

# Ab Initio Total Energy Study of Brucite, Diaspore and Hypothetical Hydrated Wadsleyite

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**Abstract.** Ab initio total energy calculations based on the local density approximation (LDA) and the generalised gradient approximation (GGA) of density functional theory have been performed for brucite,  $\text{Mg}(\text{OH})_2$ , diaspore,  $\text{AlOOH}$  and hypothetical hydrated wadsleyite,  $\text{Mg}_7\text{Si}_4\text{O}_{14}(\text{OH})_2$ . The use of a general gradient approximation (GGA) is essential to obtain a good agreement ( $\approx 1\%$ ) of the calculated lattice parameters to diffraction data. The calculated fractional coordinates of brucite and diaspore are in good agreement ( $\approx 1.5\%$ ) with experimental data. The angle of the non-linear hydrogen bond in diaspore is reproduced well, and the calculated Raman active OH stretching frequency in brucite is in very good agreement with spectroscopic data. There are no significant differences between the calculated fractional coordinates and the second derivative of the energy when GGA is used instead of standard LDA. It is concluded that the description of the static and the dynamic behavior of the OH groups in these hydroxides is very good. It is therefore inferred that the parameter free model is predictive and it has been used to evaluate a hypothetical structure of hydrated wadsleyite. The model reproduces the unusual Si-O bond length of  $1.7 \text{ \AA}$ , observed in  $\beta\text{-Mg}_2\text{SiO}_4$ . It predicts an O-H distance of  $0.97 \text{ \AA}$ , which is significantly shorter than the distance obtained from earlier model calculations.

## Introduction

Increasingly, microscopic models based on pair-potentials are used to address a large variety of problems in mineralogy, including, to name but a few, isotope fractionation, Al/Si ordering, equations of state, and lattice dynamics. Such conventional models, based mostly on empirical, but nevertheless sometimes transferable potentials (Winkler et al. 1991), can be predictive and are satisfactory for a large number of mineralogical ap-

plications. However, Winkler et al. (1991) noted that it seems unlikely that this approach will be developed much further, as the next step would be a computationally very demanding derivation of further pair potentials by fitting short-range potential parameters simultaneously to many mineral structures to maintain transferability. One way to circumvent this and other problems associated with models based on empirical pair potentials is to use *ab initio* total energy calculations. Such models are predictive and the underlying physics and constraints are well understood.

Currently a number of *ab initio* approaches are used, very useful summaries of several techniques are given in books by Devreese and van Camp (1984) and Meyer and Pontikis (1991). As quantum-mechanical calculations have been applied to minerals only recently, there has, to the best of our knowledge, not yet been a discussion of which method is best suited for a given problem. Here we use a technique based on density functional theory (DFT) in the local density approximation (LDA) and the generalised gradient approximation (GGA). LDA calculations have been used successfully to investigate structures, phonons, bulk moduli and other properties. However, in the last few years, evidence has accumulated that a further extension to standard LDA, a generalized gradient approximation, GGA, is necessary to correct for the 'overbinding' often encountered in such calculations, which leads to too short lattice constants. Perdew et al. (1992) have shown that their formulation of the GGA generally leads to significant improvements of the calculations in the prediction of physical properties.

Total energy calculations are predictive, and should, starting from a trial structure, yield the most stable structure at zero Kelvin, whose properties could then be derived from the dependence of the total energy on structural parameters, such as small atomic displacements or small changes in the lattice constants. One possible application, in which we are presently interested, is the prediction of positions and orientations of small molecules in silicates, such as water in cordierite or zeolites.

