Structure and elastic properties of Mg(OH)$_2$ from density functional theory

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Received 29 May 2010, in final form 20 September 2010
Published 22 October 2010
Online at stacks.iop.org/JPhysCM/22/445403

Abstract

The structure, lattice dynamics and mechanical properties of magnesium hydroxide have been investigated by static density functional theory calculations as well as ab initio molecular dynamics. The hypothesis of a superstructure existing in the lattice formed by the hydrogen atoms has been tested. The elastic constants of the material have been calculated with a static deformations approach and are in fair agreement with the experimental data. The hydrogen subsystem structure exhibits signs of disordered behaviour while maintaining correlations between the angular positions of neighbouring atoms. We establish that the essential angular correlations between hydrogen positions are maintained to a temperature of at least 150 K and that they are well described by a physically motivated probabilistic model. The rotational degree of freedom appears to be decoupled from the lattice directions above 30 K.

1. Introduction

Magnesium hydroxide—Mg(OH)$_2$—is a very simple mineral, called brucite, often regarded as a good example of a material with structurally bound OH group. The large number of known silicate phases with such structurally bound OH units [1, 2] creates significant interest in the role played by the OH groups and the physical properties induced by them for this type of crystal in the Earth’s interior. Brucite has been the subject of numerous experimental [3–9] and theoretical [7, 10–12] studies in the past. Despite its simple structure, its physical properties remain unexplored—in fact even its crystallographic symmetry has not yet been fully established [13], although the question of its structure has been addressed several times in the past [7, 10–12].

The crystal lattice of magnesium hydroxide is a simple, layered, hexagonal structure with layers of magnesium interlaced with layers of hydroxyl groups. This basic structure was firmly established long ago [14] as having $P\overline{3}$m1 symmetry with O–H bonds aligned on a three-fold axis (see figure 1). Further research [15] showed unexpectedly high thermal displacements of the hydrogen atoms. The models proposed previously [7, 8, 13, 16–18] deal with temporally and spatially averaged positions of the hydrogen subsystem and suggest that the hydrogen atoms are in fact displaced from the high-symmetry points on the three-fold axis to form a new lattice with $P\overline{3}$ symmetry and an averaged 1/3 occupancy of three equivalent 6i Wyckoff positions (x, 2x, z), with either $x > 1/3$ (the so called XGT arrangement) [7, 8, 13, 17, 18], or $x < 1/3$ (the so called XLT arrangement) as proposed by Megaw [16]. The schematic placement of atoms in this larger unit cell is presented in figure 2. The case for the XGT arrangement is further strengthened by the neutron diffraction experiment of Desgranges et al [19] indicating that protons are displaced into XGT positions even at ambient pressure.

All the above models could reflect true structure of the brucite crystal, but because of performing spatial and temporal averaging of the structure they may miss the dynamical aspect. In the present paper we deal with this aspect of the magnesium hydroxide structure. Firstly, we will show the results of the static, elastic constants calculations for the brucite crystal followed by those for its structural properties from density functional theory (DFT) molecular dynamics (MD) calculations. Secondly, we analyse the dynamical aspects of the structure and demonstrate that the hydrogen atoms are not frozen in their equilibrium positions but fluctuate strongly, displaying some unexpected dynamical structure characterized by long-range spatial correlations.
The paper is organized as follows. In section 2 the calculation method is presented. It serves to derive the elastic constants of magnesium hydroxide, which are reported and compared with available experimental values in section 3. Next, in section 4.1, we investigate the dynamical model of the hydrogen structure, showing that short-range correlations persist and relative hydrogen positions may be described by the simple probabilistic model presented in section 4.2. The paper is concluded in section 5.

2. Calculation set-up

We performed all the calculations of the structure and elastic properties of magnesium hydroxide using VASP [20], a DFT-based code employing the generalized gradient approximation (GGA) [21] with Perdew, Burke, and Ernzerhof (PBE) [22] projector augmented-wave (PAW) pseudopotentials [23, 21]. The reciprocal space integration was carried out over the set of special points generated according to the Monkhorst–Pack scheme [24].

