Supplemental Material for: '2D and 3D Cu/ Zn order-disorder transitions in Cu_2ZnSnS_4 from Monte Carlo simulations'

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1 Convergence of change in lattice energy with cut-off radius for Monte Carlo moves

In the Monte Carlo (MC) simulations of CZTS, we use the change in lattice energy, dE, of the system before and after performing an MC move (nearest-neighbour Cu-Zn substitution) to determine if the move should be accepted or rejected.

In a simple model of ionic crystals, it is assumed that the lattice energy is given entirely by the potential energy of classical ions of charge Z at their equilibrium positions [1]. Two oppositely charged ions separated by a distance r experience an attractive Coulomb force, F, shown in equation 1. Their Coulombic potential energy, U, is then given by equation 2 [2].

$$F = \frac{e^2 Z_+ Z_-}{4\pi\epsilon_0 r^2} \tag{1}$$

$$U = \int_{\infty}^{r} F dr = -\frac{e^2 Z_+ Z_-}{4\pi\epsilon_0 r} \tag{2}$$

Considering nearest neighbouring ions, next-nearest neighbours, etc. out to a particular cut-off and summing over pairwise contributions to the electrostatic potential gives the dominant term in the expression for the lattice energy. Here, we are neglecting short-range forces including van der Waals interactions.

For computational efficiency when performing large numbers of MC moves, we use a finite cutoff radius for the lattice energy summation. To ensure that we use a suitable r_{cutoff} for our lattice summations when calculating dE for each MC move, we calculate dE for the same move with increasing r_{cutoff}, as shown in Fig. 1. From this, we have taken 5 lattice units as a suitable value for r_{cutoff}. We use the same volume for

the lattice summation before and after performing the nearest-neighbour Cu-Zn substitution to compute dE (we called this our 'site_energy_stencil' method in the Eris source code). This method was found to be better for achieving convergence in dE when using a finite cutoff radius for the lattice energy summation.

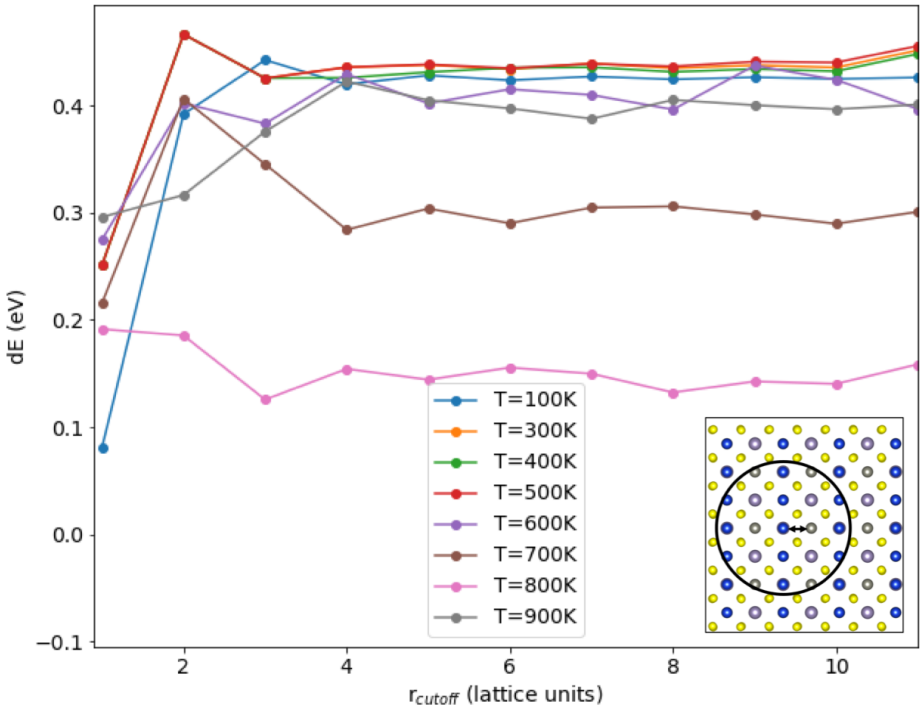

Figure 1: Convergence in the change in lattice energy (dE) for 3D Cu/ Zn disorder with respect to the cut-off radius (r_{cutoff}) for the lattice summations. The schematic shows a proposed swap between a Cu (blue) and Zn (steel grey) ion, and the circle is used to demonstrate a cut-off radius used for the lattice energy summation to obtain dE between the system before and after the proposed Monte Carlo move.

