Direct derivation of the atomic displacement parameters with molecular dynamics simulations

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Atomic displacement parameters (ADPs) are often provided as part of crystallographic structural data and may represent atomic motion, possible static displacive disorder, and thermal vibration. [1] Theoretical derivations of ADPs are typically performed indirectly through lattice dynamics analysis, where the dynamical matrix is obtained and the vibrational, or phonon, frequency of each mode is calculated. However, the lattice dynamics approach is difficult to apply in systems where disorder of elements on a (sub)lattice plays a critical role and in split-site systems.

Direct derivation of anisotropic ADPs, assuming a normal (or Gaussian) distribution, using molecular dynamics (MD) simulations is possible even for disordered systems and split site systems. The ADP is simply the (co)variances of atom positions. The very recent advances in off-the-shelf universal potentials applicable to diverse systems allow accumulation of a very large number of atom positions through classical MD simulations.

Fig. 1 shows the isotropic ADP, U_{iso}, for Mg and O in MgO. MD simulations were conducted using the Matlantis package from Preferred Networks and their PreFerred Potential (PFP), a machine-learned neural network potential trained on the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) to density functional theory (DFT). Simulations were performed on a 5×5×5 supercell with a time step of 2 fs, and the number of steps was 50,000 steps (100 ps). Positions were recorded every 100 steps, but those for the first 10,000 steps were discarded to account for initial shifting of atoms to attain equilibration. The number of atom position data is 500 atoms × 400 recordings = 200,000 each for Mg and O.

The calculated ADPs are proportional to temperature over the entire range, which is consistent with an Einstein model description where the Mg and O atoms are in a harmonic potential well. The ADP should be non-zero at 0 K because of zero-point motion, but becomes zero in the calculations because the MD simulations are based on classical dynamics without zero-point motion. The zero-point motion effect can be evaluated as a correction based on the proportionality factor, and the corrected U is shown with a dashed line in Fig. 1. The room temperature experimental values of 0.0038-0.0040 Å^2 and 0.0042-0.0046 Å^2 for Mg and O, respectively, [2-4] are reproduced well.

Application of the proposed method to systems containing atoms with large anisotropic ADPs or with partially disordered sites are discussed in the presentation.

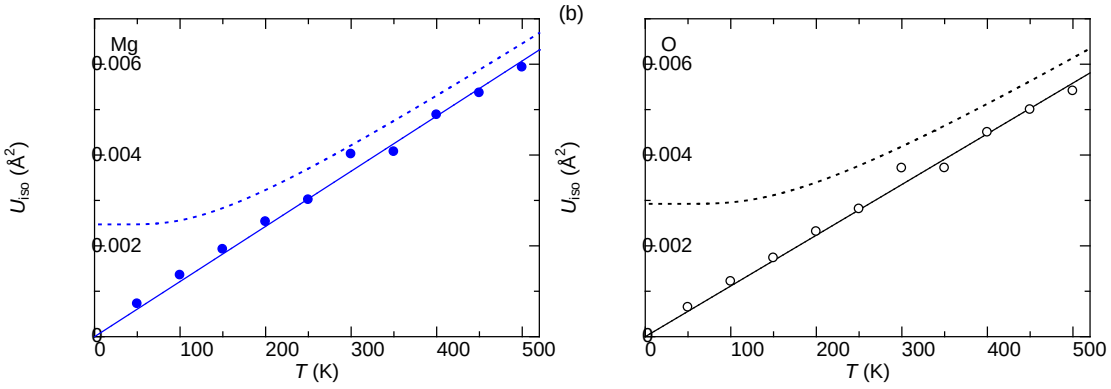

Figure 1. Calculated isotropic ADP of (a) Mg and (b) O in MgO. The linear fit to calculated points pass through the origin. The dashed lines are the corrected ADP accounting for zero-point motion.

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