Order-Disorder Transition in Kesterite Cu_2ZnSnS_4: Thermopower Enhancement via Electronic Band Structure Modification

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1. Further DFT calculations

1.1 Full band structure for ordered and disordered kesterite

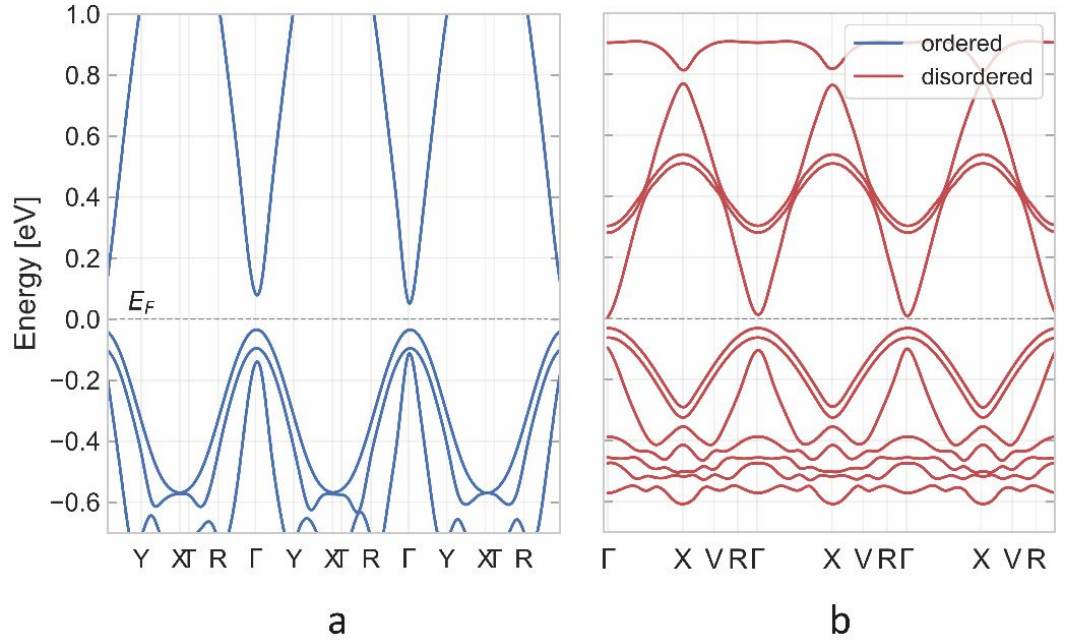

Figure S1. Full band structures for ordered (a), and disordered (b) kesterite. The reduced curvature of valence bands close to the energy gap for the disordered polymorph is clearly visible. The Fermi energy is set to 0 eV in each case. X-axis is on the same scale in k-space.

1.2 Different configurations and degrees of disorder

To allow a better understanding of the behavior of kesterite during the order-disorder transition, additional simulations were carried on with the same calculation method described in section 2.2 of the main text. A partially disordered structure was modelled by disordering half of the 64-atom supercell (Figure S2a). The relevant band structure is visible in Figure S3a, where it is possible to notice the intermediate behavior with respect to the ordered and fully disordered phase, with a closer similarity to the latter. This is consistent with the definition of random occupation of Cu and Zn cations for the disordered structure, which will also include some narrow regions of order. For what concerns the disordered structure, a 64-atom supercell cannot be representative of disorder in the real situation, which should be modelled with a computationally unfeasible much larger supercell, that accounts for additional patterns of disorder. To partially overcome this problem, we have simulated the behavior of an additional configuration of fully disordered kesterite, the supercell of which is visible in Figure S2b, and band structure in Figure S3b. The band structure shows a behavior consistent with the first simulation: although not identical, due to different cation positions and therefore a slightly different super-structure, if compared to the band structure of ordered kesterite, it is possible to observe a reduction of band gap, and flatter, more converged bands.

