



## The Hubbard $U$ correction for iron-bearing minerals: A discussion based on $(\text{Mg,Fe})\text{SiO}_3$ perovskite

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### ABSTRACT

Using iron-bearing magnesium silicate perovskite as an example, we show that the Hubbard  $U$  correction is not always necessary for calculating the structural and elastic properties of iron-bearing minerals. Instead, it is the choice of DFT functionals (LDA or GGA) that may have greater impact on the quality of the predictive calculation. For iron-bearing minerals, calculations adopting LDA (LDA +  $U$ ) are generally in better agreement with experimental data than those adopting GGA (GGA +  $U$ ) after including zero point motion and thermal vibrational effects, as demonstrated by the room-temperature compression curve of  $(\text{Mg,Fe})\text{SiO}_3$  perovskite. A criterion indicating the necessity of the Hubbard  $U$  correction is also discussed. As long as the standard DFT functional produces insulating ground state with correct orbital occupancy, the Hubbard  $U$  correction does not affect the computed structural and elastic properties.

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### 1. Introduction

Iron-bearing minerals, such as ferroperricite  $(\text{Mg,Fe})\text{O}$ , ferromagnesian silicate perovskite  $(\text{Mg,Fe})\text{SiO}_3$ , and olivine  $(\text{Mg,Fe})_2\text{SiO}_4$ , are major constituents of the Earth's mantle. A thorough knowledge of these minerals is therefore crucial for understanding mantle properties. For a long time, the strongly correlated nature of ferrous and/or ferric iron has hindered predictive electronic structure calculations with satisfactory accuracy for these minerals. In the standard density functional theory (DFT) calculations for crystalline solids, there are two very popular approximations for the exchange-correlation energy functional: the local density approximation (LDA) (Ceperley and Alder, 1980; Perdew and Zunger, 1981) and the generalized gradient approximation (GGA) (Perdew et al., 1996). While these standard DFT functionals usually provide good predictions, sometimes they do not, especially when they are applied to some transition-metal compounds. A recent breed of methods aiming to correct severe limitations of standard DFT functionals for this class of materials is the so-called DFT + Hubbard  $U$  (DFT +  $U$ ) method. In the DFT +  $U$

approach, the Coulomb interaction among electrons on a single iron (or other transitional metal) site is explicitly included in the total energy functional in a way similar to the  $U$ -term in the Hubbard model. This approach has been explored for various materials and has led to considerably more accurate results than those given by LDA or GGA (Cococcioni and de Gironcoli, 2005; Cococcioni, 2010; Hsu et al., 2009; Kulik et al., 2006; Sit et al., 2006; Zhou et al., 2004).

A recent example of a successful utilization of DFT +  $U$  in iron-bearing minerals is the calculation of spin-state crossover in ferroperricite (Tsuchiya et al., 2006; Wentzcovitch et al., 2009; Wu et al., 2009). Neither LDA nor GGA describe this phenomenon correctly. They give partially occupied 3d-orbitals in the high-spin (HS) ferrous iron and therefore produce a metallic state, rather than an insulating state observed experimentally. The equation of state of ferroperricite and the enthalpy crossing between high-spin,  $S=2$ , and low-spin (LS),  $S=0$ , states were well reproduced once the Hubbard  $U$  was determined by the first principles for each spin state at different volumes. The intermediate spin (IS),  $S=1$ , state is not found experimentally or theoretically. Another major factor in the success of this calculation was the use of LDA +  $U$  rather than GGA +  $U$ . It is a general trend in covalent/ionic normal materials, i.e., non-strongly correlated materials, that LDA gives better equations of state and structural/elastic properties than GGA for

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silicates and oxides once zero point motion energy and thermal vibrational effects are included in the calculations (Wentzcovitch et al., 2010). This result appears to hold also for DFT+ $U$  calculations (Hsu et al., 2009, 2010a; Wentzcovitch et al., 2009; Wu et al., 2009).