The static calculations were carried out with a single hexagonal unit cell shown by the grey box in figure 1, a $\sqrt{3} \times \sqrt{3} \times 1$ supercell (figure 2) and reciprocal space sampling based on a $2 \times 2 \times 2$ lattice. The calculation of the elastic constants used the standard finite deformation method described in detail in previous publications [25, 26]. We applied displacements between [0.1%; $0.1^\circ$] and [1%; $1^\circ$] for the lattice vector lengths and angles, respectively.

The static calculation of the crystal in the $2 \times 2 \times 2$ supercell is presented in figure 1 together with the numbering scheme adopted for the hydrogen atoms used later in section 5 in the analysis of inter-atomic correlations. The MD calculations were conducted with both $\sqrt{3} \times \sqrt{3} \times 1$ and $2 \times 2 \times 2$ unit cells with the standard energy cut-off, $E_{\text{cut}} = 400$ eV, determined by the pseudopotentials used. We performed several 3 ps runs with 1–1.5 fs time step for temperatures ranging from 10 to 150 K in the micro-canonical ensemble (constant total energy) with at least 10 ps thermalization runs carried out using Nosé thermostat technique [27]. The trajectories collected from the MD runs were further analysed to extract positional correlations using the computer code developed for this purpose.

To check the influence of the supercell size on the results obtained we calculated—using a standard direct method [28, 29]—the force constants matrix and full lattice dynamics for a larger (3 x 3 x 3) system as well as the smaller one used in the MD calculations (2 x 2 x 2). The obtained exponential dependence of the force constants on distance shows that the inclusion of the next layer of unit cells in the system contributes less than 1/1000 of the overall interaction between atoms in the system. Furthermore, the dispersion curves and phonon density of states spectra, calculated for both (2 x 2 x 2 and 3 x 3 x 3) systems, display no significant difference, which means that the inclusion of the additional layer of unit cells does not modify the lattice dynamics of the system in any significant way and the conclusions concerning
lattice vibrations drawn from the present calculations are robust.

3. Elastic constants

We have completed a series of static, elastic constants calculations using various sizes and symmetries of the unit cells and atomic positions: high-symmetry (P3m1) experimental unit cell [14], low-symmetry (P3) \( \sqrt{3} \times \sqrt{3} \times 1 \) supercell, both with standard (1%) and small deformations (0.1%). In general, the results for the high-symmetry unit cell exhibit peculiarities which indicate that the high-symmetry cell may be not appropriate for this system. While the values of \( C_{11} \) obtained are fairly close to the experimental ones, the calculated elastic constants \( C_{12}, C_{13} \) and \( C_{44} \) are systematically about twice the experimental values (table 1). The largest difference, close to one order of magnitude, was noticed for \( C_{13} \) at \( P \simeq 1 \) GPa. During calculations we have also observed that the system shows a high sensitivity of the elastic constants to external stress applied to the unit cell. In some cases a non-hydrostatic stress of approximately 1-2 GPa induced a two-fold change in the constants \( C_{33} \) and \( C_{13} \). However, the discrepancy between the theoretical and experimental values of the elastic constants can be resolved by lowering the symmetry to \( P\overline{3} \). The elastic tensor for the larger \( \sqrt{3} \times \sqrt{3} \times 1 \) unit cell with \( P\overline{3} \) symmetry and hydrogen atoms displaced into the XGT positions, as suggested recently by Mookherjee and Stixrude [13], is presented in table 2. This suggestion agrees also with the earlier results in the literature [7, 8, 17, 18], and the values presented in table 2 show good agreement with experiment (table 1). We have also observed a considerably weaker sensitivity of the calculated values to the external stress applied to the system.

Moreover, during optimization of the magnesium hydroxide structure, we have observed that the positions of the hydrogen atoms around the three-fold axis are not very well constrained in the system, i.e., they probably move in a very shallow potential well. This observation is in concordance with previous experimental evidence [15]. It suggests that the structure of the magnesium hydroxide crystal may be more complicated than is currently accepted.

