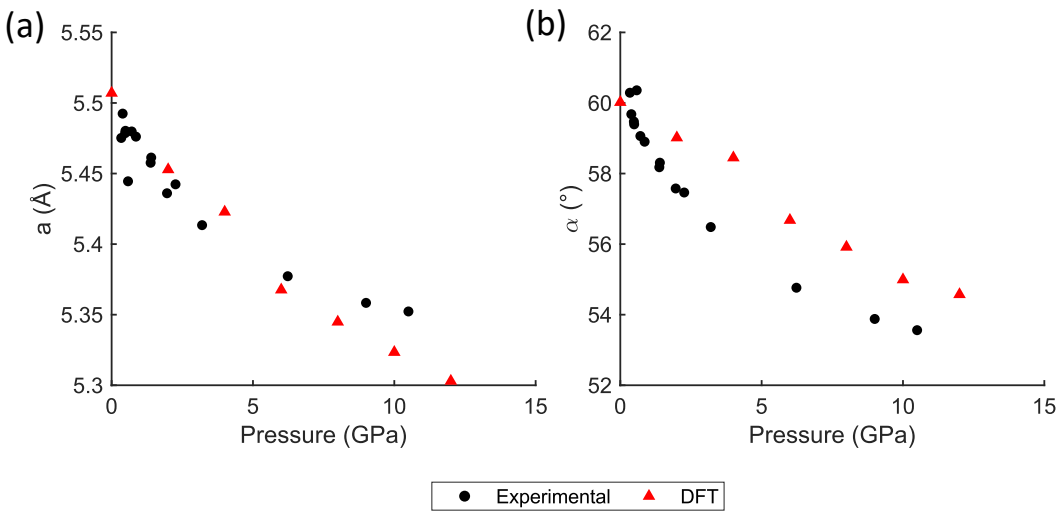

FIG. S4. The variation in DFT calculated rhombohedral unit cell parameters (a) a and (b) α with pressure compared with experimental results from Carlson *et al.*[1, 2]

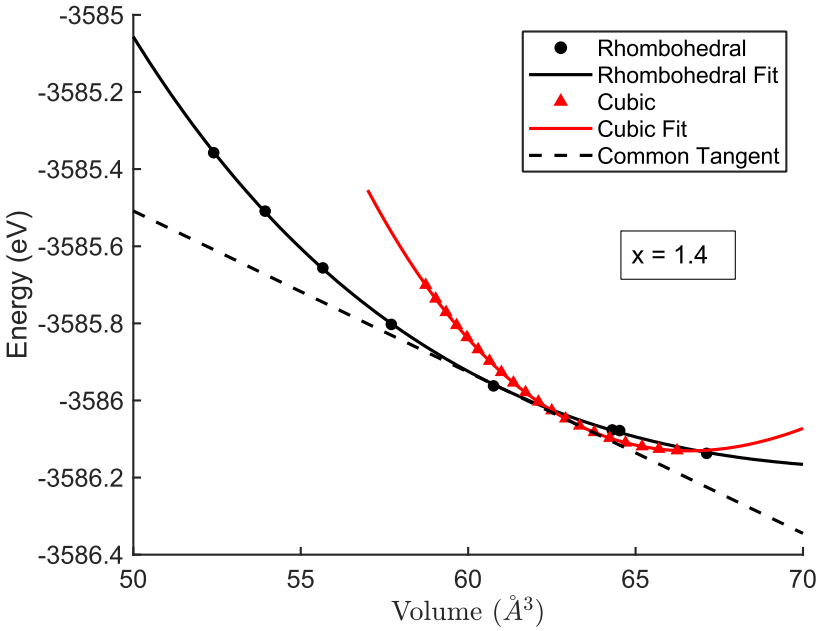

FIG. S5: Birch-Murnaghan equation of state fitting for DFT geometry optimisations of both cubic ($Pm\bar{3}m$) and rhombohedral ($R\bar{3}c$) $NbO_{0.6}F_{2.4}$ with a common tangent fit to estimate the transition pressure.

