Determination of the high-pressure properties of fayalite from first-principles calculations

Stephen Stackhouse, Lars Stixrude, Bijaya B. Karki

Abstract

We have calculated the high-pressure properties of fayalite, including band structure, magnetism, equation-of-state and elastic properties using density functional theory within the generalized gradient approximation (GGA) and using the GGA +U method. We show for the first time that the addition of an on-site Hubbard correction term to the GGA leads to improved agreement between calculated and experimental values of structural and elastic properties, as well as electronic band gap, particularly at high pressure. High-pressure elastic instability, originating in the vanishing of the elastic constant c44 and previously predicted on the basis of extrapolated experimental data, is found with the GGA +U method. Experimental measurements of the elastic constants agree better with the GGA +U method, than with the GGA, which calls for a reassessment of the structural and elastic properties of iron-bearing minerals calculated using standard density functional theory, which have hitherto been used to interpret the structure and dynamics of the mantle. The improvement can be related to the better description of magnetic structure: without the Hubbard U the magnetic moments on the iron ions decrease with pressure, whereas when it is included they remain almost constant, at least, up to the highest pressure studied. This also leads to better predictions of equation-of-state. Our calculated partial density-of-states indicate that the lowest energy excitation across the electronic band gap lies within the d-orbital manifold, and this likely renders the fundamental gap observable in optical spectroscopy at high pressure, accounting for the better agreement between theory and experiment above 20 GPa. We associate the changes in the character of the bands with a change in the crystal structure.

1. Introduction

Fayalite is the pure iron end-member of olivine, thought to be the most abundant phase in the Earth’s upper mantle (Ringwood, 1970). Olivine is expected to predominate from the base of the crust to the 410 km seismic discontinuity and may be preserved (in a metastable state) to greater depths in subducting slabs (Green and Burnley, 1989; Green and Karato, 1995). The second relevant issue concerns the nature of the thermodynamic stability of olivine, because of its unusual characteristics as compared with the other major cations, including its large mass and electronic structure dominated by d-states. These lead to it having a pronounced effect on density, elastic wave velocities and electrical conductivity and thus, in turn, on mantle dynamics and the interpretation of geophysical observations.

The high pressure behavior of fayalite allows us to explore two important issues. The first of these is the behavior of silicates as they are compressed outside their thermodynamic stability field. While the thermodynamic stability field of olivine is well known (Yagi et al., 1987), its behavior under metastable over-compression, as would occur in a kinetically hindered subducting slab is still not well understood. Pressure-induced amorphization of silicates is often observed (Richet and Gillet, 1997) and in some cases may be related to a dynamical instability of the lattice (Kingma et al., 1993). Based on extrapolation of experimental data, it has been proposed that an elastic instability occurs in fayalite at about 35 GPa (Spezie et al., 2004), and this could be related to the observed amorphization transition (Williams et al., 1990; Richard and Richet, 1990; Andrault et al., 1995). The second relevant issue concerns the nature of the insulator to metal transition in silicates. Iron-free silicates have large band gaps that apparently do not close until pressures well beyond those at the center of the Earth (Umamoto et al., 2006), but iron-
bearing silicates have much smaller band gaps that may be influenced by the spin state of the iron cation (Badro et al., 2004). Experimental studies suggest that the band gap of fayalite narrows under static compression at low temperature (Williams et al., 1990), a phenomenon that could be related to the simultaneous observation of pressure-induced amorphization.