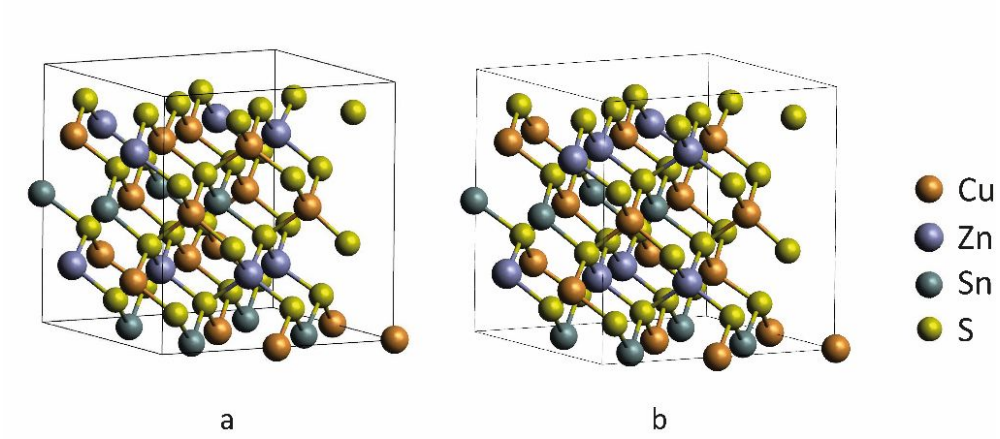

Figure S2. Supercell crystal structures of kesterite used in the additional DFT calculations simulating partial disorder, (a), and another configuration of full disorder, (b).

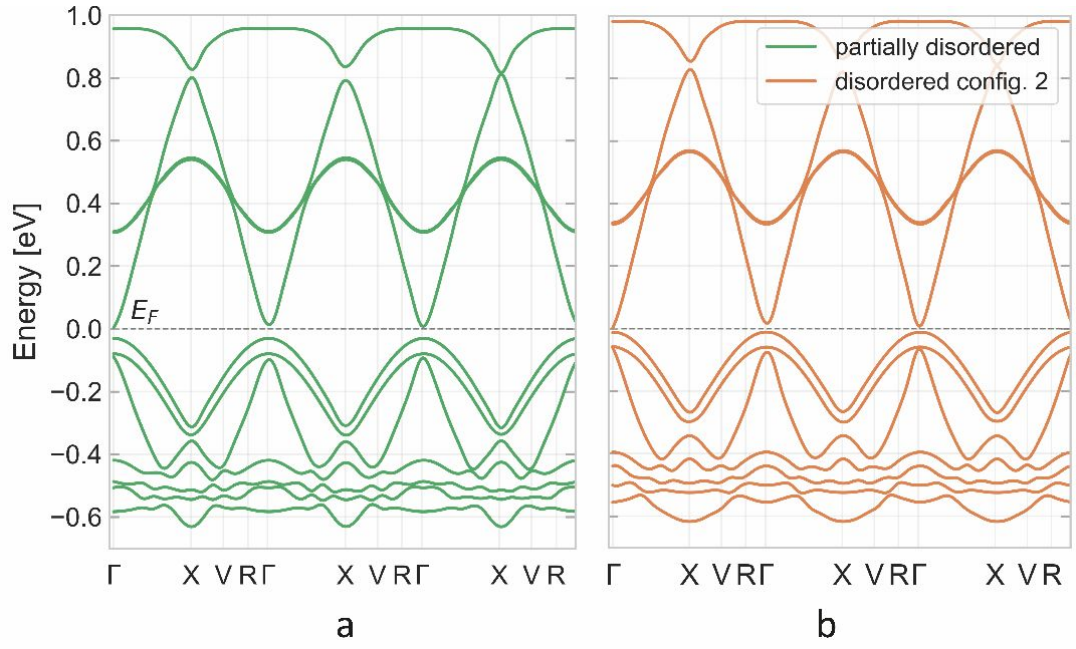

Figure S3. Band structures for partially disordered (a), and an additional configuration of fully disordered (b) kesterite. The Fermi energy is set to 0 eV in each case. X-axis is on the same scale in k-space.