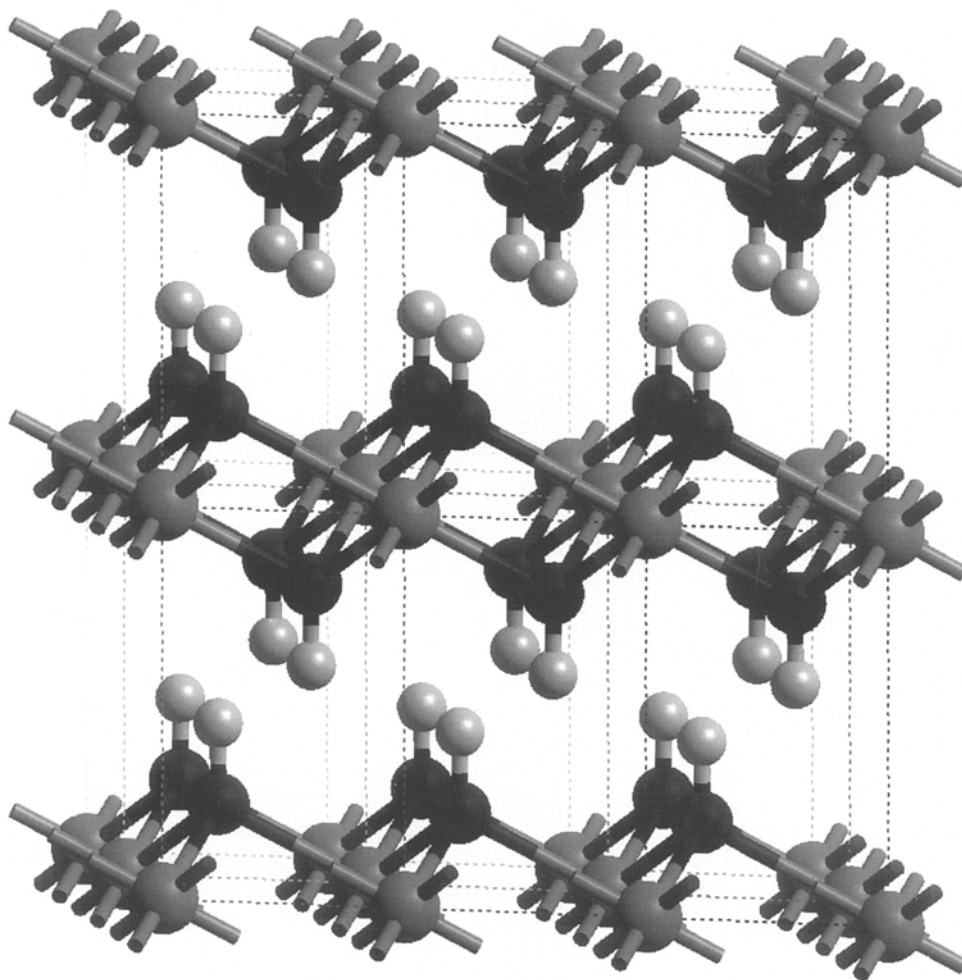


Fig. 1. The structure of brucite

The orientation of water molecules in a given structure will depend on the character of the hydrogen bonds between the 'guest' and the framework. The calculation of properties of hydrogen bonds in minerals with conventional models is not straight-forward. Results obtained with empirical rigid-ion or core-shell models generally are not totally convincing, although for some complex structures they can, at least to some extent, reproduce the static and dynamic properties (Abbott et al. 1989; Abott 1991; Collins 1990; Winkler et al. 1991). However, due to the nature of these models, their transferability is extremely limited; they have virtually no predictive power and hence, they cannot help solve problems such as those mentioned above.

As hydrogen bond strengths in silicates can differ greatly from structure to structure, or even within one structure, two systems were investigated. In the first, brucite,  $\text{Mg}(\text{OH})_2$ , the hydrogen is presumably not hydrogen-bonded at all (Fig. 1), while in the second, diasporite,  $\text{AlOOH}$ , the hydrogen is strongly hydrogen bonded (Fig. 2). Based on these two model structures, we wanted to test if the DFT calculations give acceptable results for the proton positions and vibrational frequencies. These are two properties which can easily be checked against experimental data. Brucite has only five atoms

in the unit-cell (Zigan and Rothbauer 1967). All atoms are located on special positions, and only the  $z$  coordinates of the oxygen and hydrogen atoms are not fixed by symmetry. Brucite has been modeled by Sherman (1991) and D'Arco et al. (1993) within the Hartree Fock formalism and thus we can compare two different modeling approaches. Diasporite also has a simple structure (Busing and Levy 1958; Hill 1979) with only three kinds of atoms, but with its 16 atom unit-cell it approaches the dimensions of more interesting complex silicates. The atoms in diasporite lie on two planes at  $z=1/4$  and  $3/4$ . Characteristic for the non-hydrogen bonded proton in brucite is the high O—H stretching frequency. In diasporite the hydrogen bond is non-linear, i.e. the direction of the O—H bond and the O...O vector enclose an angle of  $12^\circ$  (Fig. 2). A satisfactory model has to reproduce both these properties. Then, this model can be used to predict properties, and here we investigate if a model by Smyth (1994) for hydrous wadsleyite gives reasonable H positions.