We also consider fayalite an ideal testing ground for ab initio theory. Density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) has been applied with much success to the study of a wide range of mantle minerals (Karki et al., 2001; Brodholt and Vočadlo, 2006), but studies of iron-bearing phases have been limited. This is because transition metal oxides such as fayalite present a particular challenge to the method, due to the strong correlation of electrons in the d-states. This correlation is responsible for magnetism and insulating behavior in these systems and its effects are not fully accounted for in the most widely used approximations: the local density approximation (LDA) and generalized gradient approximation (GGA). In view of this, density functional theory can fail to predict the correct band structure of iron-bearing minerals, such as iron oxide (Isaak et al., 1993a; Alfredsson et al., 2004) and fayalite (Cococcioni et al., 2003; Jiang and Guo, 2004). In spite of this, it has continued to be used to predict the elastic properties of iron-bearing phases, such as silicate perovskite and post-perovskite (e.g. Kiefer et al., 2002; Li et al., 2005; Caracas and Cohen, 2005; Tsuchiya and Tsuchiya, 2006; Stackhouse et al., 2006), on the assumption that they are less affected. However this is unknown, since no corresponding experimental data exists with which to compare. In contrast, abundant experimental data exists for fayalite (Sumino, 1979; Graham et al., 1988; Wang et al., 1989; Isaak et al., 1993b; Speziale et al., 2004), providing the possibility to assess the accuracy of the method.

In the present work we also investigate an advanced method, referred to as GGA + U, whereby strong correlation is captured via an additional local Hubbard repulsion of magnitude \( U \). The exchange-correlation functional adhered to the PBE form of the generalized gradient approximation (GGA) (Perdew et al., 1996) and the potentials were generated using the following electronic configurations: \( 3p^6\ 3d^4\ 4s^1 \) for iron, \( 3s^2\ 3p^2 \) for silicon and \( 2s^2\ 2p^4 \) for oxygen. For all calculations the kinetic-energy cut-off for the plane-wave expansion was 800 eV, the Brillouin zone sampled using a 4 \times 4 \times 4 \) special k-point grid (Monkhorst and Pack, 1976) and the convergence criteria for structural optimization was 10⁻⁸ eV. For both the GGA and GGA + U calculations we applied Fermi (i.e., physical) smearing (Mermin, 1965) with a broadening width of 0.2 eV, except for calculation of the electronic density-of-states when the tetrahedron smearing method with Blöchl corrections (Blöchl et al., 1994) was used. These settings ensured that calculated total energies were converged to less than one meV per atom and elastic constants to within about one percent. For further information on density functional theory and its application to mineral physics, the reader is directed to a review (Stixrude et al., 1998).

The GGA + U method requires specification of an onsite exchange interaction parameter \( J \) and onsite Coulomb interaction parameter \( U \). However in the most widely used implementation employed in the present work (Dudarev et al., 1998), the results depend only on the difference between these values. It is therefore common to define an effective \( U \) parameter \( U_{\text{eff}} = U - J \) and refer to \( U_{\text{eff}} \) as simply \( U \), which is the notation adopted here. Self-consistent calculations indicate that for fayalite \( U \) should be about 4.6 eV and 4.9 eV for the two distinct iron sites (Cococcioni et al., 2003; Cococcioni and de Gironcoli, 2005). In view of this, we used \( U = 4.8 \) eV. We also explored a range of alternative values of \( U \), between 1.0 eV and 6.0 eV.

In all our calculations we assumed a ferromagnetic state of order and allowed the magnitude of the moment to vary. Fayalite is known to be a non-collinear anti-ferromagnet at low temperature with a Néel temperature of 65 K at ambient pressure, rising to 100 K at 16 GPa (Hayashi et al., 1987). But at room temperature and above, the regime of primary interest in geophysics and the comparison with high-pressure experimental data, the moments are disordered. Since non-collinear calculations are more challenging and as the magnetic state at high pressure is poorly known, ferromagnetic order seems a good first order assumption. In addition, previous studies have shown that nature of the magnetic order has only very subtle effects on crystal structure (Cococcioni et al., 2003; Jiang and Guo, 2004).

At each volume considered, the structure was optimized allowing all cell parameters and atomic positions to vary. Because of our particular interest in mechanical instability, we took the unusual step of leaving the symmetry unconstrained \(( P \neq 1 \) ), increasing the computational expense of the calculations considerably. Previous studies have shown that electronic spin transitions can be associated with symmetry breaking, with important consequences for predicted spin transition pressures (Bengtson et al., 2008). Despite this extra freedom, we find that the olivine structure was preserved during relaxation at all volumes, except for the smallest volume in the GGA calculations. To determine the athermal elastic constants three different orthorhombic and one triclinic strain of magnitude \( \pm 0.5\% \) were applied to the optimized models, and the atomic positions allowed to fully relax in the strained configurations (Karki et al., 2001). Then a second-order polynomial was fit to the relationship between applied strain and induced, calculated stress.