In contrast, standard DFT functionals still give satisfactory results for (Mg,Fe)SiO<sub>3</sub> perovskite, the most abundant mineral in the Earth. For example, LDA has given excellent results for the elastic properties (Kiefer et al., 2002), and both LDA and GGA predict the change of quadrupole splitting (QS) in iron nucleus with increasing pressure (Hsu et al., 2010b), consistent with experiments (Li et al., 2006; Jackson et al., 2005; McCammon et al., 2008). Clearly, iron in various minerals may be treated successfully with different methods. However, even with the above-mentioned success of standard DFT on (Mg,Fe)SiO<sub>3</sub> perovskite, it has still been argued by Stackhouse et al. (2010) that calculations for iron-bearing minerals with standard DFT could be in significant error, based merely on GGA and GGA+ $U$  computations in fayalite. An interesting question thus arises: Is the Hubbard  $U$  correction always necessary for calculating the structural and elastic properties of iron-bearing minerals? If not, when (and how) do standard DFT functionals provide reliable results? To properly address this issue, a systematic investigation of the effect of Hubbard  $U$  on the calculations for iron-bearing minerals is of interest. The information provided by such an investigation would be important not only for theorists to better judge whether or not to adopt DFT+ $U$ , but also for experimentalists to judge whether a DFT or DFT+ $U$  calculation is more reliable (if they are not entirely consistent) when interpreting experimental data or planning future experiments based on them.

In this paper, we start with a general discussion of the Hubbard  $U$  correction and the importance of determining  $U$  by the first principles. Then we show the effect of Hubbard  $U$  on the atomic structure, electronic structure, and the equation of states of (Mg,Fe)SiO<sub>3</sub> perovskite. Both the LDA and GGA results are analyzed. The Hubbard  $U$  and the equation of state (static and finite-temperature) are determined from the first principles. No empirical approach or experimental input is included, so the source of error and the predictive quality of each method can be clearly examined. In addition, a criterion indicating the necessity of the Hubbard  $U$  correction for calculating iron-bearing minerals' structural and elastic properties is also discussed.

## 2. DFT+ $U$ functional

The DFT+ $U$  corrective functional was introduced in the early 90s (Anisimov et al., 1991) and has evolved significantly to present days. Due to its relatively low computational cost and its simple formulation, it is now one of the most widely used computational techniques to correct the significant and well known inaccuracy of the most commonly used DFT functionals for strongly localized and correlated electronic ground states. A particularly important and appealing feature of this corrective approach consists in the fact that it allows the efficient calculation of energy derivatives as, e.g., atomic forces and stresses, and thus can be used to compute equilibrium structures, elastic properties, phonon frequencies, and other quantities related to higher order derivatives of the energy. These are very important properties for studies of transition-metal bearing minerals under realistic temperature and pressure conditions in the mantle.

The DFT+ $U$  functional consists in a simple extension of the DFT Hamiltonian that is shaped after the Hubbard model with effective electronic interactions. In a simplified version (Dudarev et al., 1998) of the rotationally invariant formulation (Liechtenstein et al., 1995),

the DFT+ $U$  energy functional is expressed as follows:

$$E_{DFT+U} = E_{DFT} + E_U = E_{DFT} + \sum_{l,\sigma} \frac{U^l}{2} \text{Tr}[\mathbf{n}^{l\sigma}(1 - \mathbf{n}^{l\sigma})], \quad (1)$$

where  $\mathbf{n}^{l\sigma}$  are the atomic occupation matrices (defined as projections of the Kohn–Sham states on a set of localized orbitals) and  $U$ , the Hubbard interaction parameter, represents the strength of the effective (screened) on-site Coulomb repulsion between electrons. Since  $U > 0$ , the Hubbard correction to the energy functional corresponds to a penalty that forces the system to have integer occupations (either 0 or 1). This feature favors a Mott-like ground state with electrons localized on atomic orbitals (if localized wave functions are chosen to be atomic). This type of ground state is normally not well represented by standard DFT functionals, which usually predict metallic behavior.

