

Design of Photoactive Metal Chalcogenide Semiconductors: From Composition to Structure with Data-mining and Global Optimisation

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(Dated: 15 November 2017)

I. SUPPLEMENTAL DATA ITEMS

A. Dynamic Stability

No negative frequency phonon modes were found at Γ for the structures predicted by global optimisation. The phonon densities of states are shown in Figure S1. The negative frequency phonon modes in the $\text{Sn}_5\text{S}_4\text{Cl}_2$ structure are at the Y , T and Z high symmetry points in the Brillouin zone. These imaginary modes would not be present if the structure was doubled along X (and Y as these are equivalent) and T were considered. Due to the practical limits of the size of the unit cell that can be considered for a global search, such a structure was not identified.

For the compounds predicted by analogy, the $\text{Cd}_5\text{S}_4\text{Cl}_2$ and Cd_4SF_6 structures both had modes with negative frequencies (imaginary modes) which indicate a lack of a restoring force when a ions are displaced along the collective mode coordinate. Although this can often indicate dynamical instability, mapping out of the modes in question can in each case provide a satisfactory explanation for their presence.

In the case of the $\text{Cd}_5\text{S}_4\text{Cl}_2$ structure, three imaginary modes were found. Mapping of the first reveals a double well potential energy surface (Figure S3a). The second and third reveal two extremely shallow degenerate double wells (Figure S3b). The structure did not relax into one of these wells during the DFT relaxation step due to limitations inherent to the numerical optimisers used for structure relaxation; if the structure is at a saddle point with some symmetry on the potential-energy surface, it is unlikely that the optimiser will break the symmetry to find a minimum, as the forces on the structure are balanced. Nudging the structure into the larger of the two wells in Figure S3a results in a slight reduction of total energy and elimination of all three imaginary phonon modes. Mapping of the one imaginary mode present for the Cd_4SF_6 structure reveals a wide, flat-bottomed potential (Figure S3c), which suggests the imaginary mode is due to anharmonicity rather than the system being a saddle point on the energy surface.

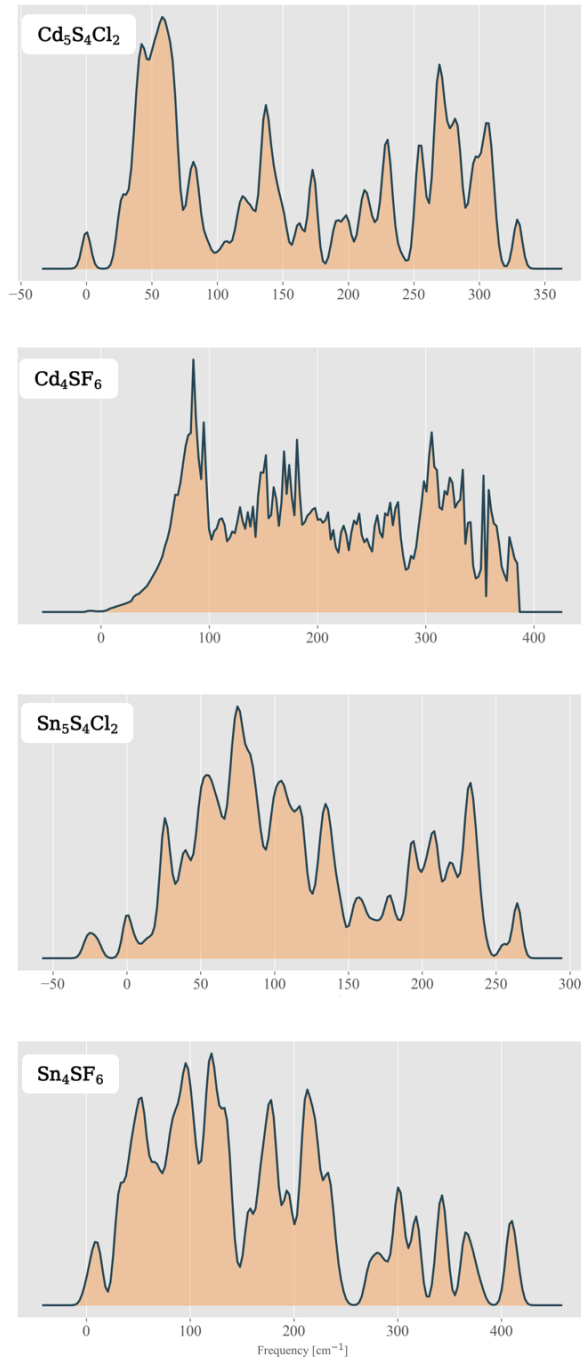


FIG. S1: Phonon densities of states for each of the structures found by global optimisation.