In order to compare with experiment, the resulting athermal values were converted to room-temperature adiabatic values making use of the thermodynamic identity:

\[
\left( \frac{dc_v}{dT} \right)_T = \left( \frac{dc_v}{dP} \right)_V + \left( \frac{dp}{dT} \right)_V \left( \frac{dc_v}{dp} \right)_T
\]

with values for the temperature derivatives of the elastic constants at constant pressure taken from Isaak et al. (1993b), that for the isochoric change in pressure with temperature from Anderson and Isaak (1995) and those for the pressure derivatives of the elastic constants at constant temperature from Speziale et al. (2004). Bulk and shear moduli were computed as the Voigt-Reuss-Hill average (Hill, 1963).

To correct our athermal calculations for the influence of phonon excitation and the well known under-binding tendency of the GGA, we report pressures as:

\[
P(V, T) = P_{\text{VASP}}(V, 0K) + P_{\text{ESP}} + P_{\text{ZPM}}(V) + P_{\text{DH}}(V, T)
\]

where \( P \) is the total pressure, \( P_{\text{VASP}}(V, 0K) \) the (athermal) pressure calculated by the VASP code at volume \( V \) and 0 K; \( P_{\text{ESP}} \) a volume- and temperature-independent empirical pressure correction; \( P_{\text{ZPM}}(V) \) the pressure associated with zero-point motion and \( P_{\text{DH}}(V, T) \) the thermal pressure at volume \( V \) and temperature \( T \) (de Koker et al., 2008). The empirical pressure correction \( P_{\text{ESP}} \) was calculated as:

\[
P_{\text{ESP}} = -P_{\text{VASP}}(V_{\text{ESP}})
\]

where \( V_{\text{ESP}} \) is the experimental volume at zero pressure and static conditions computed using the thermodynamic model of Xu et al. (2008). Values for \( P_{\text{ZPM}}(V) \) and \( P_{\text{DH}}(V, T) \) were also computed using the thermodynamic model of Xu et al. (2008). The calculated value of \( P_{\text{ESP}} \) for the GGA was \(-2.87 \) GPa. For the GGA + U method it was \(-5.36 \) GPa with \( U = 2.0 \) eV and \(-6.72 \) GPa with \( U = 4.8 \) eV. These lie within the

\[
P_{\text{VASP}}(V, 0K) + P_{\text{ESP}} + P_{\text{ZPM}}(V) + P_{\text{DH}}(V, T)
\]
range of pressure corrections calculated in previous investigations (e.g. \( P_{\text{cmax}} = -12.08 \text{ GPa for MgSiO}_3 \) perovskite using the GGA (Oganov et al., 2001) and \( P_{\text{cmax}} = +1.6 \text{ GPa for forsterite using the LDA (de Koker et al., 2008) } \) and consistent with a host of other studies of silicates that find that the LDA generally slightly overbinds and the GGA underbinds by a larger amount.

3. Results

The calculated equation-of-state and lattice parameters of fayalite are in good agreement with experimental values at low pressures, irrespective of whether they were calculated with the GGA or GGA + U method and the value of U used (Figs. 1 and 2; Table 1). The ambient pressure lattice parameters calculated using the GGA + U method vary less than 1% as \( U \) varies from 1 eV to 6 eV. The maximum difference between the lattice parameters calculated with the GGA and those of Fujino et al. (1980) is 1.07%, while the GGA + U method does a little better, with a maximum difference of 0.30% with \( U = 2.0 \text{ eV and } 0.49\% \text{ with } U = 4.8 \text{ eV.} \) Though it is significant that the GGA and GGA + U method both accurately predict the correct shape of the unit cell (i.e., c/a and b/a ratios), especially as the structure is highly elastically anisotropic, the good agreement in the zero pressure volume is due to the application of the empirical pressure correction (Eq. (3)). This correction is larger for the GGA + U pressures than the GGA pressures, which means that the well-known under-binding tendency of the GGA is somewhat exacerbated by the addition of \( U \).