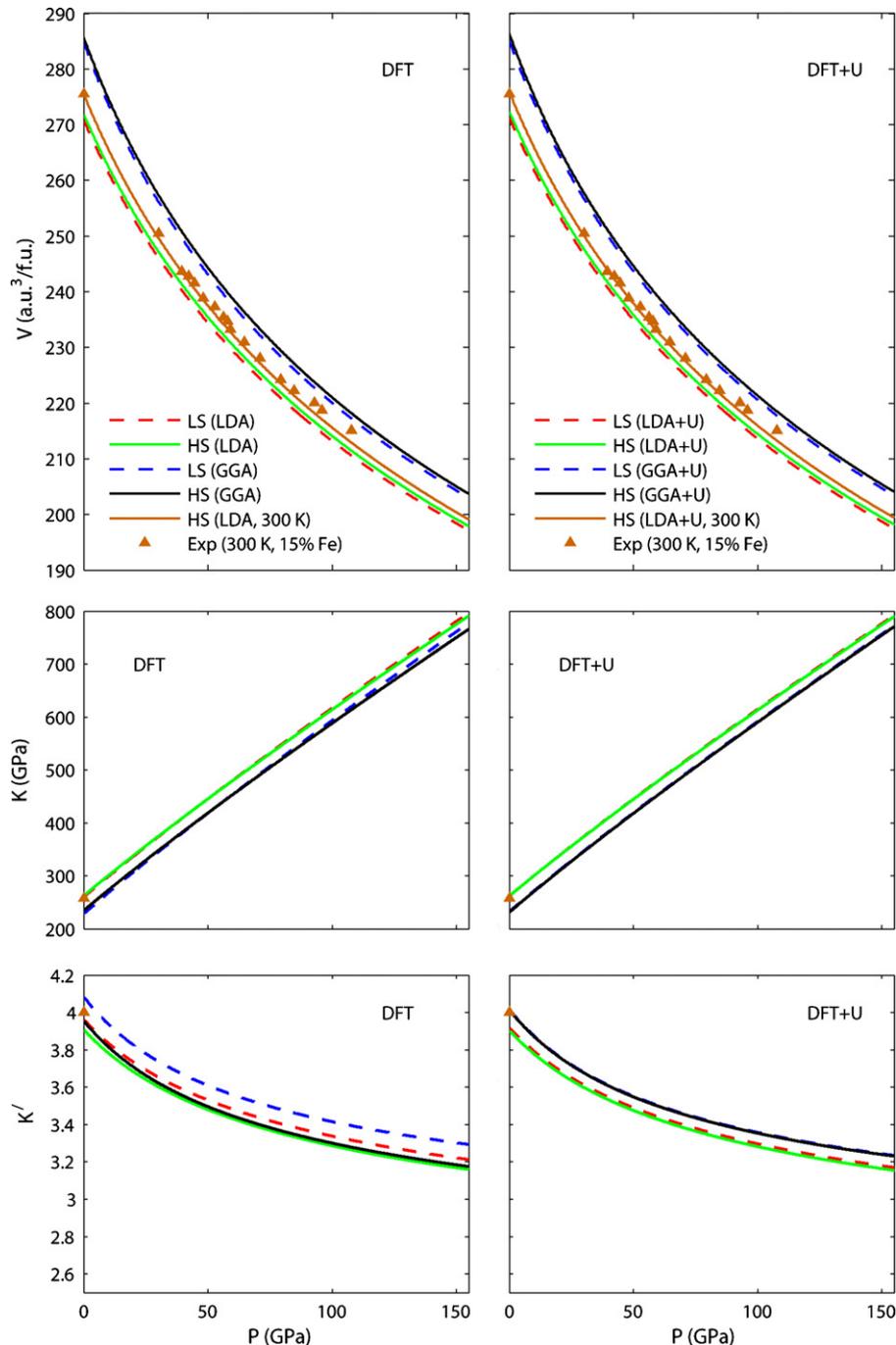
As evident from Eq. (1), the strength of the corrective functional in this approach is controlled by the Hubbard interaction parameter,  $U$ . The numerical value of  $U$ , unfortunately, is not known a priori. Although quite common in the literature, the semi-empirical evaluation of these coupling parameters, through fitting of experimental data, is not very satisfactory and fails to capture their dependence on the structure, volume or magnetic phase of the crystal. Since the formulation of this corrective scheme, a number of methods have been introduced to compute  $U$  by first principles, e.g., through constrained DFT calculations based on a localized (LMTO) basis set (Anisimov and Gunnarsson, 1991; Aryasetiawan et al., 2006; Karlsson et al., 2010; Solovyev et al., 1994). In this work, we use the formulation introduced by Cococcioni and de Gironcoli (2005), where the computation of  $U$  is based on linear-response theory. This method is particularly well suited for the pseudopotential-plane-wave implementation of DFT (Giannozzi et al., 2009) that we have routinely employed, and it has been proven very successful and accurate in a quite large number of studies focusing on transition-metal compounds. These studies show that obtaining the correct Mott insulating ground state, instead of the metallic behavior usually obtained with standard approximate DFT functional, is essential to predict other properties of these systems, including equilibrium structure and atomic environment, spin state, and elastic constant. The possibility to compute the Hubbard interaction parameters also allowed us to appreciate, in several cases, the importance of their consistency with the crystal structure, the magnetic configuration, and the electronic structure, which suggests the necessity to evaluate them “self-consistently” from a DFT+ $U$  ground state (Campo and Cococcioni, 2010). This observation is particularly true when the DFT+ $U$  induces significant changes in the electronic structure leading, e.g., to the elimination of the spurious metallic behavior. In conclusion, a corrective DFT+ $U$  functional usually introduces desirable improvements in the description of the electronic ground state of transition metal compounds whose quantitative predictive character is, however, critically dependent on the rigorous evaluation of the Hubbard  $U$ .