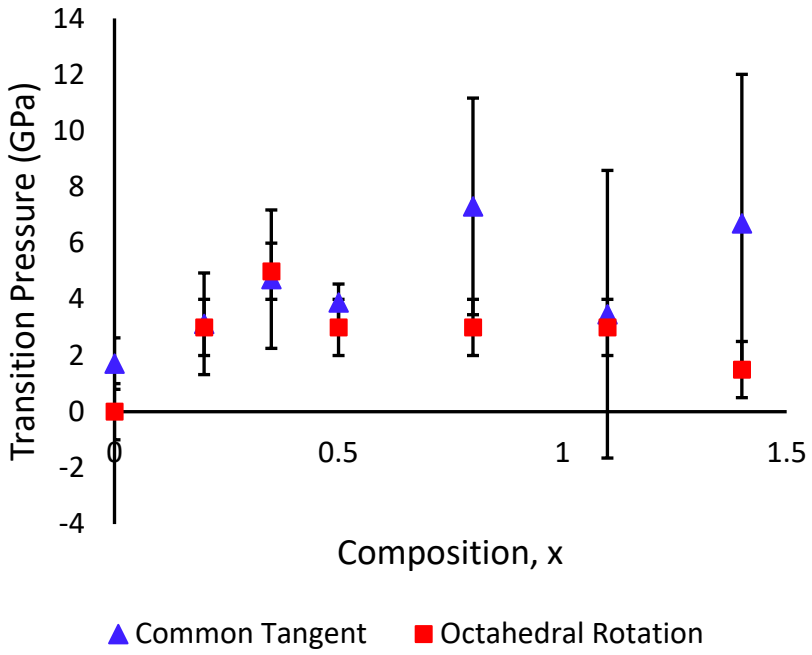

FIG. S6: Estimations of cubic to rhombohedral transition pressure for $NbO_{2-x}F_{1+x}$ determined from a common tangent approach and by comparing octahedral rotations.

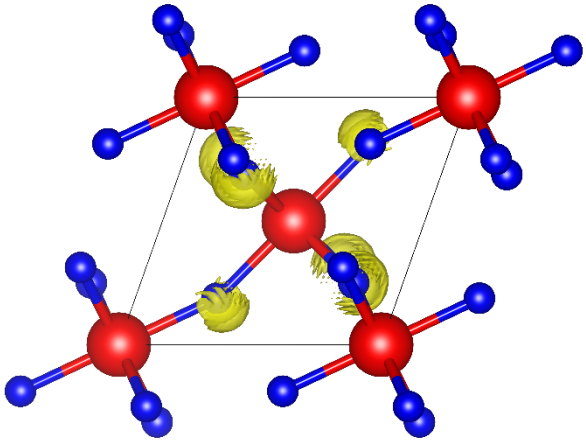

FIG. S7 Calculated electron localisation function (ELF) for NbO_2F at ambient pressure shown as an isosurface (yellow). Nb atoms are shown in red whilst O/F anions are shown in blue.