4. Dynamical structure

4.1. Correlations between hydrogen positions

In order to explore further the issue of dynamical hydrogen structure in magnesium hydroxide, we have used the DFT-based MD technique. The first calculation set-up used the \( \sqrt{3} \times \sqrt{3} \times 1, P\overline{3} \) unit cell proposed by Mookherjee and Stixrude [13]. The data were collected from measurement runs of 3 ps length, each preceded by a thermalization run of at least 10 ps, for several temperatures between 15 and 250 K.

The examination of the MD trajectories shows large amplitude hydrogen movements even for runs performed at low temperature. This result corresponds to the large thermal displacements observed in the experiment [15]. On the one hand, some experimental results [19], showing clear symmetry of the hydrogen locations, may be seen as contradicting such observations, while on the other hand, correlations between the hydrogen movements could explain this discrepancy.

To resolve this dilemma we have developed a method to quantify the angular correlations of hydrogen atoms. We extracted the correlation between positions of hydrogen atoms with respect to each other as well as with respect to the fixed reference crystal lattice. The results are presented in figure 3 for the absolute hydrogen angular distribution and in figure 4 for the relative hydrogen angular correlations. All these runs were performed in the \( \sqrt{3} \times \sqrt{3} \times 1 \) unit cell. The angle \( \psi \) is the angular position of the hydrogen atom around the three-fold axis, measured starting either from the direction of the crystal vector \( \vec{A} \) for the absolute angular distributions (red histograms), or from the direction selected by an arbitrary reference hydrogen atom (\( H_1 \left[ 4, \frac{1}{2}, z \right] \) in our case) for the relative angular distributions (blue histograms).

The high peaks seen in figure 3 suggest that there may be a lock-in of \( H_3 \) and \( H_4 \) hydrogen atom positions with respect to the crystal lattice.

The lattice lock-in still appears to be present at 244 K (upper panel in figure 3) but we must mention the fairly strong and uniform background of other positions in the histogram. In fact, most of the area in these histograms is outside the peaks. Thus, hydrogen atoms do not spend most of their time in the vicinity of their high-symmetry positions. This means that, despite distinct peaks being visible in the histograms, the angular positions of the hydrogen atoms are not locked with respect to the crystal lattice orientation.

Some of our results obtained for even lower temperatures \( T \approx 10 \) K indicate that the true lock-in with the crystal lattice may appear at or below \( T = 15 \) K—at this temperature we have observed Gaussian-shaped peaks and a diminished background in the histograms (not shown). Unfortunately, due to the difficulties of the MD calculations performed at low temperature we were unable to collect enough evidence to confirm this indication.

Table 1. Elastic constants of magnesium hydroxide for increasing pressure \( P \) (all quantities in GPa), measured by Jiang et al [30] with Brillouin scattering.

| \( P \) (GPa) | \( C_{11} \) (GPa) | \( C_{33} \) (GPa) | \( C_{12} \) (GPa) | \( C_{13} \) (GPa) | \( C_{44} \) (GPa) |
|----------|--------|--------|--------|--------|--------|
| 0.01     | 130.6  | 48.5   | 70.3   | 10.0   | 20.4   |
| 0.96     | 133.5  | 51.9   | 67.8   | 9.8    | 24.2   |
| 2.0      | 143.4  | 82.6   | 73.4   | 17.7   | 29.3   |
| 3.0      | 150.0  | 93.5   | 76.3   | 15.7   | 32.9   |
| 4.0      | 153.9  | 104.2  | 76.1   | 22.1   | 36.6   |

Table 2. Elastic constants for increasing pressure \( P \) (all quantities in GPa) obtained for the low-symmetry (\( P\overline{3} \)) unit cell of magnesium hydroxide.