## 3. Computation method

All atomic structures presented in this paper were fully optimized using damped variable cell shape molecular dynamics (Wentzcovitch et al., 1993) implemented in the quantum-*espresso* package (Giannozzi et al., 2009). Both LDA and GGA calculations were performed. The spin- and volume-dependent Hubbard  $U$  adopted in the paper was calculated by Hsu et al. (2010b) from the LDA and GGA ground states using linear response theory (Cococcioni and de Gironcoli, 2005). The pseudopotentials of Fe, Si, and O were generated by Vanderbilt's method (Vanderbilt, 1990) with valence electronic configurations of  $3s^2 3p^6 3d^{6.5} 4s^1 4p^0$ ,  $3s^2 3p^1$ , and  $2s^2 2p^4$ , and core radii (for all quantum numbers  $l$ )

of 1.8, 1.6, and 1.4 a.u., respectively. The pseudopotential of Mg was generated by von Barth–Car’s method. Five configurations,  $3s^2 3p^0$ ,  $3s^1 3p^1$ ,  $3s^1 3p^{0.5} 3d^{0.5}$ ,  $3s^1 3p^{0.5}$ , and  $3s^1 3d^1$ , were used, with decreasing weights 1.5, 0.6, 0.3, 0.3, and 0.2, respectively. Core radii for all quantum numbers  $l$  were 2.5 a.u. The energy cutoff is 40 Ry for the wave function and 160 Ry for the charge density. When performing structural optimizations, a  $2 \times 2 \times 2$   $\mathbf{k}$ -point grid was used for the 40-atom  $(\text{Mg}_{0.875}\text{Fe}_{0.125})\text{SiO}_3$  cell. Structural optimizations were terminated when interatomic forces were smaller than  $2 \times 10^{-4}$  Ry/a.u. A finer  $\mathbf{k}$ -point grid ( $4 \times 4 \times 4$ ) was used in the calculations of the density of states (DOS), except for LDA, where a  $10 \times 10 \times 10$   $\mathbf{k}$ -point grid was used for better resolution. The

compression curves are fitted to the 3rd-order Birch–Murnaghan equation of states. The 300 K equation of state was obtained using quasiharmonic theory (Wallace, 1972) in conjunction with first principles phonons calculated using density function perturbation theory (Baroni et al., 2001). The vibrational density of states (VDoS) of  $(\text{Mg}_{0.875}\text{Fe}_{0.125})\text{SiO}_3$  was computed as the direct average of those of  $\text{MgSiO}_3$  and ordered  $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{SiO}_3$ , where a  $2 \times 2 \times 2$  phonon  $\mathbf{q}$ -point grid was used to compute the interatomic force constants, from which the dynamical matrix at any  $\mathbf{q}$ -point can be generated. A  $4 \times 4 \times 4$  grid is used to compute their VDoS. The VDoS averaging procedure for  $(\text{Mg}_{0.875}\text{Fe}_{0.125})\text{SiO}_3$  will be discussed in greater detail elsewhere (Umemoto and Wentzcovitch,



**Fig. 1.** The compression curves  $V(P)$ , bulk moduli  $K(P)$ , and their derivatives  $K'(P) \equiv dK/dP$  of HS and LS  $(\text{Mg}_{0.875}\text{Fe}_{0.125})\text{SiO}_3$  determined by LDA, LDA+U, GGA, and GGA+U. The inclusion of Hubbard  $U$  does not make a significant difference; the choice of exchange–correlation functional does. The numerical values of Hubbard  $U$  are adopted from Hsu et al. (2010b), and the experimental data are cited from Lundin et al. (2008). When the effect of phonon is included, LDA (LDA+U) gives better result than GGA (GGA+U).

in preparation). At finite temperatures, magnetic and configuration entropies also contribute to alter the free energy, but in a simple ideal solid solution model (Wentzovitch et al., 2009), they are volume independent and do not alter isothermal compression curves.

