



The influence of electronic structure on diffusion in periclase: the crystal field effect.

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Periclase is the second most abundant mineral in Earth's lower mantle and is a key to understanding chemical exchange mechanisms and diffusive length scales at the core-mantle boundary. The crystal field effect has long been known to influence the partitioning of first-row transition metals in minerals, but its influence on diffusion has not previously been considered. Transition metal cations with partially filled *d*-orbitals are stabilized on octahedral sites by the crystal field effect; this crystal field stabilization may increase the energy barrier for the migration of cations to adjacent vacancies.

To investigate the influence of the crystal field effect on diffusion in periclase, ideally one would hold all variables constant except for electronic structure. Two cations exist, Cr^{3+} and Ga^{3+} , which are essentially twins; they possess identical charge, nearly identical radii (0.615\AA for Cr^{3+} and 0.62\AA for Ga^{3+}), and very similar dipole polarizability (1.45\AA^3 for Cr^{3+} and 1.50\AA^3 for Ga^{3+}). However, Cr^{3+} contains only three *d*-orbital electrons whereas the *3d*-shell of Ga^{3+} is full. Experiments were performed to determine rates of diffusion, the activation energy, and the energy of binding between the trivalent cation and vacancy in periclase at 1 atm and 2 GPa and temperatures between 1563K and 2273K. Theoretical diffusion profiles were calculated numerically, and were fit to the experimental profiles through a chi-square minimization procedure to extract the binding energy and impurity-vacancy pair diffusivity. Despite the similarities between Cr^{3+} and Ga^{3+} , our experiments show that Ga^{3+} diffuses more than an order of magnitude faster than Cr^{3+} , has lower activation energy, and binds more tightly to the adjacent vacancy. All of these observations can be explained by the crystal field stabilization of Cr^{3+} on octahedral cation sites in MgO. The partial filling of the *d*-orbitals in Cr^{3+} leads to a lowering of energy; the three *d*-electrons occupy t_{2g} orbitals that experience less repulsive interaction with the electrons of the six surrounding oxygen atoms. This crystal field stabilization increases the activation energy for Cr^{3+} migration to an adjacent vacancy. It also may explain the lower binding energy of vacancies to Cr^{3+} —the crystal field stabilization is greatest for perfect octahedral symmetry, and there is an energy cost associated with the presence of an adjacent symmetry-breaking vacancy.

The crystal field effect may also explain a trend seen in the diffusion of first-row divalent transition metals in periclase; diffusion coefficients are smaller for elements with larger crystal field stabilization energy. The crystal field stabilization of Fe^{2+} , Mn^{2+} , or Co^{2+} may be enhanced through high-spin to low-spin transitions. If such spin transitions occur in the deep mantle, we expect that the diffusivity of these cations may slow significantly, perhaps by several orders of magnitude.