In the following, we present some technical aspects of the calculations. Then we describe the results for brucite, diasporite and wadsleyite in more detail. Finally, we summarize our findings.

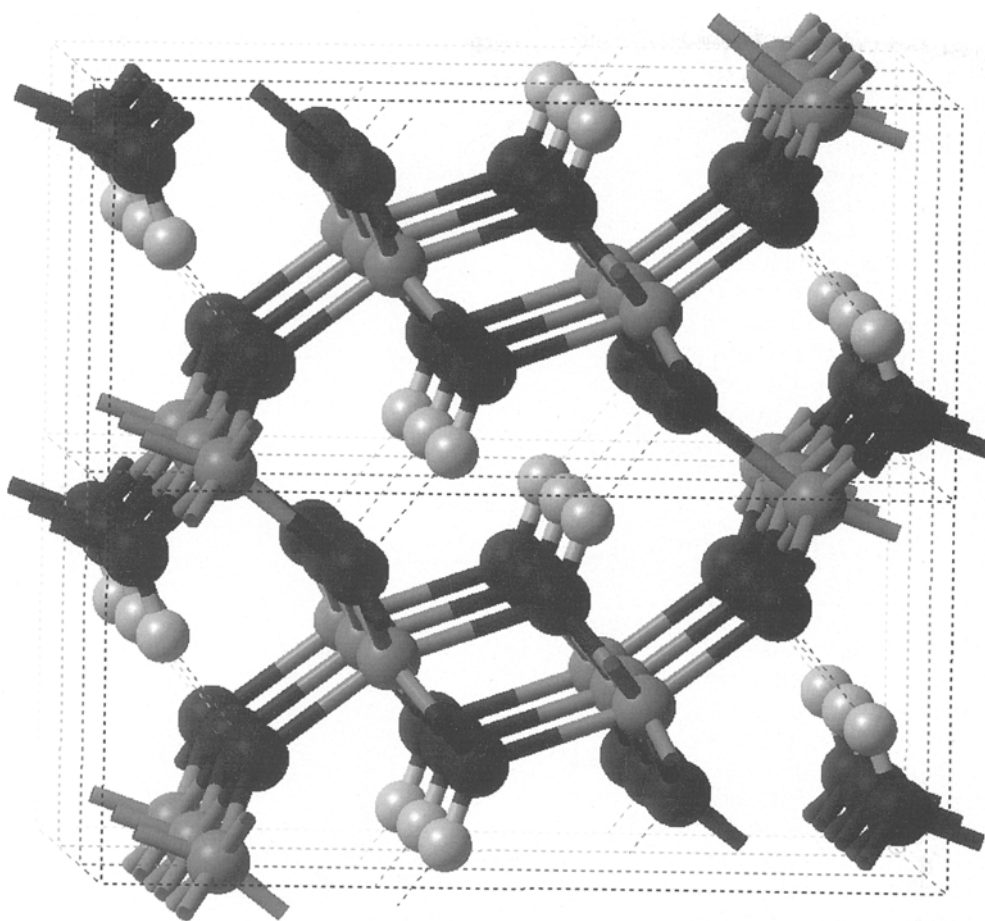


Fig. 2. The structure of diaspore

### Technical Details

The software package CASTEP (Cambridge Serial Total Energy Package), which has been described elsewhere (Teter et al. 1989; Payne et al. 1992), and associated programs for symmetry analysis, were used for the calculations presented here. Preliminary calculations have been performed with an earlier public domain version, while for the final calculations a commercial version from Molecular Simulations Ltd. has been used. CASTEP is a pseudopotential total energy code which employs special points integration over the Brillouin zone, and a plane-wave basis set for the expansion of the wave-functions. The calculations were performed using norm conserving nonlocal pseudopotentials of the form suggested by Kleinman and Bylander (1982), where the pseudopotentials were taken from the CASTEP data base.