#### 4. Results and discussion

Ferrous iron in (Mg,Fe)SiO<sub>3</sub> perovskite can be in LS, IS, and two energetically competing HS states with distinct QSs (Bengtson et al., 2009; Hsu et al., 2010b). Theory, at the level of sophistication applied to investigations so far, predicts the fraction of IS iron to be negligible (Hsu et al., 2010b; Umemoto et al., 2010). The two competing HS states, differing in the equilibrium position of iron in the 8–12 coordinated cage, have essentially the same lattice parameters (Hsu et al., 2010b). Also, at lower-mantle pressures (23–135 GPa), the HS state with higher QS dominates. Therefore, only the LS and high-QS HS states are addressed in this paper.

The compression curves  $V(P)$ , bulk moduli  $K(P)$ , and their derivatives  $K'(P) = dK/dP$  of (Mg<sub>0.875</sub>Fe<sub>0.125</sub>)SiO<sub>3</sub> perovskite (in LS and HS states) as functions of pressure  $P$  determined using standard DFT and the DFT+ $U$  methods are shown in Fig. 1. Equation of state parameters,  $V_0$ ,  $K_0$ , and  $K'_0$ , are listed in Table 1. The Hubbard  $U$  correction does not affect these parameters significantly for all these cases. Instead, the choice of the standard DFT functional does. As expected, LDA gives a smaller static equilibrium volume. When vibrational effects are included at 300 K, compression curves determined using LDA and LDA+ $U$  agree with experimental data (Lundin et al., 2008) quite well. One can notice that the experimental data deviate from the predicted compression curve at pressures around 100 GPa or higher. This may not be necessarily a flaw of LDA or LDA+ $U$ . It is more likely to result from the known questionable accuracy of the Au pressure scale adopted in the experiment (Lundin et al., 2008) in this pressure range ( $P > 100$  GPa). Since GGA already overestimates static volume, including phonon effect

**Table 1**

Static equation of state parameters of (Mg<sub>0.875</sub>Fe<sub>0.125</sub>)SiO<sub>3</sub>. For each spin state and each exchange–correlation functional, the inclusion of Hubbard  $U$  does not make a significant difference.

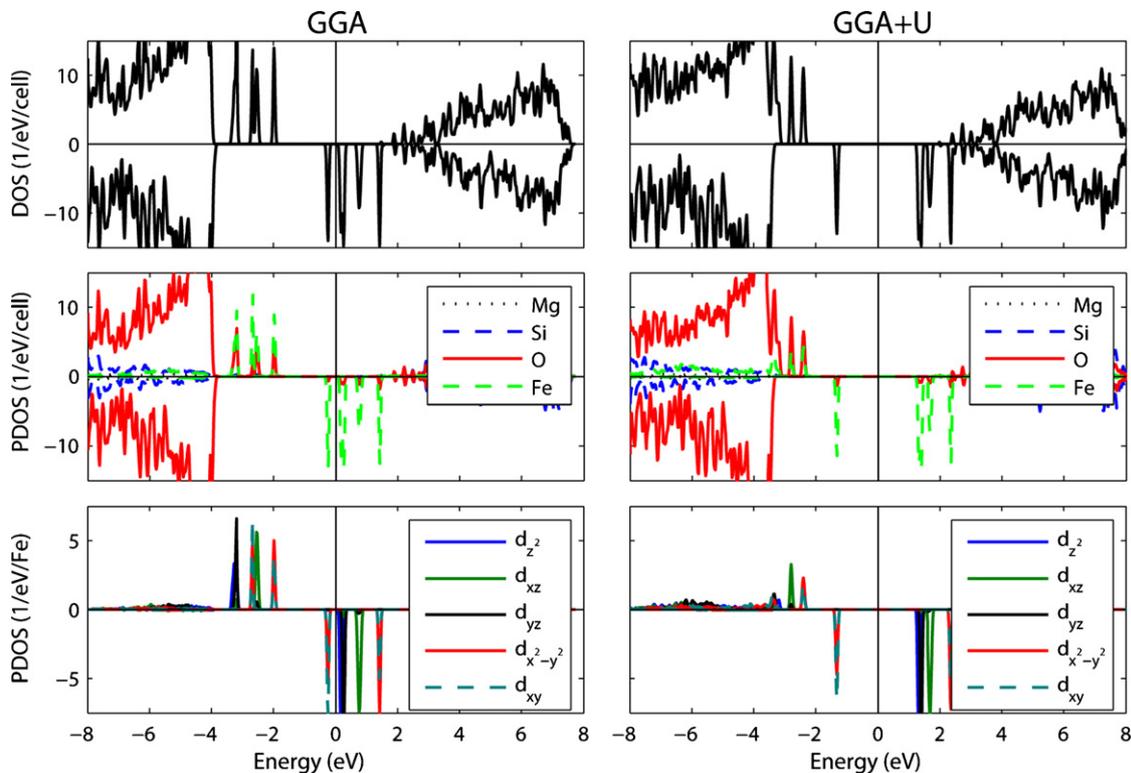
	$V_0$ (a.u. <sup>3</sup> /f.u.)	$K_0$ (GPa)	$K'_0$
HS (LDA)	271.91	262	3.91
HS (LDA+ $U$ )	272.44	262	3.90
LS (LDA)	270.83	260	3.96
LS (LDA+ $U$ )	271.32	262	3.92
HS (GGA)	285.67	235	3.95
HS (GGA+ $U$ )	286.39	231	4.01
LS (GGA)	284.85	228	4.08
LS (GGA+ $U$ )	285.12	232	4.02
Exp. (15% iron, $T = 300$ K)	275.50	257	4.00