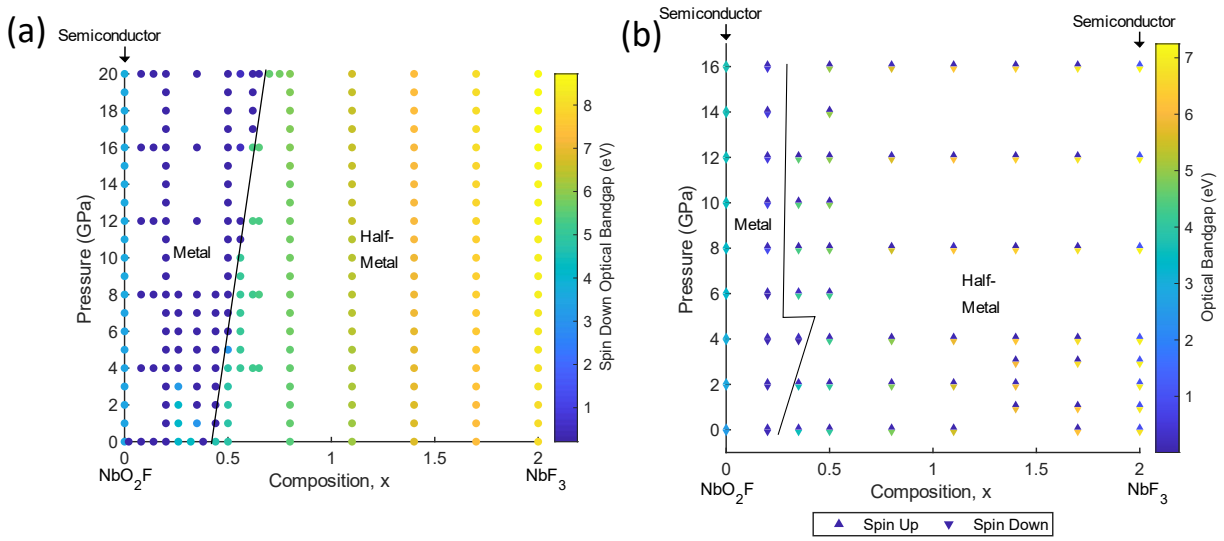

FIG. S8 DFT Calculated optical band gaps for a) cubic and b) rhombohedral $NbO_{2-x}F_{1+x}$ at each composition and external pressures up to 20 GPa.

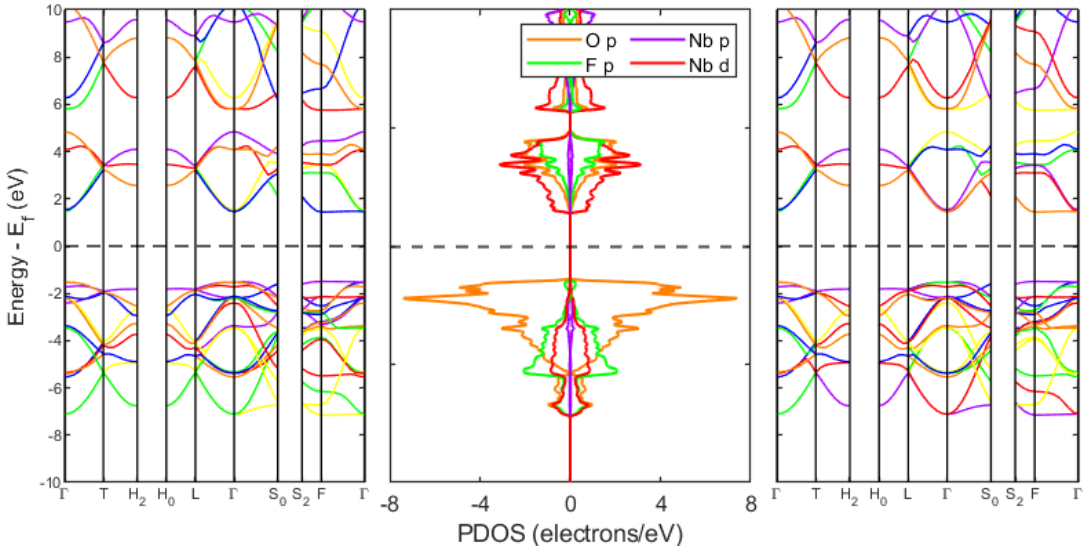

FIG. S9. DFT calculated band structure and PDOS for rhombohedral NbO_2F at an external pressure of 4 GPa.