An application of the pseudopotential method for first-row elements has long been a problem. In these atoms there are no core states of the same symmetry as the valence 2p orbitals. As a result there is no effective screening and valence electrons feel the full potential of the ionic core. It is still possible to apply formally any standard scheme (Kerker 1980; Bachelet et al. 1982) and construct a pseudopotential for p angular momentum. This potential will be very deep, but still softer than the pure Coulomb potential of the ion. The same procedure can be also used to generate a hydrogen pseu-

dopotential (Bachelet et al. 1982). The problem with thus constructed potentials comes from the fact that we are using a plane wave basis set, and the representation of a very hard potential requires an exceedingly large number of plane waves. For hydrogen it has been shown that the use of a pseudopotential is not advantageous compared to the Coulomb (local) potential (Needs 1992).

Therefore, the main difficulty here is a poor convergence of the oxygen pseudopotential. We employed the optimization scheme based on the minimization of the kinetic energies of pseudoorbitals beyond a certain critical wave vector (Lin et al. 1993). This approach has been shown to produce a reliable oxygen pseudopotential for studies of oxides (De Vita et al. 1992a, b). For Mg and Al no optimization is needed, as the original Kerker (1980) scheme produces soft potentials, and the overall convergence of the calculations for minerals with respect to the number of plane waves depends mainly on the properties of oxygen and hydrogen potentials. All these potentials have been shown to be transferable over the required energy range and free of the "ghost" states which are sometimes introduced by the Bylander-Kleinman representation (Gonze 1990).

In addition to the total energy, the calculations also yield the residual forces on the atoms. The forces are used to compute the necessary shifts of the atomic coordinates during the energy minimization. As this is done

very efficiently, a constant volume minimization of relatively large structures is possible. The Monkhorst-Pack scheme (Monkhorst and Pack 1976) was used to sample the Brillouin zone. Four to eight points were used in the irreducible wedge of the Brillouin zone for both structures. The symmetries of the structures were generally maintained by using an option to symmetrise the wave functions or by using constraints for the displacements of atoms on special positions. Some calculations have been performed without these constraints and gave identical results. Methods to obtain phonon dispersion curves have recently been described by Wei and Chou (1992). In the present study we only calculate the frequency of one high frequency phonon at the  $\Gamma$  point, using the 'frozen phonon' approach (Kunc 1985).

## Results

### Convergence

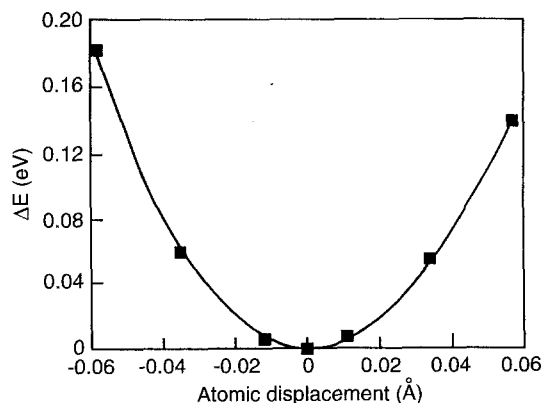
The application of LDA calculations to minerals is crucially dependent on the possibility of using relatively low kinetic energy cut-offs, as otherwise the computational resources needed to address mineralogical problems, typically involving large unit cells, will not be available. We have investigated the dependence of structural parameters and the total energy as a function of the cut-off energy extensively for brucite. A comparison of the total energy in a variety of calculations performed up to a cut-off of 1000 eV showed that the total energy was already converged to within 0.5 eV of the value for a 1000 eV cut-off when using a cut-off of 500 eV. Structural parameters are well converged with a 500 eV cut-off, a typical example is the O–H distance which changes by less than 0.01 Å when increasing the cut-off from 500 to 1000 eV. Most calculations have been performed using cut-offs between 600 and 800 eV, only in wadsleyite did the system size impose the use of a 500 eV cut-off.

