Supplemental Material for: 'Thermodynamically limited Cu-Zn order 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, ΔE, 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, V, is then given by equation 2 [2].

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

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

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.

To ensure that we have use a suitable r_{cutoff} for our lattice summations when calculating ΔE for each MC move, we calculate ΔE 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}.

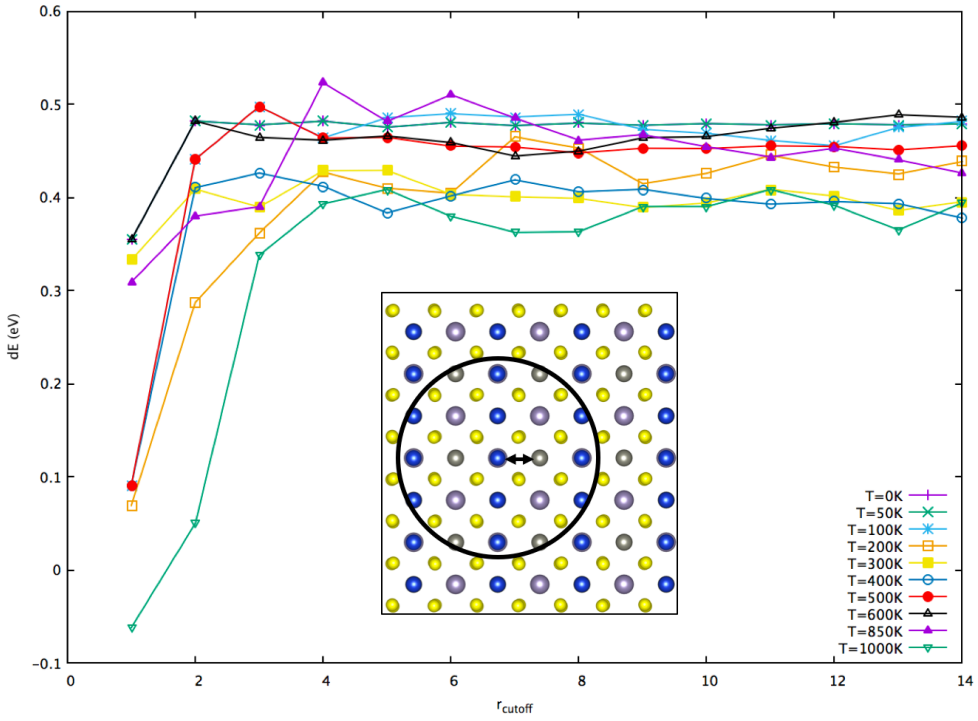

Figure 1: Convergence in the change in lattice energy (ΔE) with respect to the cut-off radius (r_{cutoff}) for the lattice summations. The schematic shows a proposed swap between a Cu (blue) and Zn (steel grey) ion, and the circle is used to demonstrate a cut-off radius used for the lattice energy summation for the ΔE.

2 Convergence in lattice potential with cut-off radius for equilibration test

We take a value of 10 lattice units as suitable r_{cutoff} for lattice potential calculations in equilibration tests using the variance in distribution of Sn potentials calculated in Fig. 2.

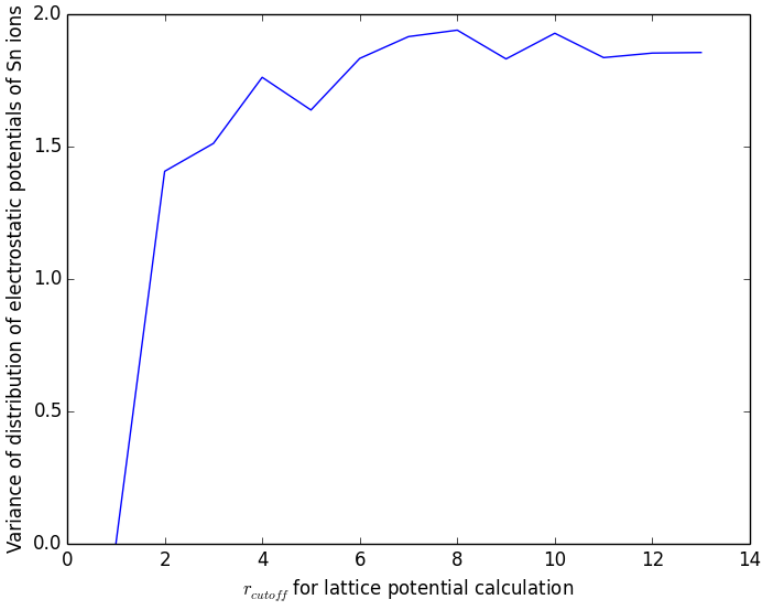

Figure 2: Convergence in the variance of the distribution of on-site electrostatic potentials of Sn ions calculated by our custom code with increasing cut-off radius for each calculation of lattice potential. Simulation run at T= 1050K and allowed to evolve from an ordered initial lattice.

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.