The situation is quite different at high pressures where the lattice parameters and equation-of-state calculated using the GGA and GGA + U method diverge. The GGA predicts lattice parameters and an equation-of-state that differ from experimental values at high pressures. In particular, the GGA predicts an equation-of-state that is much too soft. In contrast, the two sets of GGA + U values are in good agreement with experimental values and each other at nearly all pressures. In particular, the GGA + U values agree with experiment to within experimental uncertainty, except for the highest pressure volume measurements of Andrault et al. (1995) and the highest pressure measurements of the \( b \) axis of Williams et al. (1990). However it is likely that these high-pressure experimental data are biased by non-hydrostaticity (Speziale et al., 2004).

The calculated ambient pressure elastic constants of fayalite depend greatly on the value of \( U \) used (Fig. 3). The elastic constants increase with increasing \( U \) at fixed volume, except for the off-diagonal elastic constants (\( c_{12}, c_{13}, c_{23} \)), which change little with increasing \( U \). Best agreement with the experimental values, listed in Table 1, is found with \( U = 2.0 \text{ eV (Table 2)} \). Using this value the largest discrepancies are in the off-diagonal elastic constants (close to 20%). The other elastic constants agree to within an average of 6%. The predicted Voigt-Reuss-Hill bulk modulus is 10% higher than the average experimental value, while the Voigt-Reuss-Hill shear modulus is almost identical.

![Fig. 1. Equation-of-state of fayalite calculated using the GGA and GGA + U method, with \( U = 2.0 \text{ eV or } 4.8 \text{ eV.} \) and corresponding experimental data. Note that, Kudoh and Takeda (1986) studied an (Fe_{0.920}Mn_{0.055}Mg_{0.020}Si_{0.005})_{2}SiO_{4} composition; Williams et al. studied an Fe_{2}SiO_{4} composition; Andrault et al. (1995) studied an (Fe_{0.99}Mn_{0.01})_{2}SiO_{4} composition; and Zhang (1998) studied an Fe_{3}SiO_{4} composition.](image)

![Fig. 2. Lattice parameters of fayalite as a function of pressure, calculated using the GGA and GGA + U method, with \( U = 2.0 \text{ eV and } 4.8 \text{ eV, and corresponding experimental data. Note that, Kudoh and Takeda (1986) studied an (Fe}_{1-0.19}Mn_{0.19})_{2}SiO_{4} composition; Williams et al. studied an Fe_{2}SiO_{4} composition; Andrault et al. (1995) studied an (Fe_{0.99}Mn_{0.01})_{2}SiO_{4} composition; and Zhang (1998) studied an Fe_{3}SiO_{4} composition.](image)

