Supporting Information for:
Structural Transition in Layered $As_{1-x}P_x$ Compounds: A Computational Study

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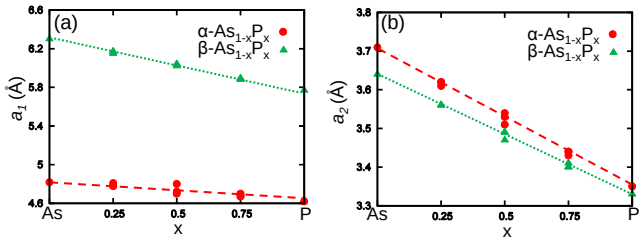

Figure S1: Equilibrium lattice constants (a) a_1 and (b) a_2 in the α (or $A17$) and β (or $A7$) phase of $As_{1-x}P_x$ compounds with changing composition. a_1 is aligned with the soft and a_2 with the hard direction. All structures are represented by rectangular unit cells containing 4 atoms.

Lattice constants of $As_{1-x}P_x$ compounds

As mentioned in main manuscript, the equilibrium lattice constants of $As_{1-x}P_x$ compounds depend sensitively on the composition. As seen in Figure S1, we find that the lattice constants decrease almost linearly with increasing phosphorus concentration. Since the primitive unit cell of the α (or $A17$) phase is rectangular and that of the β (or $A7$) phase is hexagonal, we projected the primitive unit cells of all structures, irrespective of composition and phase, onto conventional rectangular unit cells containing four atoms and spanned by the lattice vectors a_1 and a_2. As seen in Figure S1(a), this results in the effective lattice constant a_1 becoming longer in the β phase than in the α phase in the entire composition range. The situation reverses for the lattice constant a_2, which is longer in the α than in the β phase according to Figure S1(b). Clearly, the difference between the two structural phases is much larger for a_1 than for a_2.

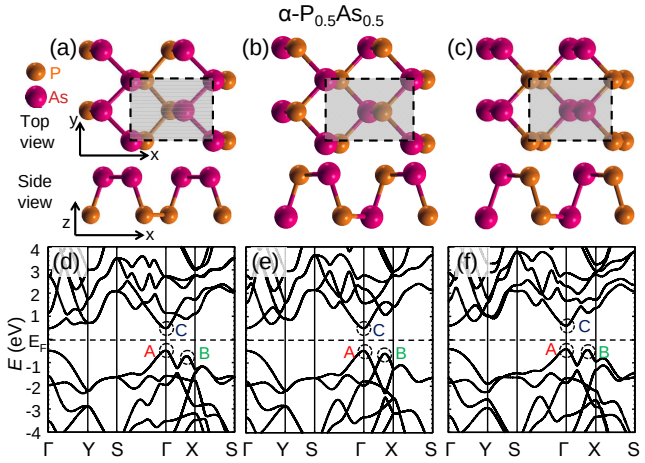

Figure S2: Electronic band structure of $As_{0.5}P_{0.5}$ structural allotropes in the α (or $A17$) phase with different relative arrangements of As and P atoms. Panels [(a) through (c)] show different atomic arrangements. Panels [(d) through (e)] show the electronic band structure for the structures in the panels above.

Electronic band structure of $As_{0.5}P_{0.5}$ compounds

In the main manuscript, we have shown that the electronic properties of $As_{1-x}P_x$ compounds depend on composition. Still, for a given stoichiometry, the electronic band structure depends on the local arrangement of As and P atoms within the unit cell. This is illustrated in Figure S2 for three different structures with the same composition $As_{0.5}P_{0.5}$ in the α phase. The electronic structure of these systems differs not only in the absolute value of the fundamental band gap, but also in the location of the valence band maxima in the conduction band. In analogy to the main manuscript, we label the valence band maximum at Γ by "A", another prominent valence band maximum by "B", and the conduction band minimum at Γ by "C". All three structures display a direct fundamental band gap at Γ. Still, depending on the structure, the energy difference between the valence band maxima at "A" and "B" decreases significantly from the structure in Figure S2(a) to that in Figure S2(c). Since the states corresponding to peaks "A" and "B" have a different character, changing atomic arrangement will be accompanied by a change in the valence frontier states. For structural arrangements not considered here, peak "B" could become the valence band maximum, changing a direct gap to an indirect gap. As discussed in the main manuscript, this transition is also expected to occur in compounds with a larger phosphorus concentration.