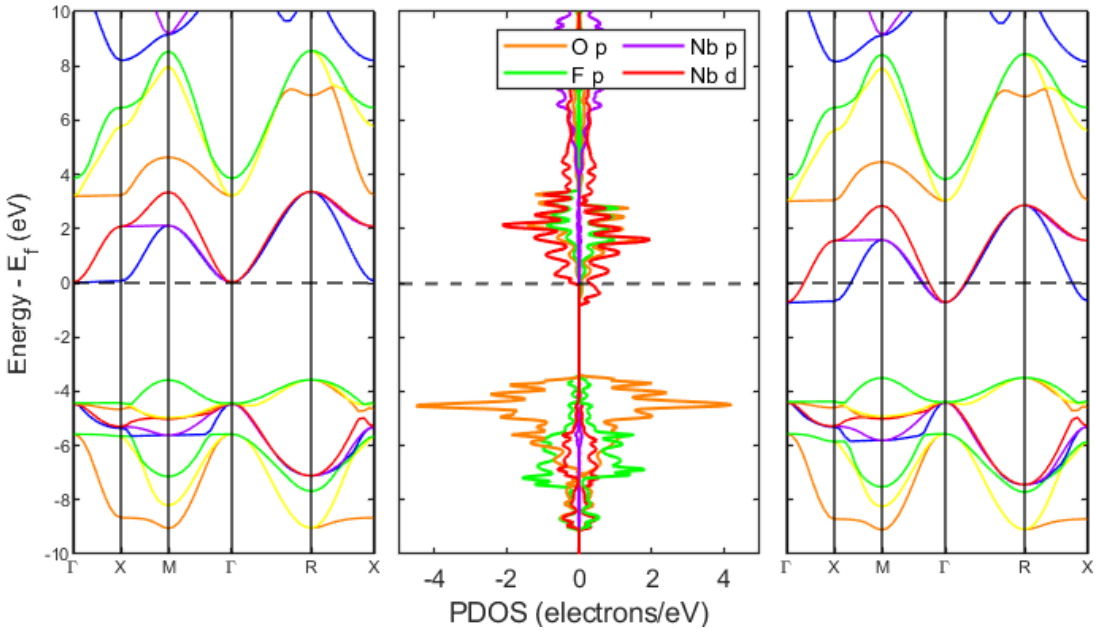

FIG. S10. DFT calculated band structure and PDOS for cubic $NbO_{1.65}F_{1.35}$ at an external pressure of 4 GPa.

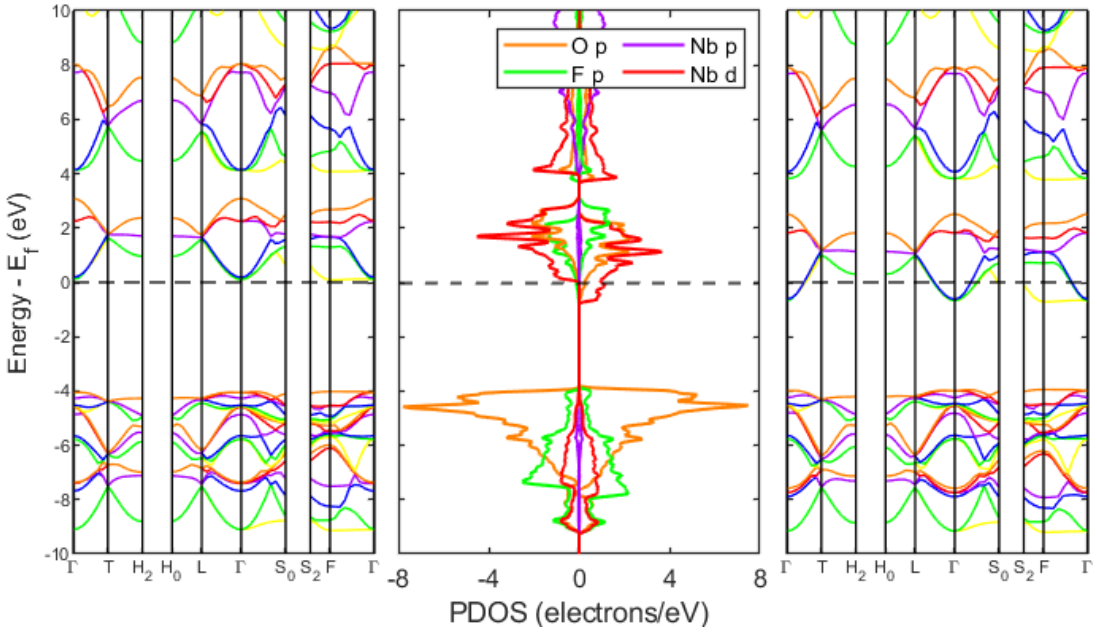

FIG. S11. DFT calculated band structure and PDOS for rhombohedral $NbO_{1.65}F_{1.35}$ at an external pressure of 6 GPa.