<table>
<thead>
<tr>
<th>( U ) (eV)</th>
<th>( \rho ) (g cm(^{-3}))</th>
<th>( V ) (Å(^3))</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Theoretical values</strong>&lt;br&gt; This work (^{a})</td>
<td>GGA</td>
<td>0.0</td>
<td>4.402</td>
<td>307.424</td>
<td>4.901</td>
</tr>
<tr>
<td>This work (^{a})</td>
<td>GGA + U</td>
<td>2.0</td>
<td>4.402</td>
<td>307.424</td>
<td>4.834</td>
</tr>
<tr>
<td>This work (^{a})</td>
<td>GGA + U</td>
<td>4.8</td>
<td>4.402</td>
<td>307.424</td>
<td>4.834</td>
</tr>
<tr>
<td>Coccocci</td>
<td>LDA</td>
<td>4.765</td>
<td>284.054</td>
<td>4.757</td>
<td>10.176</td>
</tr>
<tr>
<td>et al., 2003 (^{b})</td>
<td>Coccocci</td>
<td>LDA</td>
<td>4.904</td>
<td>276.027</td>
<td>4.985</td>
</tr>
<tr>
<td>et al., 2003 (^{c})</td>
<td>Coccocci</td>
<td>LDA</td>
<td>4.339</td>
<td>311.912</td>
<td>4.874</td>
</tr>
<tr>
<td>et al., 2003 (^{b})</td>
<td>Coccocci</td>
<td>LDA</td>
<td>4.370</td>
<td>309.710</td>
<td>4.953</td>
</tr>
<tr>
<td>et al., 2003 (^{c})</td>
<td>Coccocci</td>
<td>LDA</td>
<td>4.443</td>
<td>304.666</td>
<td>4.956</td>
</tr>
<tr>
<td>Jiang and Guo, (^{a})</td>
<td>GGA</td>
<td>3.6</td>
<td>4.383</td>
<td>308.849</td>
<td>4.878</td>
</tr>
<tr>
<td>Jiang and Guo, (^{a})</td>
<td>GGA + U</td>
<td>3.6</td>
<td>4.402</td>
<td>307.424</td>
<td>4.820</td>
</tr>
</tbody>
</table>

**Table 1.** Density, volume and lattice constants of fayalite at ambient conditions.

\(^{a}\) Ferromagnetic configuration — unit cell optimized at fixed volume.<br>\(^{b}\) Antiferromagnetic configuration 1.<br>\(^{c}\) Antiferromagnetic configuration 2.
The pressure dependencies of the elastic constants predicted with the GGA + U method show good agreement with experimental data with both values of U used, with the possible exception of c_{44} (Fig. 4). In particular, the large negative curvature in the pressure dependence of c_{44} is reproduced. Fayalite shows an elastic instability at high pressure using both the GGA and GGA + U method. The GGA calculations converge poorly as the instability is approached and the precise location or nature of the instability is not easy to determine. The poor convergence using the GGA is also responsible for the rapid oscillations in the values of the elastic constants with increasing pressure as the instability is approached. In the case of the GGA + U method, the range of experimental values listed in Table 2 agree with the theoretical predictions.

Fig. 3. Elastic constants and bulk and shear moduli of fayalite calculated using the GGA + U method, as a function of U value. GGA values correspond to U = 0.0 eV. The shaded bands represent the range of experimental values listed in Table 2.

Table 2
Elastic constants and bulk and shear moduli of fayalite at ambient conditions (in GPa).

<table>
<thead>
<tr>
<th>U (eV)</th>
<th>c_{11}</th>
<th>c_{12}</th>
<th>c_{13}</th>
<th>c_{22}</th>
<th>c_{23}</th>
<th>c_{33}</th>
<th>c_{44}</th>
<th>c_{55}</th>
<th>c_{66}</th>
<th>K</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>GGA</td>
<td>0.0</td>
<td>257</td>
<td>169</td>
<td>191</td>
<td>116</td>
<td>125</td>
<td>97</td>
<td>40</td>
<td>49</td>
<td>52</td>
</tr>
<tr>
<td>This work</td>
<td>GGA + U</td>
<td>2.0</td>
<td>262</td>
<td>176</td>
<td>238</td>
<td>113</td>
<td>113</td>
<td>107</td>
<td>39</td>
<td>47</td>
<td>56</td>
</tr>
<tr>
<td>This work</td>
<td>GGA + U</td>
<td>4.8</td>
<td>275</td>
<td>184</td>
<td>247</td>
<td>113</td>
<td>113</td>
<td>111</td>
<td>46</td>
<td>54</td>
<td>63</td>
</tr>
</tbody>
</table>

**Theoretical values**

**Experimental values**

| Sumino, 1979 | 267 | 174 | 239 | 95 | 99 | 98 | 32 | 48 | 57 | 138 | 51 |
| Graham et al., 1988 | 267 | 160 | 222 | 92 | 81 | 88 | 32 | 47 | 57 | 129 | 50 |
| Wang et al., 1989 | 260 | 168 | 234 | 94 | 93 | 89 | 33 | 46 | 55 | 132 | 50 |
| Speziale et al., 2004 | 269 | 172 | 233 | 94 | 97 | 94 | 32 | 47 | 57 | 136 | 51 |

a. Ferromagnetic configuration.

b. Rectangular parallelepiped resonance technique — values as reported by Isaak et al., 1993b.

c. Superposition ultrasonic interferometry method — samples contained trace amounts of MnO.

d. Brillouin scattering — (Fe_{0.94}Mn_{0.06})SiO_{4} composition.

e. Rectangular parallelepiped resonance technique — samples contained trace amounts of MnO.

