

Absolute ionic diffusion in MgO-computer calculations via lattice dynamics

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Computer calculations based upon lattice dynamics have enabled us to calculate self-diffusion coefficients (D_{sd}) in MgO, a significant component of the lower mantle. We have employed the supercell method to study the mechanisms governing the diffusion process thereby enabling us to calculate values for activation enthalpies and entropies for migration and formation.

There are several approaches to predicting the atomic jump frequencies of diffusing species. They can simply be estimated as being typical of lattice modes (i.e. $\sim 10^{13} \text{s}^{-1}$) or they can be calculated from reaction rate theory, Green functions or dynamical theory. In this study we have chosen to use Vineyard theory, since it has proved successful in the past and is one of the more efficient methods for determining the pre-exponential factor in the diffusion equation.

Vineyard theory is based upon absolute rate theory, and enables us to obtain an estimate for the jump rate, v^* , which is defined by:

$$v^* = \frac{\prod_{j=1}^{3N} \omega_j}{\prod_{j=1}^{3N-1} \omega'_j}$$

where ω_j are the lattice frequencies in the perfect lattice and ω'_j are those in the defective lattice containing N-1 species; here v^* is related to the attempt frequency, v , in the diffusion equation via:

$$v^* = v e^{\frac{\Delta S_m}{k}}$$

This relation is valid only within the harmonic approximation, since motions near the saddle point are treated by the theory of small oscillations, and therefore the anharmonicity that may arise at the saddle surface is not adequately

treated by this theory and may require an anharmonic correction.

Thus for Mg or O diffusion in a phase such as MgO, diffusion is expected to be along the $\langle 110 \rangle$ direction, and the jump distance is therefore $a/\sqrt{2}$, where a is the cubic cell parameter. The self-diffusion coefficient may be written, therefore, as:

$$D_{sd} = \frac{ZN_v v^*}{6} \left(\frac{a}{\sqrt{2}} \right)^2 e^{-\frac{H_m}{kT}}$$

where N_v is the vacancy concentration. In order to calculate an absolute self-diffusion equation for Mg^{2+} and O^{2-} diffusion in MgO, we need to obtain appropriate values for ΔH_m , v^* and N_v . This we did this using well established potential models and the PARAPOCS code.

In the intrinsic régime we calculate:

$$\text{Magnesium: } D_{sd} = 1.46 \times 10^{-6} \exp\left(\frac{-5.70}{kT}\right)$$

$$\text{Oxygen: } D_{sd} = 8.25 \times 10^{-6} \exp\left(\frac{-5.72}{kT}\right)$$

and in the extrinsic régime we calculate:

$$\text{Magnesium: } D_{sd} = N_v 1.89 \times 10^{-6} \exp\left(-\frac{1.985}{kT}\right)$$

$$\text{Oxygen: } D_{sd} = N_v 1.06 \times 10^{-6} \exp\left(-\frac{2.003}{kT}\right)$$

where N_v is the extrinsic defect concentration. We have also confirmed that for this system the diffusion path is not simple, but there is a predicted bifurcation of the saddle surface. Our results are comparable with previous embedded defect calculations, and suggest that current experimental data is unable to probe the intrinsic régime.