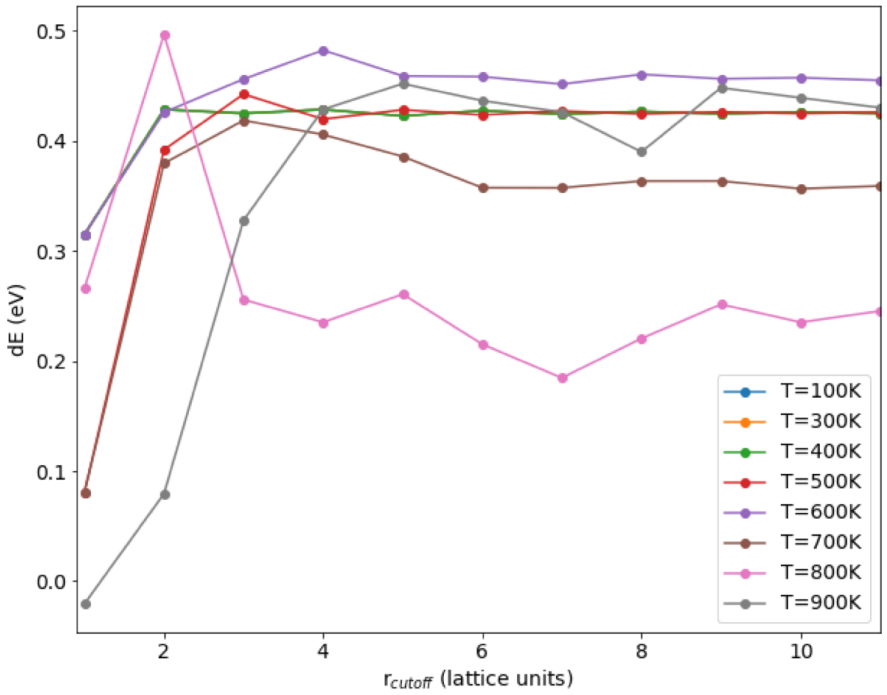

Figure 2: Convergence in the change in lattice energy (dE) for 2D Cu/ Zn disorder with respect to the cut-off radius (r_{cutoff}) for the lattice summations.