The evolution of the band gap in our calculations is very different from that observed experimentally. In order to explore the origin of this difference further, we have computed the partial densities-of-
states (Fig. 6). These calculations show that the lowest energy excitation across the gap lies within the d-orbital manifold. While the top of the valence band also has slight oxygen character, the bulk of the oxygen p- and s-states lie at lower energy.

In order to understand the strong influence of U at high pressure, we have examined the influence of compression on magnetic structure (Fig. 7). We find that iron in both iron sites is in a high-spin state at ambient pressure. The calculated spin magnetic moments are 3.53 μB (Fe1) and 3.65 μB (Fe2) with the GGA. For the GGA + U method, the values are 3.64 μB (Fe1) and 3.69 μB (Fe2) with U = 2.0 eV and 3.75 μB (Fe1) and 3.77 μB (Fe2) with U = 4.8 eV. The magnetic moments on the different iron sites become more similar with increasing values of U used. Our values are nearly identical to those obtained in previous studies that assumed an antiferromagnetic arrangement (Cococcioni et al., 2003; Jiang and Guo, 2004; Cococcioni and de Gironcoli, 2005), although slightly lower than the experimental value of 4.4 μB. The difference between theoretical and experimental values of the magnetic moment may be due to the assumption in this and previous studies of a co-linear spin arrangement whereas experimentally the spins are known to be non-collinear. In the case of the GGA the magnetic moments remain nearly constant up to 10 GPa and then begin to decrease with increasing pressure. The decrease is pronounced, ending in partial magnetic collapse at the highest pressure studied (not shown). Upon reaching 32.3 GPa (Volume = 245,000 Å³) the magnetic symmetry is broken and the moments on two of the four iron ions in Fe2 sites collapse, while the remaining Fe2 moments and all of the Fe1 moments retain finite values. In contrast, using the GGA + U method, the decrease in magnetic moment is very small with both U values, up to the highest pressure studied.

Numerical values for all results are included as supplementary material.

4. Discussion

The addition of local Coulomb interactions significantly improves agreement between theory and experimental measurements of the band gap, crystal structure, equation-of-state, and elastic constants. This success is significant because it means that the GGA + U method, originally motivated by the tendency of density functional theory to under-predict the band gap, improves other physical properties as well. The degree of improvement is not large and this is consistent with previous studies of transition metal oxide systems using standard density functional theory, which have often found reasonable agreement with experiment, even though it wrongly predicts the band structure (Isaak et al., 1993a; Alfredsson et al., 2004). This suggests some cancellation of errors in density functional theory. While agreement with experimental data is reasonably good for our GGA + U calculations, in particular with U = 2.0 eV, it is not as good as found in previous studies of transition metal free systems with standard density functional theory (Oganov et al. 2001; Karki et al., 2001). This suggests that GGA + U, while an important improvement, does not fully capture the relevant physics of strongly correlated systems such as fayalite. The mixed success of the GGA + U method in describing the different properties of fayalite points to the importance of continued development of more exact methods such as Quantum Monte Carlo (Foulkes et al. 2001) in studies of iron-bearing insulators, which, at present, are applicable only to much simpler systems (Kolorenc and Mitas, 2008).
The improvement in predicted elastic properties upon the addition of the local Coulomb repulsion calls for a re-examination of the predicted elastic properties of major mantle iron-bearing species. To date, these predictions have been based on standard density functional theory, without $U$, which the present results suggest could be in significant error.