| \( P \) (GPa) | \( C_{11} \) (GPa) | \( C_{33} \) (GPa) | \( C_{12} \) (GPa) | \( C_{13} \) (GPa) | \( C_{44} \) (GPa) |
|----------|--------|--------|--------|--------|--------|
| 10\(^{-4}\) | 159.0(16) | 49.5(7) | 43.3(17) | 11.1(25) | 22.8(4) |
| 1.1(1)   | 164.1(10) | 59.2(7) | 45.5(8)  | 12.3(8)  | 25.2(3) |
| 2.1(1)   | 169.3(9)  | 73.2(7) | 46.2(8)  | 16.6(7)  | 28.9(3) |
| 3.5(1)   | 179.6(10) | 94.0(8) | 52.0(9)  | 22.1(8)  | 33.4(3) |
| 4.8(1)   | 184.3(8)  | 110.0(6)| 53.1(6)  | 28.2(5)  | 36.8(3) |
Figure 3. Absolute angular hydrogen distribution in the $P\bar{3}$ unit cell. The top and bottom panels show the results obtained from the MD run at 244 K and at 46 K, respectively. The maxima at angle $\varphi \simeq 120^\circ$ obtained for $H_2$ ($H_5$) atoms are 2.05 and 1.2 (1.2 and 1.57) at high and low temperature, respectively. The positions of the hydrogen atoms with labels $H_1$, $H_2$, ..., $H_6$ are shown in figure 1.

The relative angular distribution results displayed in figure 4 show quite a different picture. On the one hand, there is a strong correlation, indicated by distinct peaks, of angular position between hydrogen atoms in the same layer ($H_1$, $H_2$, and $H_3$ positions are as in figure 2). On the other hand, no visible correlations were found for the atoms in the next layer ($H_4$, $H_5$, and $H_6$). This means that the hydrogen atoms maintain the relative orientations shown in figure 2, keeping their angular positions 120° apart—similar to the angular positions in the XGT/XLT structures mentioned in section 1—but only if we consider atoms which belong to the same layer of the structure. On the contrary, the neighbouring layer positions appear only loosely coupled. These relations are maintained up to the highest temperature we have investigated (300 K), but broadening of the peaks observed at 244 K (upper panel of figure 4) suggests that the peaks may disappear at higher temperatures, as one would expect.

The above result supports, to some extent, the conclusions of the previous work on brucite crystal [7, 8, 13, 15, 17–19], except that the hydrogen–hydrogen correlations do not appear for all atoms, but only for neighbouring atoms in the same layer. Furthermore, the lock-in of hydrogen positions to the lattice is not well confirmed by the above results and probably vanishes above the relatively low temperature of $T = 15$ K. These discrepancies motivated us to investigate the system further under less constraining conditions.
Figure 4. Relative angular hydrogen distribution in the $P\bar{3}$ unit cell. The H1 box shows the absolute angular distribution of the H1 atom. The top and bottom panels show the results obtained from the MD run at 244 K and at 46 K, respectively. The positions of the hydrogen atoms with labels H1, H2, ..., H6 are shown in figure 1.

The results of the calculation performed for the larger $2 \times 2 \times 2$ unit cell at temperature $T = 16$ K are presented in figure 5. It is quite clear that the correlations seen in the smaller unit cell are changed by the increase of the unit cell. We were unable to identify clearly any lock-in effect of the hydrogen positions with respect to the crystal lattice for temperatures above 30 K (figure 6) but below this temperature the signal arising from locked-in hydrogen positions is distinct and robust (figure 5). We have performed the calculations for several temperatures in the low temperature regime and for different starting conditions and obtained the same result in all cases.

The relative angular correlations are still present when a larger unit cell is investigated, but they are also modified with respect to the ones found before with the smaller unit cell. The histograms seen in figure 6 show the distributions of the angular positions of hydrogen atoms relative to the crystal lattice and those shown in figure 7—relative to an arbitrarily selected reference atom H1, see figure 1. For the low temperature run (figure 5) we can easily identify obvious non-uniformities in the distribution of absolute angular positions of most of the hydrogen atoms. The absence of distinct peaks for some atoms may be interpreted as a result of the relatively short simulation time (6 ps) and insufficient statistics due to the difficulty of performing adequate sampling of configuration space at low temperatures. We have verified that the overall picture remains in fact similar for different runs, but the individual peaks disappear for different atoms.

