Understanding the Difference in Cohesive Energies between Alpha and Beta Tin

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The transition temperature between the low-temperature alpha phase of tin to beta tin is close to the room temperature ($T_{trans} = 130C$), and the difference in cohesive energy of the two phases at 0 K of about $\Delta E_{coh}=0.02 \text{ eV/atom}$ is at the limit of the accuracy of DFT (density functional theory) with available exchange-correlation functionals. It is however critically important to model the relative phase energies correctly for any reasonable description of phenomena and technologies involving these phases, for example, the performance of tin electrodes in electrochemical batteries. Here, we show that several commonly used and converged DFT setups using the most practical and widely used PBE functional result in $\Delta E_{coh}\approx 0.04 \text{ eV/atom}$, with different types of basis sets and with different models of core electrons (all-electron or pseudopotentials of different types), which leads to a significant overestimation of T_{trans} . We show that this error is due to the errors in relative positions of s and p –like bands, which, combined with different populations of these bands in alpha and beta Sn can be obtained with the same computational scheme. We quantify for the first time the effects of anharmonicity on ΔE_{coh} and find that it is negligible.



Figure 1. Crystal structures of alpha (left) and beta tin.