Predictions based on density functional theory form an important part of our understanding of the structure of the upper and lower mantle (Stixrude and Lithgow-Bertelloni, 2005; Stackhouse and Brodholt, 2008). In particular, the properties of iron-bearing phases are particularly critical in arguments concerning the non-thermal origin of deep mantle heterogeneity, for which lateral variations in iron-content have been proposed (Kiefer et al., 2002; Trampert et al., 2004; Brodholt et al., 2007). Our results indicate that the GGA strongly underestimates the shear modulus of fayalite at high pressure (Fig. 4), which would lead to an underestimation of the amount of iron in the upper mantle.

The calculated elastic instability in fayalite is most likely to be the origin of experimentally observed pressure-induced amorphization (Williams et al., 1990; Richard and Richet, 1990; Andrault et al., 1995). The pressure at which $c_{44}$ vanishes in our GGA + $U$ calculations, with $U = 2.0$ eV, coincides with that of a sudden reduction in the amplitude of X-ray diffraction peaks in diamond anvil cell experiments. The vanishing of $c_{44}$ means that fayalite violates one of the Born stability criteria and cannot be preserved even in a metastable state. It must spontaneously transform to a new structural state. This state need not be one of thermodynamic equilibrium. Indeed a simple shear cannot

---

**Fig. 6.** Calculated partial density-of-states using the GGA + $U$ method, with $U = 4.8$ eV. A: Partial density-of-states for Fe1(3$d$), Fe2(3$d$) and O(2$p$) at ambient pressure. B: Partial density-of-states for Fe1(3$d$) and Fe2(3$d$) as a function of increasing pressure. The solid and dashed lines differentiate respectively the spin-up and spin-down components for Fe1(3$d$) and Fe2(3$d$).

**Fig. 7.** Magnetic moment of the two iron sites in fayalite calculated using the GGA and GGA + $U$ method, with $U = 2.0$ eV or 4.8 eV. In the GGA calculations, two out of the four iron atoms in site 2 underwent a spin transition to a low-spin state upon compression beyond the highest pressure shown.

---

transform fayalite to the stable assemblage of wüstite and stishovite at 40 GPa. It is plausible that the mismatch between the un-restored shear associated with vanishing $c_4$ and the stable thermodynamic state produces frustration that leads to amorphization. Pressure-induced amorphization has been associated with unstable phonon modes in other systems (Wentzcovitch et al., 1998).

The influence of iron on the shear modulus is stronger at high pressure than at low pressure (Fig. 4). The addition of iron to mantle silicates and oxides reduces the shear-wave velocity by increasing the density and decreasing the shear modulus. We find that the shear modulus of fayalite depends much more strongly on pressure than that of forsterite. This causes the shear moduli of the two end-members to diverge on compression. The effect of iron on the seismic properties of olivine will be particularly large near the bottom of a metastable olivine wedge.

We argue that the band gap in fayalite at ambient pressure is closer to our theoretical prediction of between 0.85 eV ($U=2.0$ eV) and 2.52 eV ($U=4.8$ eV) than previous experimental measurements of the optical absorption edge (Mao and Bell, 1972; Nitsan and Shankland, 1976; Smith and Langer, 1982). We suggest that the fundamental gap is not observed at ambient pressure because the signal in the optical spectrum is too weak. We find that the fundamental gap involves a transition from Fe2(3d) in the valence band to Fe1(3d) in the conduction band (Fig. 6). This transition is dipole forbidden and likely to have very small amplitude (Jiang and Guo, 2004). In contrast, the higher energy transitions from O(2p) in the valence band to Fe1(3d) in the conduction band, which have the greatest intensity above 4 eV (Jiang and Guo, 2004) will have a much larger amplitude, and this is likely the lowest energy peak that was observed in optical spectra.

The nature of the gap changes at high pressure due to the broadening of the 3d manifold: Fe1(3d) states become more prominent at the valence band maximum, and Fe2(3d) states become more prominent at the conduction band minimum (Fig. 6). These changes in the electronic structure likely render the fundamental gap observable in optical spectroscopy at high pressure, accounting for the reasonable agreement between theory and experiment above 20 GPa (Fig. 5).