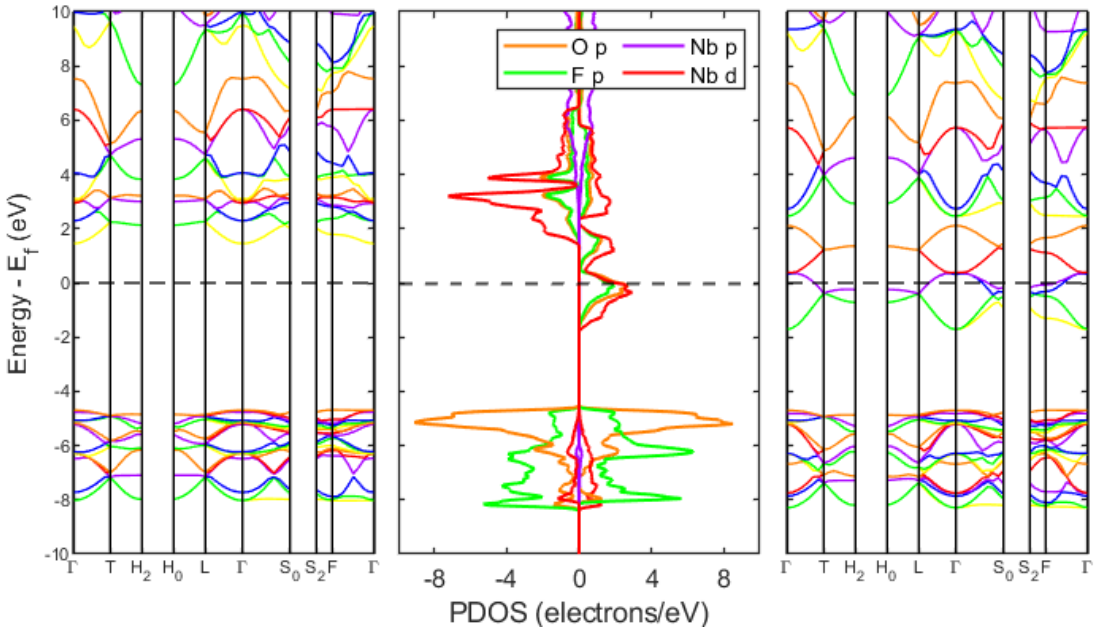

FIG. S12. DFT calculated band structure and PDOS for rhombohedral $NbO_{0.3}F_{2.7}$ at ambient pressure.

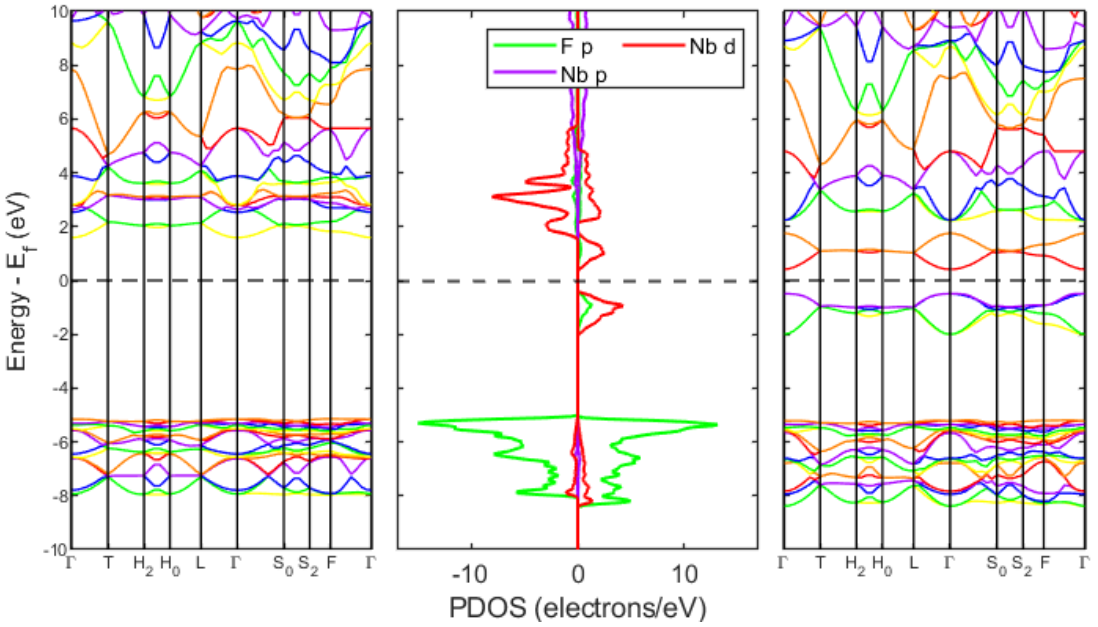

FIG. S13. DFT calculated band structure and PDOS for rhombohedral NbF_3 at ambient pressure.

