Crystal chemistry of forsterite: A first-principles study

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ABSTRACT

We present a first-principles study (local density approximation) of the structural properties of forsterite under pressure. This highly anisotropic magnesium orthosilicate is the most abundant phase of the Earth’s upper mantle, and its elastic properties determine the rheology of this region. We perform full structural optimizations and investigate its compressive behavior up to 25 GPa. We obtain a pressure dependence of lattice parameters that agrees well with experiments to 17.2 GPa. We predict that the coordination polyhedra compress essentially isotropically, and we explain the anisotropy of forsterite in terms of the nonuniform distribution of coordination polyhedra having different but nearly uniform compressibilities. In agreement with Brodholt et al. (1996), we do not find theoretical evidence for sudden changes in compression mechanisms in this mineral as had been suggested from experiments. Our results support the hypothesis that such compressive anomalies are caused by solidification of the pressure medium.

INTRODUCTION

The magnesium orthosilicate polymorphs are the dominant mineral phases of the top-most 660 km of Earth’s mantle. The low-pressure phase olivine is the major phase of the upper mantle, which represents nearly 20% of the planet’s volume. The composition of olivine in the upper mantle consists of ~90% forsterite, the Mg end-member. The properties and behavior of forsterite have been intensively studied because they determine the elasticity and rheology of the asthenospheric mantle and, in turn, plate-tectonic processes. An important observational constraint on the nature of flow in the sub-lithospheric mantle comes from seismological observations of anisotropy, which originate in the intrinsic elastic anisotropy of olivine. Moreover, the pressure-induced transformation of forsterite to wadsleyite under equilibrium conditions is largely responsible for the seismic discontinuity observed at depths of 400 km within the Earth. Lower temperatures suppress this transformation, however, and forsterite may persist metastably to much higher pressures and may be present in subducted lithospheric slabs to depths as great as 660 km (24 GPa) (Sung and Burns 1976; Rubie and Ross 1994).

The need to understand the structure and behavior of the upper mantle and of subducted lithospheric slabs has prompted numerous experimental investigations of the properties of forsterite at high pressure. Experimental X-ray diffraction and vibrational spectroscopy studies have both found evidence for a sudden change in the compressional behavior of forsterite near 9 GPa (Kudoh and TakeÂuchi 1985; Chopelas 1990). However, the compressional anomalies seen in single-crystal X-ray diffraction experiments have not been reproduced by more recent experiments that used a more hydrostatic pressure medium (Downs et al. 1996). An understanding of these results is essential because rapid changes in compression mechanism have important consequences for the elastic constants, and therefore for the seismic wave velocities of this geophysically important mineral.

In this paper we present a first-principles study of forsterite’s behavior under compression at zero temperature. The aim is to elucidate the origin of the anisotropic behavior under pressure and to investigate the nature of the compressional anomaly, if any, at the atomic scale.

COMPUTATIONAL METHOD

We use the plane-wave pseudopotential method (e.g., Cohen and Chelikowsky 1988) to solve the equations of density functional theory (Kohn and Sham 1965) in the local density approximation (LDA). An important issue in computations of complex structures, such as that of forsterite, is the efficient determination of the ground state (equilibrium) arrangement of the atoms. To find the equilibrium structure of forsterite at each pressure, we have used a first-principles implementation (Wentzcovitch 1995) of a variable cell-shape molecular dynamics (VCSMD) algorithm (Wentzcovitch 1991). This method has been successfully used to determine the compressive and elastic behavior of other minerals under compression (Wentzcovitch et al. 1995a, 1995b). It is a quite conventional implementation of first principles molecular dynamics (MD) in which forces and stresses are calculated self-consistently (Wentzcovitch and Martins 1991) at every time step by resorting of iterative diagonalization