### Brucite

Starting from the experimentally determined structure (Zigan and Rothenbauer 1967) we performed a number of calculations with different lattice constants, using both gradient corrected and standard LDA. After our calculations had been performed, Catti et al. (1995) published new structural data, which differed in some respects from the data by Zigan and Rothbauer (1967). In Table 1 our calculated values are compared to those of Zigan and Rothbauer (1967) and Catti et al. (1995). Our results are in better agreement with the structural parameters of Catti et al. (1995) than with the data of Zigan and Rothbauer (1967). Especially the calculated O–H distance agrees very well with the new experimentally determined value. Irrespective of the chosen cut-off for the plane wave expansion, the calculations without the gradient corrections gave equilibrium lattice parameters which were significantly too small, namely  $a =$

**Table 1.** The experimentally determined (Zigan and Rothbauer 1967; Catti et al. 1995) and calculated structure of brucite. The experimentally determined frequency of the OH stretching vibration is from Ryskin (1974)

|                                                   | exp.<br>Zigan and<br>Rothbauer<br>(1967) | exp.<br>Catti et al.<br>(1995) | calc.<br>LDA | calc.<br>GGA |
|---------------------------------------------------|------------------------------------------|--------------------------------|--------------|--------------|
| $a$ [Å]                                           | 3.142 (1)                                | 3.14979 (4)                    | 3.00         | 3.13         |
| $c$ [Å]                                           | 4.766 (2)                                | 4.7702 (1)                     | 4.57         | 4.71         |
| $c/a$                                             | 1.517                                    | 1.500                          | 1.523        | 1.505        |
| O(z)                                              | 0.2216 (7)                               | 0.2203                         | 0.2201       | 0.2201       |
| H(z)                                              | 0.4303 (12)                              | 0.4415                         | 0.4356       | 0.4209       |
| O–H [Å]                                           | 0.99                                     | 0.958 (3)                      | 0.985        | 0.946        |
| $\nu_{\text{OH}}$ , Raman<br>[ $\text{cm}^{-1}$ ] | 3653                                     |                                | 3633         | 3625         |



**Fig. 3.** Change of the total energy of brucite as a function of the displacement of the proton along [001] from its equilibrium position

3.10 Å and  $c = 4.45$  Å while with the use of a gradient corrected exchange potential the respective results were in much better agreement with experiment. We obtained  $a = 3.13$  Å and  $c = 4.71$  Å which is 0.7%–1.3% smaller than the room temperature values of Zigan and Rothenbauer (1967), and Catti et al. (1995).

Brucite is a simple structure where the Mg atom is located on a special position. This simplifies the derivation of the eigenvector of the OH stretching vibration. The structure is centro-symmetric (point group  $D_{3d}$ ), hence modes which are Raman active (all gerade modes) are not infrared active (all ungerade modes) and vice versa. Factor group analysis shows that there are two OH stretching vibrations, one Raman ( $A_{1g}$ ) and one infrared ( $A_{2u}$ ) mode, which have a simple eigenvector where both oxygen and protons move only  $\parallel$  [001]. We simplified the eigenvectors further by taking into account the fact that oxygen has a much larger mass than hydrogen. Hence the total energy was calculated as a function of a hydrogen displacement parallel to [001] only, while all other structural parameters were fixed. Both hydrogens were displaced in the same sense relative to the respective oxygen, this corresponds to the eigenvector of the  $A_{1g}$  mode. The resultant  $\Delta E = f(u)$  curve obtained from the standard LDA calculations is shown

in Fig. 3. In the harmonic approximation the change in energy,  $\Delta E$ , is related to the mass weighted displacements,  $m_i |u_i|^2$  of the  $i$ -atoms and the frequency,  $\omega$ , of the corresponding the phonon by:

$$\Delta E = \frac{1}{2} \omega^2 \sum m_i |u_i|^2 \quad (1)$$

which, for the eigenvector used here, i.e. for two protons having the same displacement vector,  $u$ , and the mass,  $m$ , simplifies to:

$$\Delta E = \omega^2 m u^2 \quad (2)$$

The change of the energy can be expanded in terms of  $u$ :