For higher temperatures, above 30–40 K, the absolute angular positions of hydrogen atoms are completely decoupled from the directions of the crystal lattice (figure 6) but we can
still observe fairly strong correlations in the relative angular positions of hydrogen atoms—these correlations are robust and persist even in the regime of rather high temperature. Figure 8, obtained for a temperature $T = 150$ K, presents an essentially unchanged picture of the distribution of hydrogen atoms’ relative positions. One can notice that weaker correlations with atoms from the first and from the last row seem to have disappeared. However, this may be due to the smaller statistics of the sample (18 ps versus 39 ps) and higher noise in the data obtained for this case.

4.2. Angular distribution of hydrogen positions

We have constructed a simple probabilistic model to describe the measured angular distribution of hydrogen atoms. As a starting point it is reasonable to assume a Gaussian distribution around one location accompanied by a constant background filling for the rest of the histogram. In periodic angular coordinates the standard Gaussian distribution in angle $\varphi$ centred at $\mu$ with width $\sigma$,

$$P_\sigma(\varphi) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left[-\frac{(\varphi - \mu)^2}{2\sigma^2}\right].$$

should be summed up over periodic repetitions of itself, which leads to

$$\frac{1}{\sigma \sqrt{2\pi}} \sum_{k=-\infty}^{\infty} \exp\left[-\frac{(\varphi - \mu + 2\pi k)^2}{2\sigma^2}\right] = \frac{1}{2\pi} \phi_3\left(\frac{\varphi - \mu}{2}, e^{-\frac{\sigma^2}{4}}\right).$$

Figure 5. Absolute angular distribution of hydrogen atoms in the $2 \times 2 \times 2$ supercell. The results are obtained from a 6 ps MD run at 16 K. The positions of the hydrogen atoms with labels H1, H2, …, H16, are shown in figure 1.
Figure 6. Absolute angular distribution of hydrogen atoms in the $2 \times 2 \times 2$ supercell. The results are obtained from a 39 ps MD run at 30 K. The positions of the hydrogen atoms with the labels H1, H2, ..., H16 are shown in figure 1.

Here $\vartheta_3$ is an elliptic Jacobi function of the third kind. Thus, the angular distribution we introduce here reads:

$$F_{\sigma}(\phi) = N \left[ (1 - \alpha) \frac{1}{2\pi} \vartheta_3 \left( \frac{\phi - \mu}{2}, e^{-\frac{\phi^2}{2}} \right) + \alpha \right],$$

where $N$ is a normalizing factor. It consists of the correlated part given by equation (2) with intensity $(1 - \alpha)$ and the background with intensity $\alpha$.

One can notice that in the case of 30 K (figure 7) as well as for 150 K (figure 8) the model for the angular distribution given by equation (3) fits the obtained numerical data remarkably well—it indicates the existence of a single potential minimum in the relative motion of individual hydrogen atoms. This demonstrates that the relative angular distribution reflects the correlated behaviour of the hydrogen atoms, with a single optimal angular position for each hydrogen atom. This is obviously not the case in the absolute angular positions depicted in figure 5, where a two-peaked distribution would be required to describe the data.

We should also note that the atoms \{H9, H10, H11, H12\} are characterized by strongly correlated movement with respect to the atom H1. They are located in the same structure layer as the reference (H1) atom. Also the position of a single out-of-plane atom H5, located directly above the reference atom H1 on the same three-fold axis, is strongly correlated with that of atom H1. Moreover, it is clear that the directions of the peaks do not strongly follow the 60° grid present in the smaller unit cell. The strongest signal indicates the same/opposite direction arrangement of the direct neighbour (atom H9) of the reference atom and its images in the neighbouring unit cells.
Figure 7. Relative angular distribution of hydrogen atoms in the $2 \times 2 \times 2$ supercell. The results are obtained from a 39 ps MD run at 30 K. Solid line shows the function $F_\sigma(\phi)$ given by equation (3) fitted to the data. The positions of the hydrogen atoms with labels H1, H2, ..., H16 are shown in figure 1.