Experimental values are cited from Lundin et al. (2008).

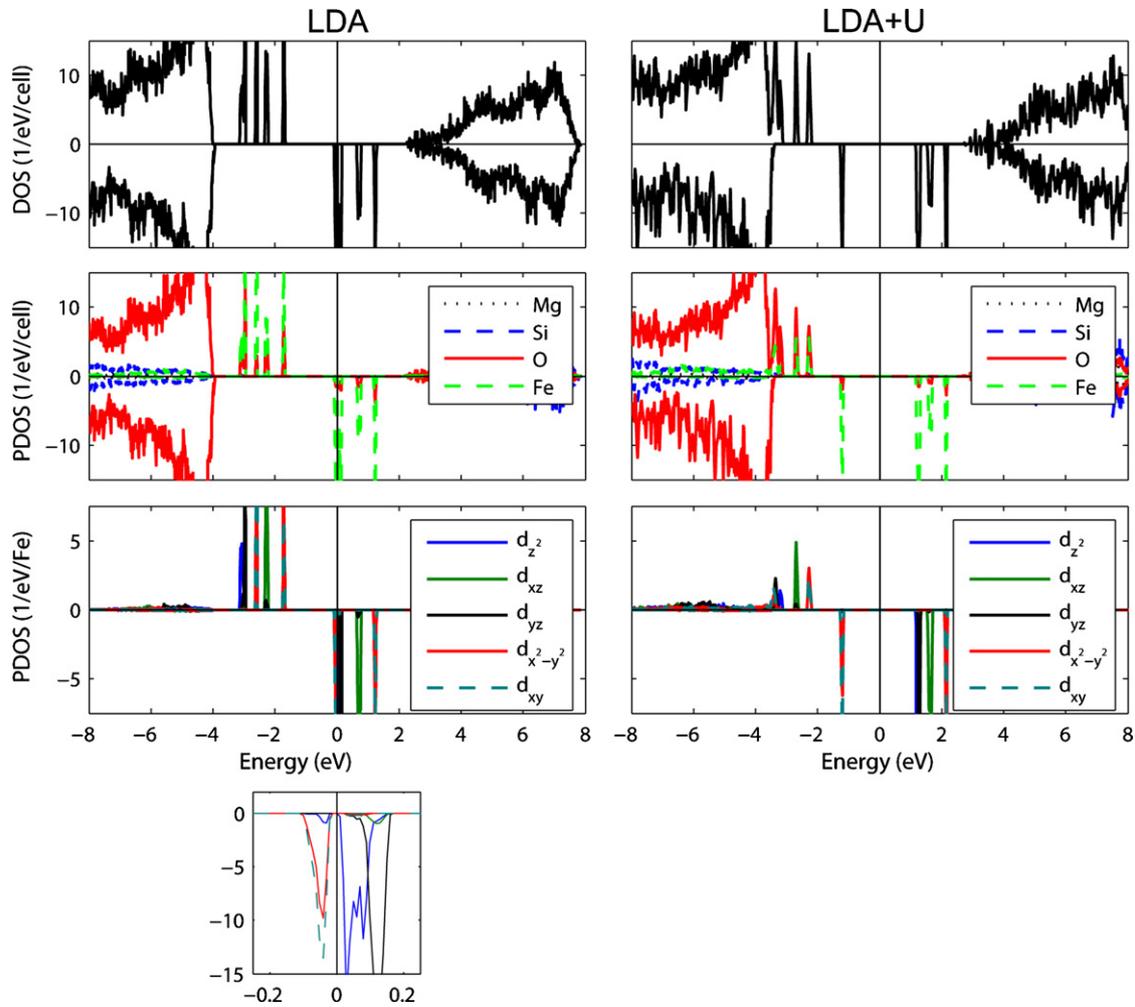
would just make it worse. In fact, the volume overestimation resulting from GGA is quite common, as can be seen in fayalite (Cococcioni et al., 2003; Stackhouse et al., 2010) and LaCoO<sub>3</sub> (Hsu et al., 2009).