$$\Delta E = a u^2 + b u^3 + \dots \quad (3)$$

where a fit of  $\Delta E = f(u) = a u^2 + b u^3$  is also shown in Fig. 3. From the excellent fit ( $R = 0.999$ ) we obtain  $a = 48.5(5) \text{ eV/\AA}^2$ , and  $b = -86(8) \text{ eV/\AA}^3$ . In the harmonic approximation only the quadratic term is retained, and the phonon frequency is:

$$f = \frac{\omega}{2\pi} = \frac{\sqrt{\frac{a}{m}}}{2\pi} \quad (4)$$

This corresponds to a Raman frequency of  $3633 \text{ cm}^{-1}$ , which is, within the accuracy of the calculations, the same as the result obtained with the GGA,  $3625 \text{ cm}^{-1}$ . The experimental value is  $3653 \text{ cm}^{-1}$  (Ryskin 1974). While the experimental value has been obtained at room temperature, the present calculations give physical properties at 0 K. However, the ratio of the experimentally obtained stretching frequencies for the protonated and deuterated compounds is very close to the ideal value based on the mass difference only, and this, together with the absence of any significant hydrogen bonding, indicates that the OH group behaves as a harmonic oscillator, which would imply a very weak temperature dependence of the stretching frequency. Even in much more anharmonic systems, such as diaspore, temperature induced shifts of the OH-stretching frequency only amount to about  $10\text{--}20 \text{ cm}^{-1}$ , which is negligible in the current context. Furthermore, a temperature decrease generally leads to a decrease of the OH stretching frequency, as it corresponds to an increase in the hydrogen bond strength. Hence the results of low temperature measurements would most probably be in even better agreement with the calculated data.

### Diaspore

The calculations performed for diaspore (Fig. 2) are computationally considerably more expensive than those for brucite. Hence we did not minimize the energy with respect to the lattice constants, but we relaxed all the atomic positions using GGA and LDA. The calculated atomic coordinates are given in Table 2. A comparison of the calculated to the observed (Busing and Levy 1958) fractional atomic coordinates shows that, again similar to brucite, the topology of the structure is reproduced well. For the OH distance the experimental value cor-

**Table 2.** The experimentally determined (Busing and Levy 1958) and calculated structure of diaspore

|                                             | exp.       | calc.  |        |
|---------------------------------------------|------------|--------|--------|
|                                             |            | LDA    | GGA    |
| a [Å]                                       | 4.401 (1)  | fixed  | fixed  |
| b [Å]                                       | 9.421 (4)  | fixed  | fixed  |
| c [Å]                                       | 2.845 (1)  | fixed  | fixed  |
| Al (x)                                      | 0.0451 (8) | 0.0449 | 0.0517 |
| Al (y)                                      | 0.8554 (3) | 0.8561 | 0.8560 |
| O1 (x)                                      | 0.7120 (5) | 0.7109 | 0.6998 |
| O1 (y)                                      | 0.1989 (2) | 0.1986 | 0.1953 |
| O2 (x)                                      | 0.1970 (5) | 0.1944 | 0.1914 |
| O2 (y)                                      | 0.0532 (2) | 0.0527 | 0.0566 |
| H (x)                                       | 0.4095 (9) | 0.4145 | 0.4036 |
| H (y)                                       | 0.0876 (4) | 0.0891 | 0.0912 |
| O–H [Å]                                     | 0.990 (4)  | 1.03   | 0.99   |
| angle H–O <sub>II</sub> –O <sub>I</sub> [°] | 12.1       | 11.8   | 11.3   |

rected for thermal motion ( $1.005 \text{ Å}$ ) has been taken from the work of Busing and Levy (1958). The non-linearity of the OH ... O group has been mentioned before. In the model the observed angle is  $\approx 11.5^\circ$ , this agrees well with the experimental value of  $12.1^\circ$ . For diaspore, the OH-stretching frequency cannot be calculated using a simplified eigenvector, as there will be no pure stretching motion along the direction of the O–H bond in this non-linear strongly hydrogen bonded system.