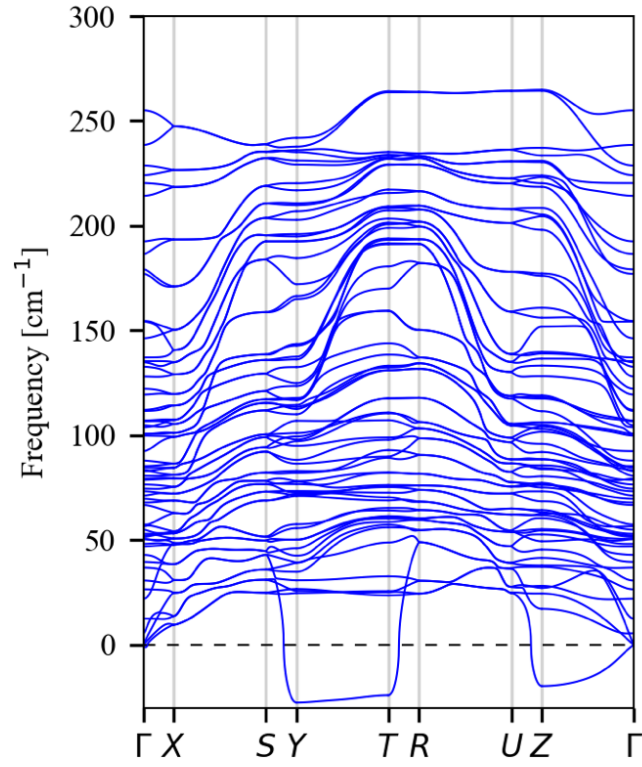


FIG. S2: Phonon band structure from a $1 \times 2 \times 2$ supercell of the $\text{Sn}_5\text{S}_4\text{Cl}_2$ crystal structure found by global searching.

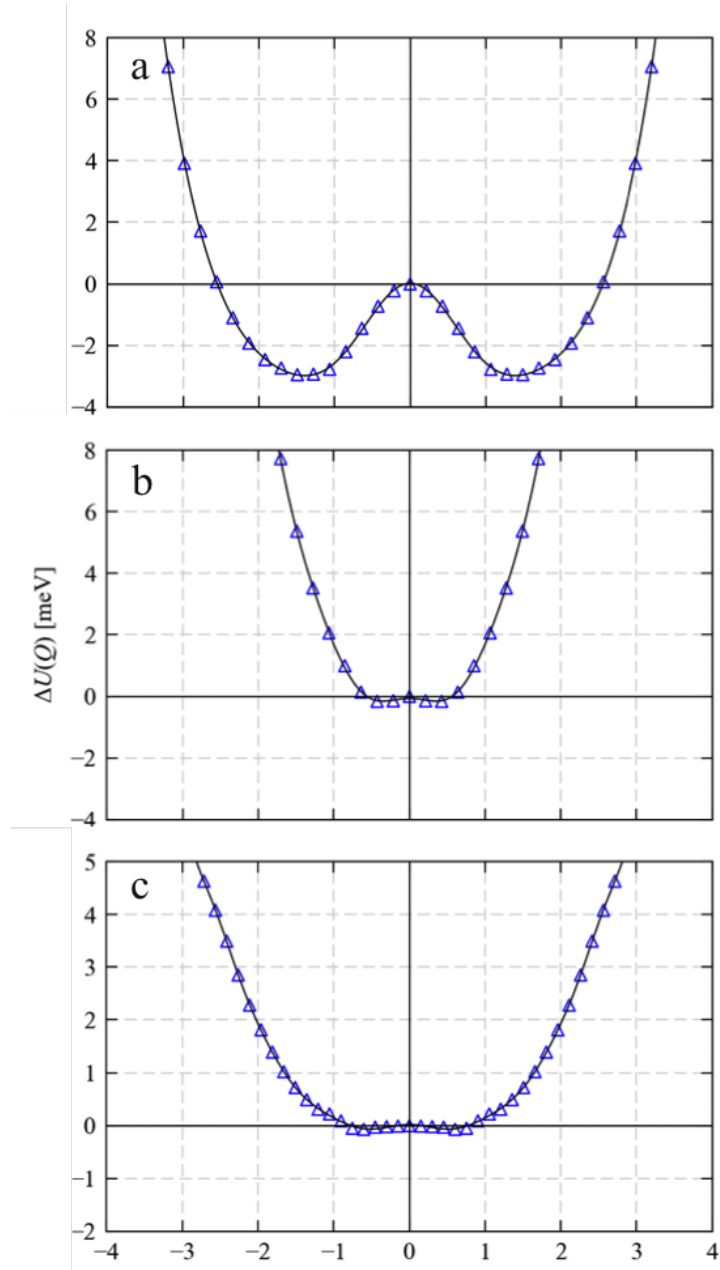


FIG. S3: Potential energy mapping of the imaginary phonon modes in the $\text{Cd}_5\text{S}_4\text{Cl}_2$ (a and b) and Cd_4SF_6 structures (c) found by analogy with known structure types.