2 Equilibration check for 2D Cu/ Zn disorder

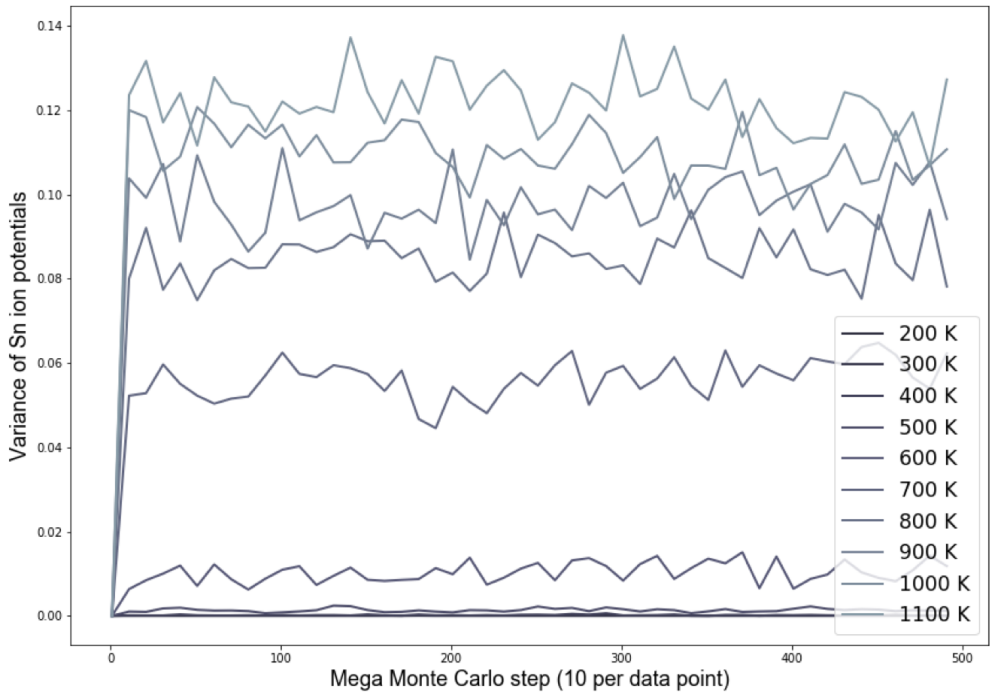

Figure 3: Variance in the distribution of the on-site electrostatic potential of Sn ions in a 24×24×24 Cu_2ZnSnS_4 system (containing 13,824 ions in total) across a range of simulation temperatures with 3D Cu/ Zn disorder. Each mega Monte Carlo step corresponds to sweeping across the lattice and attempting 100 trial moves per lattice site.

3 Finite-size check for 2D Cu/ Zn disorder

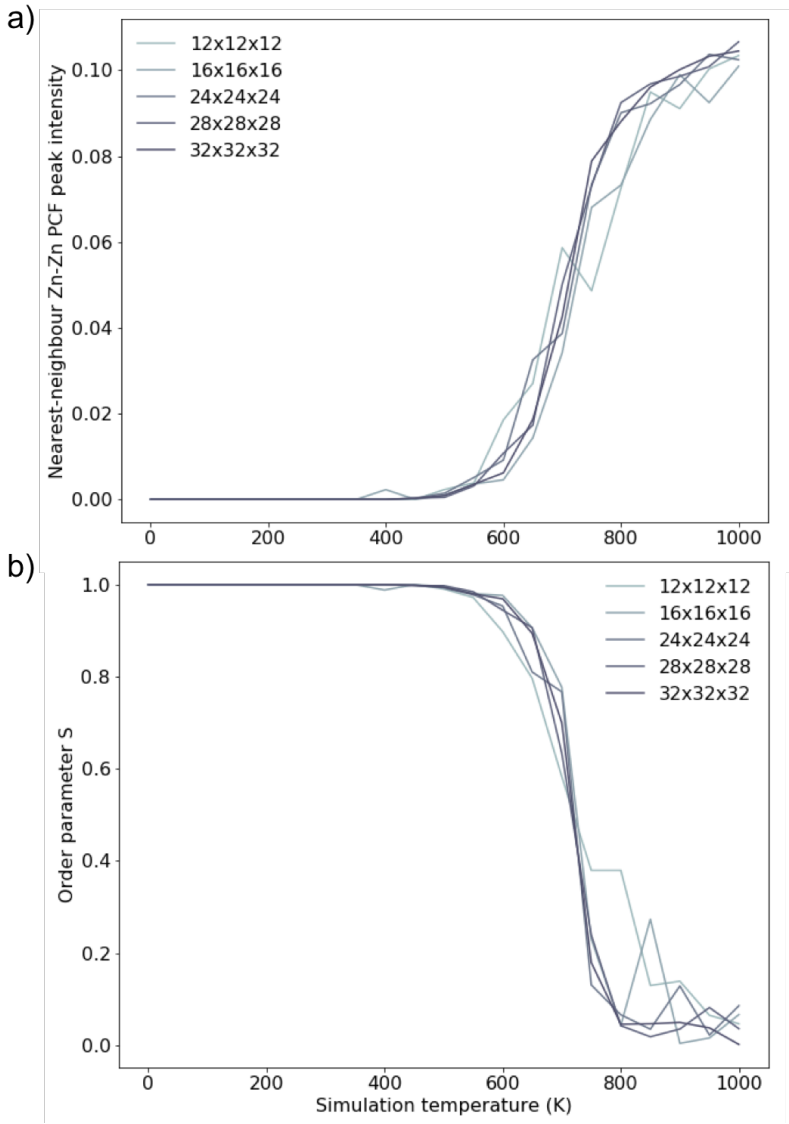

Figure 4: Two order parameters to assess finite-size effects for 2D Cu/ Zn disorder. Order parameters discussed further in the manuscript.

References

[1] N. Ashcroft and N. Mermin. *Solid State Physics*. Saunders College Publishing, 1976.

[2] A. West. *Bonding in Solids*. John Wiley & Sons, Ltd., 1999.