(H10–H12). However, if we look closer at the distributions presented in figure 7, we can notice a slight preference for image atoms (H2–H4) to cluster around the 120° and 240° directions. This result does not offer strong support for the XGT/XLT arrangement hypothesis but the preferred directions are compatible with this type of arrangement.

In light of these results we conclude that the angular correlations in the atomic distribution obtained for the small unit cell are probably just an artefact of the constraints imposed on the system by the $\sqrt{3} \times \sqrt{3} \times 1$ unit cell. We also believe that it is still possible that the real physical system exhibits one of the symmetries proposed before [7, 8, 13, 16–18], but we emphasize that it does not show these symmetries for system size up to the $2 \times 2 \times 2$ supercell.

5. Summary and Conclusions

We have performed extensive calculations to determine the structure and elastic properties of magnesium hydroxide. The static calculations confirm the main result of the previous research that the static average structure with hydrogen atoms on the three-fold axis is absent in the brucite crystal. Further static calculations of the elastic constants of brucite also support the conclusions from previous papers [7, 8, 13, 17–19] suggesting the existence of a superstructure, probably with the $P\bar{3}$ symmetry, and an XGT arrangement of the hydrogen atoms [13]. This, however, does not exclude any other possibilities that would still be consistent with the available experimental evidence.
Figure 8. Relative angular distribution of hydrogen atoms in the $2 \times 2 \times 2$ supercell. The results are obtained from a 18 ps MD run at 150 K. Solid line shows the function $F_\sigma (\phi)$ given by equation (3) fitted to the data. The positions of the hydrogen atoms with labels H1, H2, ..., H16 are shown in figure 1.

In the present paper we have investigated one such possibility—the existence of a hydrogen sublattice possibly almost decoupled from the rest of the crystal. The results from the MD calculations in the small supercell support this hypothesis. Furthermore, the calculations performed in the larger $2 \times 2 \times 2$ cell revealed correlations between neighbouring hydrogen atoms at temperatures between 30 and 150 K. We have not found any lock-in behaviour of the hydrogen system above $T = 30$ K, while below this temperature we have identified strong correlations between the angular positions of the hydrogen atoms and the orientation of the lattice vectors. This result indicates that the rotational (around the three-fold axis) degree of freedom of the hydrogen system becomes decoupled from the crystal lattice around temperature $T = 30$ K, which may be considered as a characteristic energy scale for the onset of hydrogen–lattice coupling.

The $2 \times 2 \times 2$ supercell (shown in figure 1) is the largest one available for practical use at the moment, and additional calculations of lattice dynamics performed for the $3 \times 3 \times 3$ supercell indicate that the long-range interactions do not modify lattice dynamics in any significant way. Thus, we expect that the main qualitative conclusions on the crystal symmetry and hydrogen angular correlations either will not change, or could even strengthen, once technology and algorithms have developed to the point that larger systems can be investigated.

The results presented above demonstrate that the angular coordinates of the hydrogen atoms in the brucite crystal are probably decoupled from the crystal lattice above the estimated characteristic temperature $T \approx 30$ K. We have provided evidence that, in spite of this partial disorder in the hydrogen subsystem, the angular correlations between the positions...
of hydrogen atoms are robust and survive also in the high temperature regime $T \simeq 150$ K. We believe that these results will stimulate further research and the issue of inter-hydrogen correlations in brucite and related crystals should be further investigated using theoretical as well as experimental methods. We suggest that nuclear magnetic resonance spectroscopy could be a useful experimental tool in this context.

Acknowledgments

This work was partially supported by the Marie Curie Research and Training Network under Contract No. MRTN-CT-2006-035957 (c2c) and Polish Ministry of Science and Education Grant No. 541/6.PR UE/2008/7. A M Oleś acknowledges support by the Foundation for Polish Science (FNP).

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