### Hypothetical Hydrous Wadsleyite

Based on earlier work on  $\beta\text{-Mg}_2\text{SiO}_4$  (Horiuchi and Sawamoto 1981; Finger et al. 1993) Smyth (1994) suggested a hypothetical ordered fully hydrated wadsleyite as a possible source of water in the mantle. We used his structural data and the lattice constants of Finger et al. (1993) to investigate if the suggested proton positions were reasonable from a quantum mechanical point of view. The constant volume relaxation was performed using space group Pmmb and a cut-off of 500 eV. The structure was relaxed starting from the positional parameters suggested by Smyth (1994). The calculated atomic positions are compared to those by Smyth (1994) in Table 3. The fact that the internal coordinates could be relaxed without any problem in a full quantum mechanical calculation supports the notion that such a structure could exist. Generally, there is good agreement between the model by Smyth (1994) and the calculation presented here. The present calculations reproduce the very long Si–O bond distance of  $\approx 1.7 \text{ Å}$  present in  $\beta\text{-Mg}_2\text{SiO}_4$  (Finger et al. 1993). The structure of Smyth (1994) and our results differ in the OH distance. Here, these are calculated to be  $d(\text{O–H}) = 0.97 \text{ Å}$ , i.e. they are 9% shorter than the distances  $d(\text{O–H}) = 1.05 \text{ Å}$  suggested by Smyth (1994). The range of distances in the other coordination polyhedra are in reasonable agreement to those of  $\beta\text{-Mg}_2\text{SiO}_4$  and those in Smyth's (1994) model.

**Table 3.** Comparison of computed structural parameters of hydrous wadsleyite to atomic coordinates suggested by Smyth (1994). For each atom the first row gives the data of Smyth (1994), the second row are the values obtained in the present study. The lattice parameters  $a = 5.6921 \text{ \AA}$ ,  $b = 11.460 \text{ \AA}$ ,  $c = 8.253 \text{ \AA}$  have been taken from Finger et al. (1993) and have not been varied. The symmetry was constrained to Pmmn

|      |               |               |               |     |               |               |               |
|------|---------------|---------------|---------------|-----|---------------|---------------|---------------|
| Mg1a | 0             | 0             | 0             | O1a | 0             | $\frac{1}{4}$ | 0.2187        |
|      | 0             | 0             | 0             |     | 0             | $\frac{1}{4}$ | 0.2356        |
| Mg1b | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | O1b | $\frac{1}{2}$ | $\frac{3}{4}$ | 0.7187        |
|      | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ |     | $\frac{1}{2}$ | $\frac{3}{4}$ | 0.7136        |
| Mg2  | 0             | $\frac{1}{4}$ | 0.9702        | O2a | 0             | $\frac{1}{4}$ | 0.7168        |
|      | 0             | $\frac{1}{4}$ | 0.9504        |     | 0             | $\frac{1}{4}$ | 0.7058        |
| Mg3  | 0.2500        | 0.1264        | 0.2500        | O2b | $\frac{1}{2}$ | $\frac{3}{4}$ | 0.2168        |
|      | 0.2538        | 0.1135        | 0.2522        |     | $\frac{1}{2}$ | $\frac{3}{4}$ | 0.2000        |
| Ha   | 0             | $\frac{1}{4}$ | 0.3459        | O3a | 0             |               | 0.9895 0.2556 |
|      | 0             | $\frac{1}{4}$ | 0.3532        |     | 0             |               | 0.9823 0.2522 |
| Hb   | $\frac{1}{2}$ | $\frac{3}{4}$ | 0.5915        | O3b | $\frac{1}{2}$ |               | 0.4895 0.7556 |
|      | $\frac{1}{2}$ | $\frac{3}{4}$ | 0.5957        |     | $\frac{1}{2}$ |               | 0.4843 0.7628 |
| Sia  | 0             | 0.1201        | 0.6166        | O4a | 0.2698        | 0.1229        | 0.9929        |
|      | 0             | 0.1203        | 0.6086        |     | 0.2626        | 0.1242        | 0.9980        |
| Sib  | $\frac{1}{2}$ | 0.6201        | 0.1166        | O4b | 0.7608        | 0.6229        | 0.4929        |
|      | $\frac{1}{2}$ | 0.6244        | 0.1130        |     | 0.7730        | 0.6181        | 0.5029        |

