Ab initio calculations on point defects in forsterite (Mg$_2$SiO$_4$) and implications for diffusion and creep

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ABSTRACT

Ab initio calculations on simple ionic vacancies in forsterite show that there are large energetic differences between vacancies on nonequivalent sites. Oxygen defects on the O3 site are between 1 and 3 eV lower in energy than on the O2 and O1 site, respectively. Magnesium defects on M1 sites are 0.8 eV lower in energy than on the M2 sites. These large energy differences mean that there are many orders of magnitude fewer vacancies on the less-favored sites. In the case of magnesium, where diffusion is thought to occur by means of a vacancy-hopping mechanism, the observed anisotropy with respect to crystallographic orientation can be rationalized by the fact that jumps must only be from M1 to M1 sites.

INTRODUCTION

Point defects are of considerable interest to geologists because they have an essential role in diffusion, electrical conduction, creep, and seismic attenuation in minerals. For example, diffusion most commonly occurs by a vacancy method, whereby ions jump into neighboring vacancies. At high temperatures electrical conductivity may occur by ionic diffusion, whereas at lower temperatures defects can introduce electronic states in the band gap. Under certain conditions, diffusional creep may be the dominant deformation mechanism, and even when dislocation creep is dominant it may be rate-limited by climb, which again is a diffusion mechanism mediated by vacancies. To understand and be able to make predictions about these processes requires a detailed knowledge of the defect types, their concentrations, and how they affect diffusion.

In this paper we present first-principles quantum mechanical calculations on vacancies in forsterite, Mg$_2$SiO$_4$. We find that for both Mg and O large differences in energy exist between vacancies on different nonequivalent sites. This finding agrees with previous pair-potential calculations and means that Mg vacancies in forsterite occur essentially on only the M1 site and that O vacancies only occur on the O3 site.

CALCULATIONS

Calculations were performed using the parallel density functional theory (DFT) code CETEP (Payne et al. 1992). This code uses the generalized gradient approximation (GGA) for the exchange correlation (Perdew et al. 1992) and ab-initio norm-conserving non-local Kleinman-Bylander type pseudopotentials for the valence-core electron interactions (Kleinman and Bylander 1982; Lin et al. 1993). The use of pseudopotentials means that only the valence electrons are handled explicitly, which results in significant savings in computational requirements. Full periodic boundary conditions are employed, and the valence orbitals are represented by a plane-wave expansion. There are no adjustable parameters at this level of theory other than those used in constructing the pseudopotential, and no experimental data are used except for the mass and charge of the electron and Planck’s constant. The only significant approximation in these calculations is that of the exchange-correlation functional. A substantial advantage of the plane-wave basis set is that forces and stresses may be easily evaluated using the Hellman-Feynman theorem (Payne et al. 1992) and used to relax both the atomic coordinates and the unit-cell parameters to minimize the total energy (Wentzcovitch et al. 1993). This is especially important with defects because there are significant energy differences (> 1.0 eV) between relaxed and unrelaxed defect structures.

All calculations were performed on one unit cell of 28 atoms containing one charged defect (either Mg$^{2+}$, O$^{2-}$, or Si$^{4+}$). We used a four k-point sampling set chosen using the Monkhorst-Pack scheme (Monkhorst and Pack 1976). Plane waves up to an energy of 600 eV were accepted, which gives a basis set of about 10,000 plane waves for each k point. We tested for the likely error due to the 600 eV cutoff by comparing energies for the perfect lattice obtained using the 600 eV cutoff with those using 700 and 800 eV cutoffs. The absolute difference between lattice energies obtained using 600 and 700 eV cutoffs is 0.07 eV; between 600 and 800 eV cutoffs it is 0.09 eV. These values suggest that the likely absolute error in any one calculation because of the finite number of plane waves is about 0.1 eV. The error in defect energies is substantially smaller, however, because energy differences converge much faster than absolute energies, and they are negligible in comparison with the size of the defect energies (~1 eV). We also tested for the effect of