In this paper, the pressure is determined from the fitted free energy vs. volume curve,  $F(V)$ , using  $P = -dF/dV$  (at finite temperatures, only the electronic and vibrational free energies contribute to  $-dF/dV$ ). No empirical corrections, for example, a manual shift in the calculated pressure to better fit experimental data, is adopted. If such a pressure shift was adopted here, all four compression curves (and bulk moduli) of (Mg,Fe)SiO<sub>3</sub> perovskite determined by different approaches would be similar, and the equilibrium volume would be the same as the experimental one. A desirable discussion should be based on parameter-free first-principles calculations, so the method that makes more accurate predictions can be better determined.

To understand in detail the effect of the Hubbard  $U$  on the structural and electronic properties, we compare lattice parameters and electronic density of states (DOS) calculated with GGA and GGA+ $U$  ( $U = 2.91$  eV) for HS (Mg<sub>0.875</sub>Fe<sub>0.125</sub>)SiO<sub>3</sub> perovskite at  $V = 285.17$  a.u.<sup>3</sup>/f.u. Fig. 2 shows the total and projected DOS. Both



**Fig. 2.** Total and projected density of states of high-spin (Mg<sub>0.875</sub>Fe<sub>0.125</sub>)SiO<sub>3</sub> calculated with GGA and GGA+ $U$  ( $U = 2.91$  eV) at  $V = 285.17$  a.u.<sup>3</sup>/f.u.



**Fig. 3.** Total and projected density of states of high-spin  $(\text{Mg}_{0.875}\text{Fe}_{0.125})\text{SiO}_3$  calculated with LDA and LDA+ $U$  ( $U=31.9$  eV) at  $V=271.37$  a.u.<sup>3</sup>/f.u. The detail of projected density of states on Fe-3d orbitals around the Fermi level is shown in the extra panel.

GGA and GGA+ $U$  produce a non-metallic HS state. The main difference is the width of the energy gap: 0.16 and 2.3 eV for GGA and GGA+ $U$ , respectively. The orbital occupancies of the Fe-3d spin-down electron are essentially the same for both calculations: a linear combination of real spherical harmonics  $d_{xy}$  and  $d_{x^2-y^2}$ , resulting in similar QSs within GGA and GGA+ $U$  (Hsu et al., 2010b). With Hubbard  $U$ , we also see a downward shift in the energy of the occupied Fe-3d states. This shift, however, has very little effect on the lattice parameters. With GGA, the lattice parameters (in  $Pbnm$  symmetry) are  $a=9.149$ ,  $b=9.348$ , and  $c=13.210$  a.u.; with GGA+ $U$ , they are  $a=9.150$ ,  $b=9.437$ , and  $c=13.211$  a.u. On the contrary, the Hubbard  $U$  correction significantly changes the calculated lattice parameters of  $\text{LaCoO}_3$  (Hsu et al., 2009), fayalite (Cococcioni and de Gironcoli, 2005; Stackhouse et al., 2010), and  $\text{Fe}_2\text{O}_3$  post-perovskite (Stackhouse and Brodholt, 2008) in which standard DFT methods fail to give correct orbital occupancy and insulating ground state.

Fig. 3 shows a similar comparison for HS  $(\text{Mg}_{0.875}\text{Fe}_{0.125})\text{SiO}_3$  computed with LDA and LDA+ $U$  at  $V=271.37$  a.u.<sup>3</sup>/f.u. Both LDA and LDA+ $U$  ( $U=31.9$  eV) produce a non-metallic state. The energy gaps are 0.04 and 2.2 eV within LDA and LDA+ $U$ , respectively. The effect of Hubbard  $U$  is similar to that in the GGA case: an increase of the band gap and a downward shift in the energy of the occupied 3d-orbitals, while leaving the orbital occupancies and structural parameters unchanged. The lattice parameters are (in  $Pbnm$  symmetry)  $a=9.008$ ,  $b=9.293$ , and  $c=12.967$  a.u. with LDA;  $a=9.009$ ,  $b=9.291$ , and  $c=12.968$  a.u. with LDA+ $U$ .