Pressure-induced changes in the character of the bands are associated with a change in the crystal structure. We find that at high pressure, the chains of M1 octahedra straighten out so that Fe–Fe pairs are nearly co-planar with the shared octahedral edge (Fig. 8). This change in the crystal structure will lead to increased Fe–Fe bonding, accounting for the broadening of the Fe(3d) band. Fe–Fe interactions across shared octahedral edges have also been invoked to explain the observed rhombohedral distortion in wüstite (Isaak et al., 1993a).

Magnetic collapse appears not to take place in fayalite prior to the mechanical instability near 40 GPa. While the GGA predicts partial magnetic collapse, the GGA + $U$ results show full magnetic moments up to the elastic instability. The effect of $U$ is expected: the local Coulomb repulsion strengthens correlation, making spin pairing less favorable and tending to inhibit magnetic collapse. Experimental measurements of the magnetic moments in fayalite have not yet been performed at high pressure. However the excellent agreement between the GGA + $U$ calculations and experiment and the poor agreement between the GGA and experiment in the pressure regime of the GGA magnetic collapse, indicates that the GGA + $U$ method provides the more accurate picture.

It is interesting to note that although we presume the GGA results are inaccurate, they reveal an aspect of magnetic collapse that may be observable in other iron-bearing oxides and silicates: the two symmetrically inequivalent iron atoms behave differently, with one showing more rapid magnetic collapse than the other upon compression. The situation is quite different from heterovalent compounds, such as iron-bearing MgSiO3 perovskite which may contain both ferrous and ferric iron. High-to-low-spin transitions of two or more symmetrically inequivalent ferrous iron ions have not yet been observed in oxides or silicates at high pressure. The distinct character of iron on the two sites in fayalite is also highlighted by the nature of magnetic transitions at temperatures below the Néel temperature (Aronson et al., 2007), and the magnetic properties of pressure-amorphized fayalite glass (Kruger et al., 1992).

5. Conclusions

Theoretical prediction of the properties of transition metal bearing insulators remains a fundamental challenge in condensed matter physics. Many of the new techniques that have been developed to study them are still far too expensive and cumbersome to treat even relatively simple crystal structures, like fayalite. Our results show that the GGA + $U$ method is a valuable tool for exploring such systems and is much more accurate than the GGA alone, even though the accuracy is still not as high as in studies of transition-metal-free mantle phases with standard density functional theory. This calls for a re-examination of the elastic properties of iron-bearing phases determined with standard density functional theory methods, ($U=0$ eV), which could be inaccurate, leading to inaccurate estimates of the concentration of iron in mantle phases.

Our results show a range of interesting phenomenon in fayalite upon compression, including narrowing, but not closing of the band gap on compression, broadening of the d-bands that likely produce changes in experimentally observed optical spectra, and an elastic instability that may be the cause of amorphization in the phase.

The change in electronic structure is known to be associated with an increase in the conductivity of fayalite on compression (Williams et al., 1990), that is likely to be important in understanding geophysical observations of mantle electrical conductivity (Toffelmier and Tyburczy, 2007). Our result suggest that olivine is not likely to amorphize in a subducting slab, even taking into account the possible influence of non-hydrostatic stress (Wu et al., 1992), as fayalite amorphizes at pressures well beyond the extent of the proposed metastable wedge (Green and Burnley, 1989), and experimental results show that increasing the forsterite component raises the pressure at which amorphization occurs (Andrault et al., 1995).

Acknowledgement

The bulk of the calculations were performed at the Center for Advance Computing at the University of Michigan and HECToR, the U.K. national high-performance computing service. In addition, some of the initial calculations were carried out on a Linux cluster belonging to the group of Todd Ehlers at the Department of Geological Sciences at the University of Michigan. The work supported by the U. K. National Environmental Research Council, and the U. S. National Science Foundation under grant number EAR-0635815.
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the

References