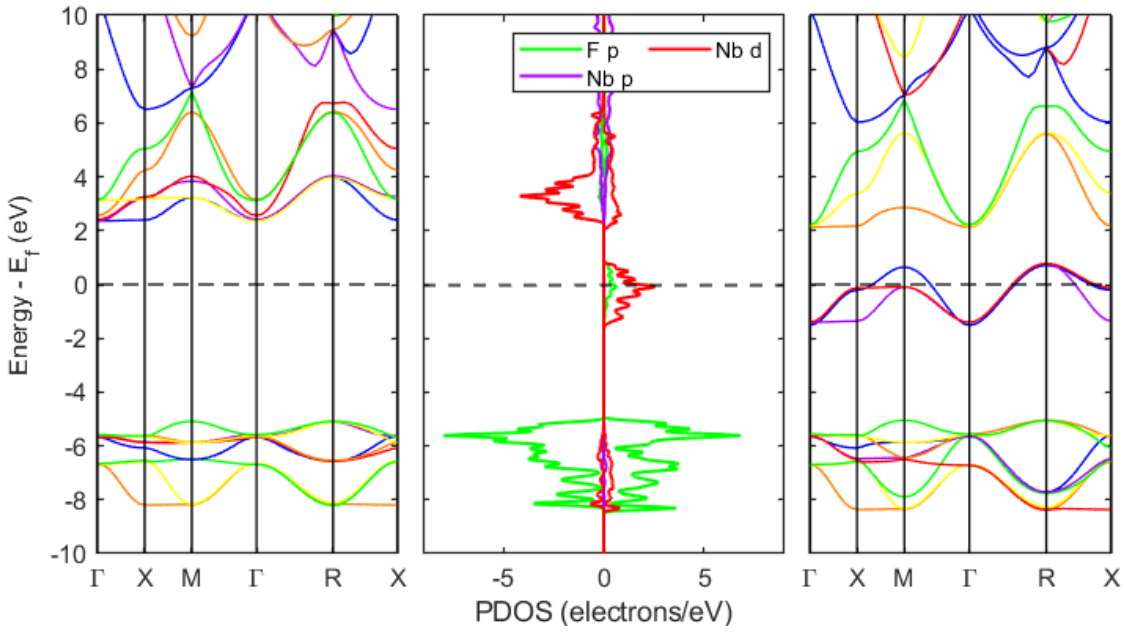

FIG. S14. DFT calculated band structure and PDOS for cubic NbF_3 at ambient pressure.