B. Electronic Band Structures

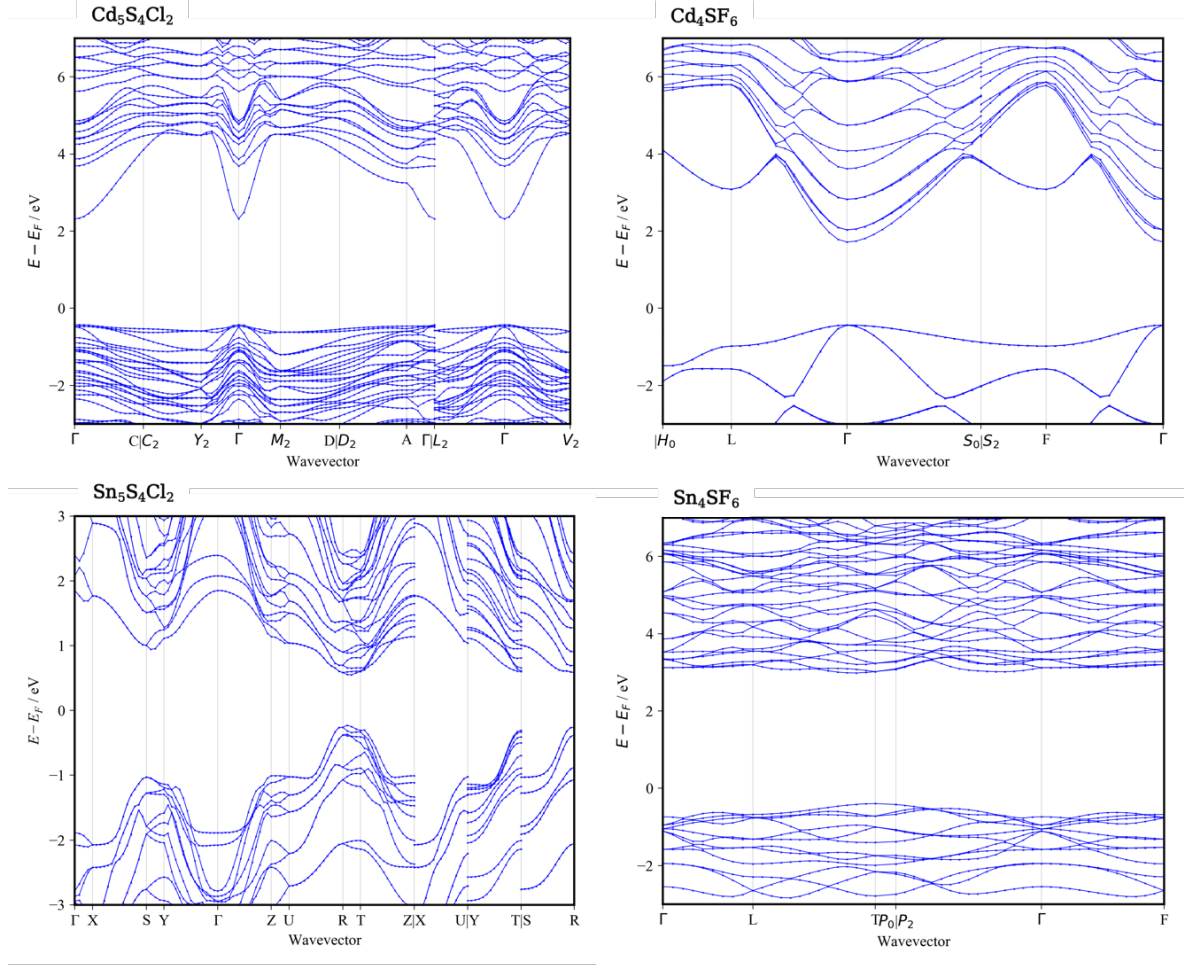


FIG. S4: Electronic band structures of the proposed chalcogenide compounds calculated using DFT and the HSE06 hybrid functional.