## Discussion

In agreement with earlier findings by Perdew et al. (1992), our calculations show that the GGA improves results compared to LDA calculations significantly, reducing the 'overbinding' often encountered in LDA. This mainly affects the lattice parameters, in the present calculations the internal coordinates converge to similar fractional coordinates irrespective of which description of the exchange-correlation energy is used. The GGA results, however, are in better agreement with the new experimental data of Catti et al. (1995). This is also true for the second derivative of the energy with respect to atomic displacements, as in brucite the calculated frequency of the OH stretching mode did not depend significantly on whether GGA or standard LDA was used. Also, the calculations reproduce the  $a/c$  ratio of the layered structure of brucite both with and without the gradient approximation, and hence the dispersive forces are correctly described even in standard LDA. That the atomic coordinates were reproduced to about 1% is especially encouraging in the case of the non-linear hydrogen bond in diasporite, as this is a result which cannot easily be obtained using conventional models. For brucite the calculations yield a stretching frequency of the O—H group very close to the observed value. To the best of our knowledge there exists no transferable empirical potential model which is able to achieve this. In summary, the calculations of brucite and diasporite have shown that GGA calculations can be used as a reliable tool to calculate structural properties in systems with hydrogen bonds. This is in agreement with the finding of Lee et al. (1992) for ice, and the results obtained for a large variety of other structures without hydrogen bonds (Perdew et al. 1992 and references cited therein).

We have then used this predictive method to evaluate a model for hydrous wadsleyite proposed by Smyth (1994). With the exception of a significantly shorter hydrogen bond, our results are in good agreement with those from Smyth (1994) and the structural parameters obtained for  $\beta\text{-Mg}_2\text{SiO}_4$  by Finger et al. (1993). There have been no problems relaxing the internal degrees of freedom in a constant volume calculation, which supports the ideas of Smyth (1994). The high stretching frequencies obtained by vibrational spectroscopy (McMillan et al. 1991) indicate that the hydrogens are weakly hydrogen bonded in nominally anhydrous wadsleyite. A comparison of the calculated OH distance in hydrous wadsleyite to that obtained for brucite is consistent with this idea, as the calculated O—H bond distance in brucite,  $d(\text{O—H}) = 0.95 \text{ \AA}$  is slightly shorter than the O—H bond distance in hydrous wadsleyite,  $d(\text{O—H}) = 0.97 \text{ \AA}$ , and hydrogen bonding causes an elongation of the O—H bond within the hydroxyl group. The stronger hydrogen bond in diasporite leads to  $d(\text{O—H}) = 0.99 \text{ \AA}$ . A more detailed investigation based on constant pressure relaxations is currently in progress.

It has been mentioned in the introduction, that currently a number of *ab initio* approaches are employed in parallel. Sherman (1991) used Hartree-Fock calculations to obtain the structure, electron distribution and other properties of brucite. However, D'Arco et al. (1993) could not fully reproduce the results of Sherman (1991), even though they used a very similar approach. The calculations of D'Arco et al. (1993) showed that the neglect of dispersion forces in layer structures will lead to wrong interlayer spacings, i.e. in the case of brucite to a very wrong  $c/a$  ratio. However, D'Arco et al. (1993) also demonstrated convincingly that 'a posteriori' corrections will lead to results which are in good agreement with experiment. Sherman (1991) obtained a stretching frequency of the Raman active mode of  $3897 \text{ cm}^{-1}$  which is significantly too high, and the LDA method used here seems to give a more realistic picture of the interatomic forces.

It is obvious that an increasing use of any *ab initio* method in mineralogy will crucially depend on the development of code for the effective minimization of the energy with respect to atomic coordinates and unit-cell parameters, and for this, the calculations of forces and stress tensors is a prerequisite. The implementation of such calculations seems to be easier to achieve for DFT than for HF calculations, which we see as a significant advantage of the former method. With all-electron calculations NMR, NQR and Moessbauer parameters can be calculated to within 10% of the experimental values (Blaha et al. 1985), which is of course not possible with the pseudopotential approach. The latter, however, should in principle be much faster. Therefore, the different approaches complement each other.

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