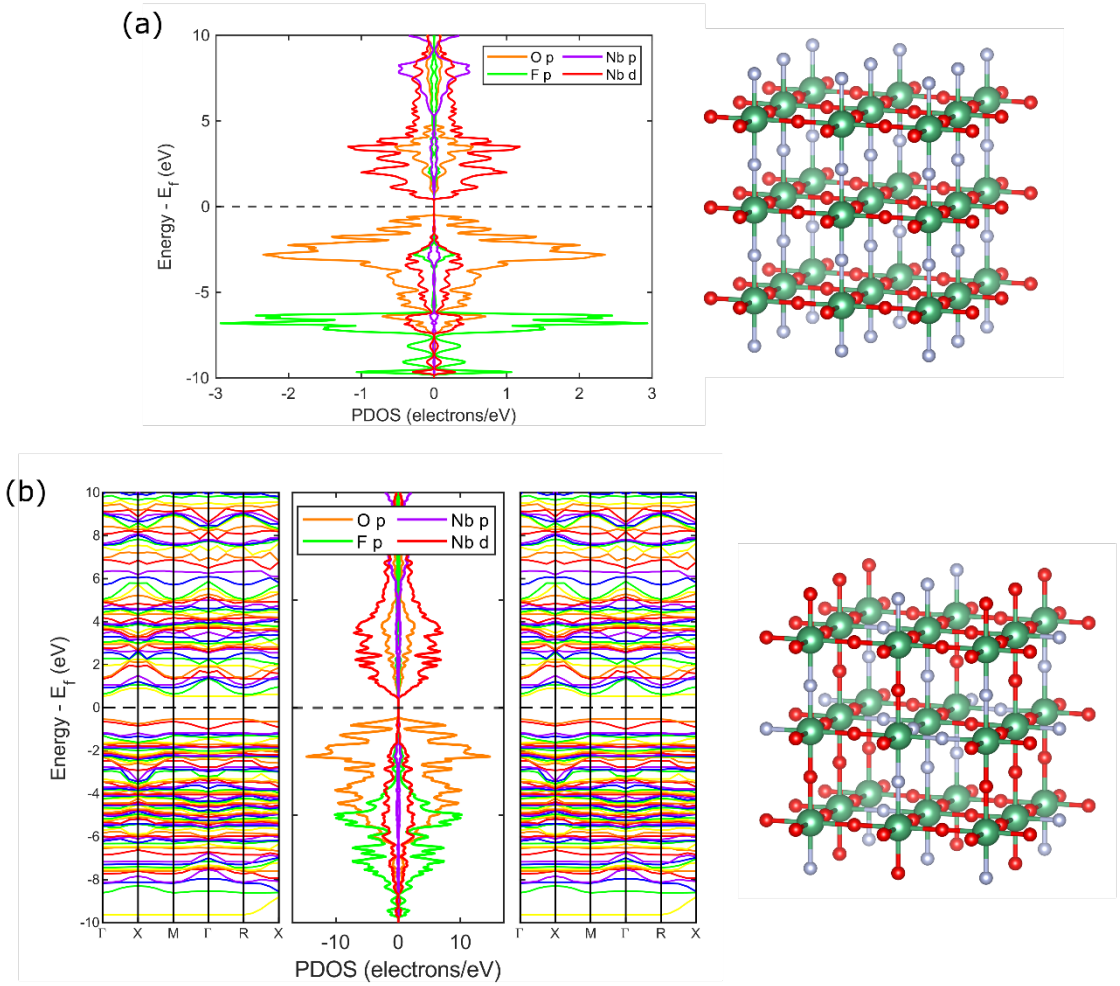

FIG. S15. DFT calculated electronic structure for anion-ordered supercell of cubic NbO_2F at ambient pressure (a) PDOS and supercell structure anions ordered in layers (b) PDOS and bandstructure with more disordered supercell structure.

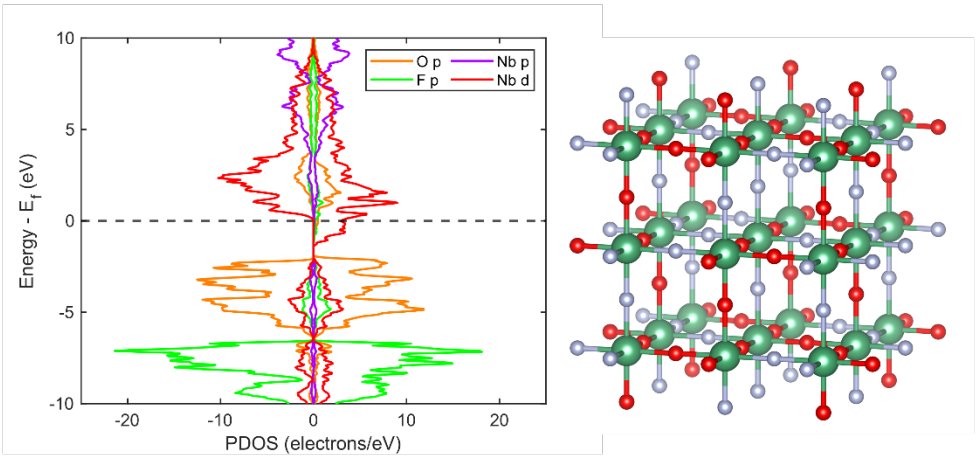

FIG. S16. DFT calculated PDOS and supercell structure for anion-ordered cubic $NbO_{1.5}F_{1.5}$ at ambient pressure with oxygen and fluorine anions ordered over alternating sites.