The reason why the Hubbard  $U$  correction barely affects the predicted structural properties of  $(\text{Mg,Fe})\text{SiO}_3$  perovskite is that standard DFT functionals already predict a small gap and the correct occupancy of the 3d-orbitals of iron, which lead to a reasonably accurate charge density. The gap is indeed underestimated, but that does not affect the orbital occupancy and charge density significantly. When the charge density, which is fundamental for the description of structural and elastic properties, can be correctly predicted by standard DFT ( $U=0$ ), inclusion of Hubbard  $U$  should not strongly affect the structural and elastic properties. Indeed, the elastic constant tensor  $C_{ij}$  and shear modulus  $G$  are not calculated in this paper. However, since the atomic structure, equation of states, bulk modulus, and charge density obtained with DFT and DFT+ $U$  are essentially the same, it can be expected that  $C_{ij}$  and  $G$  should not be strongly affected by Hubbard  $U$ . On the contrary, in systems like  $\text{LaCoO}_3$ , ferropericlase, or fayalite where standard DFT functionals fail to give a correct insulating ground state, correct orbital occupancy, and accurate charge densities, standard DFT predictions of structural parameters will not be accurate enough. The rhombohedral distortion of  $\text{LaCoO}_3$  predicted by LDA and GGA is too much. Also, both LDA and GGA fail to predict the Jahn–Teller distortion in the HS ferropericlase. For these systems, including the Hubbard  $U$  correction to enforce the correct orbital occupancy (and thus accurate charge density) is necessary for the accurate prediction of structural and elastic properties. One interesting example worthy of mention is  $\text{Fe}_2\text{O}_3$  post-perovskite. While the Hubbard  $U$  correc-

tion changes the predicted lattice parameters, electronic structures, and each elastic constant  $C_{ij}$ , it barely changes the aggregate elastic moduli,  $K$  and  $G$ , of this material (Stackhouse and Brodholt, 2008).

This series of calculations suggests a criterion to assess the necessity of the Hubbard  $U$  correction for computing the structural and elastic properties of iron-bearing minerals. In the low concentration regime where irons barely interact, as long as standard DFT functionals give correct orbital occupancy, thus stabilizing the desired spin state and a nonzero gap for insulating minerals, standard DFT produces results similar to those produced by DFT +  $U$ . On the other hand, when the iron concentration is high enough to induce iron–iron interaction, or when standard DFT fails to predict a nonzero gap for the insulating mineral, DFT +  $U$  with spin- and volume-dependent  $U$  leads to more accurate results.

Another effect of the Hubbard  $U$  is the total energy shift, and thus a shift in the enthalpy. When there are more than one phase involved so the phase transition may be an issue (e.g., more than one spin state), adopting DFT +  $U$  with  $U$  determined by first principles for each phase is important for computing more appropriate relative free energies and therefore transition pressures, even if the Hubbard  $U$  does not affect the structural/elastic properties of each phase. For example, as shown by Hsu et al. (2010b), LDA +  $U$ , GGA, and GGA +  $U$  consistently predict HS (Mg,Fe)SiO<sub>3</sub> stable in the lower mantle, i.e., up to and beyond 135 GPa, while LDA predicts a HS–LS crossover at ~100 GPa.

## 5. Conclusions

Using ferromagnesium silicate perovskite as example, we have compared its static and  $T=300$  K structural properties obtained using standard DFT functionals, LDA and GGA, and their DFT +  $U$  counterparts. Our calculations indicate that if the standard DFT functionals give correct orbital occupancies and insulating states, their predictions of structural/elastic properties are essentially unaffected by the Hubbard  $U$ . In this case, the choice of DFT functional is the main factor affecting the accuracy of the prediction. On the other hand, the Hubbard  $U$  correction is important when DFT gives incorrect metallic state and incorrect orbital occupancy, which lead to less accurate charge density and less accurate predictions for structural/elastic properties.

Based on this series of calculations and others we have carried out in the past, we expect that for iron-bearing minerals (usually with low concentration of iron), calculations adopting standard DFT methods can offer similar results for structural and elastic properties to those obtained by DFT +  $U$  functionals, as long as the DFT functional produces insulating ground states with correct orbital occupancies.

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