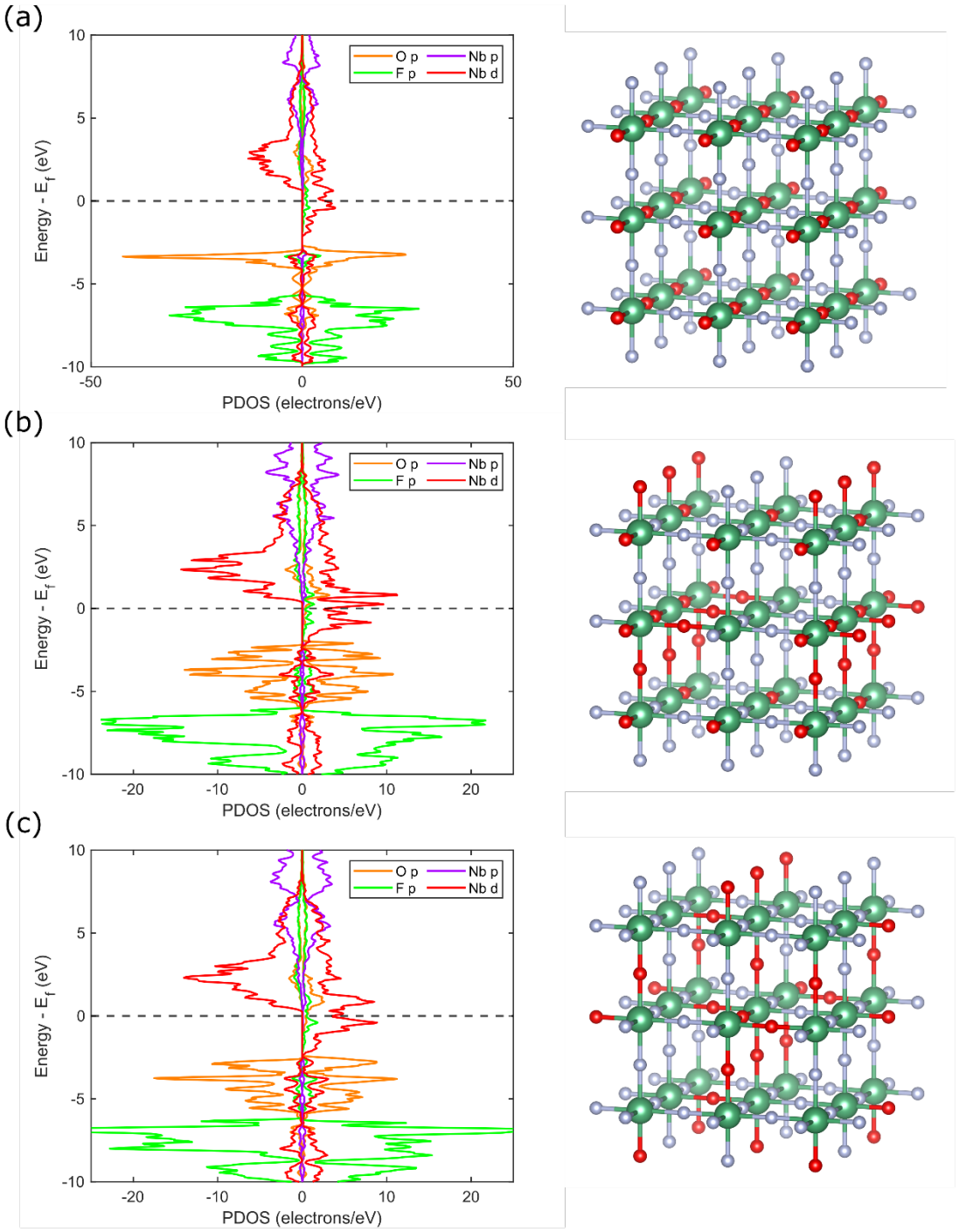

FIG. S17. DFT calculated PDOS and supercell structures for anion-ordered cubic $NbOF_2$ at ambient pressure (a) anions ordered in layers (b) more disordered anion structure (c) analogue of S15(b) anion structure with fluorine and oxygen sites reversed.

References

1. S. Carlson, *J. Appl. Crystallogr.*, 2000, **33**, 1175-1176.
2. S. Carlson, A.-K. Larsson and F. E. Rohrer, *Acta Crystallogr. Sect. B*, 2000, **56**, 189-196.