Hydrogen Bonding in $M(\text{OD})_2$ Compounds Under Pressure

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The structures of the deuterated hydroxides $M(\text{OD})_2$; $M=\text{Mg, Ca, Mn, Ni, Co}$ have been refined using the Rietveld method and neutron powder diffraction data collected at high pressure. There is no statistically significant increase in the O-D interatomic distance at increased pressure while the hydrogen bonding interaction $\text{D}\cdots\text{O}$ increases as this distance decreases and the O-D $\cdots$ O angle increases. The intramolecular O-D bond valences, determined indirectly from the intermolecular D $\cdots$ O distances, decrease steadily for all materials as pressure is increased.

[neutron diffraction, hydroxides, CdI_2 structure, brucite structure, crystal structure]

1. Introduction

Hydrous minerals play a major role in low temperature geochemistry and are increasingly implicated in deep earth processes such as mantle convection and deep focus earthquakes [1, 2]. For example, layered hydrous phyllosilicates such as the clays, amongst the most common minerals at the earth's surface, are thought to be involved in the dehydration of the down going slab in subduction zones. Nominally anhydrous [3] as well as novel high pressure magnesium silicates have been suggested as phases for water storage in the mantle [3-18]. Finally, the strengths and rheological properties of the hydrogen-containing forms of the polymorphs of Mg_2SiO_4 suggest they might provide mechanisms for storage of stress in the mantle (Weidner, unpublished results) and that dewatering processes in these and other hydrous phases may lead to the reactivation of faults in the lithosphere [2]. The properties of these minerals then impact a variety of surface and deep earth processes. The presence of hydrogen bonding in solids can determine their stability and properties [19, 20] and the nature of this bond, its contribution to the stability of the dense high pressure hydrous phases, has been alluded to in some recent investigations [21-23]. {Other issues addressed include the phase relations in the hydrous high pressure "letter" phases and determination of the structures and elastic properties of some of these materials [6, 7, 14, 24-31].}

The precise role of hydrogen bonding in the stabilization, elastic properties and structural complexity observed in the dense hydrous magnesium silicates (DHMS) is difficult to ascertain. Simple correlations between the bulk modulus of these high pressure phases (Fig. 1) suggest that the role played by hydrogen is only as a modifier to such bulk properties as density. However, close inspection of these correlations reveals a divergence between the behavior of hydrates containing main group and those containing transition elements (Fig. 1). Further, hydrogen can introduce unexpected anisotropy not revealed when only bulk properties are considered [32, 33]. The structural details of H-bonding in these structures and its interaction with nearest neighbor cations is therefore important. The hydrogen is present at the level of only a few weight percent in the DHMS phases and, since they are synthesized at high pressures, samples are available in only limited quantities. This makes difficult the use of neutron diffraction, the most reliable technique for the characterization of crystalline hydrous materials [34], especially when *in situ* studies under high pressure conditions are desirable. The crystallographic complexity along with disorder in many of these structures also

limits the resolution with which the geometry of the hydrogen bond can be investigated [35, 36].

Fig. 1. Variation in bulk modulus with density for selected hydroxides [37, 38] and dense hydrous magnesium silicates [35, 36]; data for $\text{Ni}(\text{OD})_2$ derived from Table 1.

2. Materials

Simple layered hydroxides with the CdI_2 structure such as the hydroxides or deuterides of Mg, Ca, Co, Mn, Ni and Zn are interesting model systems for the investigation of hydrogen bonding in solids [37, 38] (Fig. 2). These are layered structures in which the X-H $\cdots$ Y group [20] is isolated from the other structural elements and is therefore more amenable to study. For example brucite, $\text{Mg}(\text{OH})_2$, has been investigated extensively by a number of theoretical and experimental techniques at both ambient conditions and at high pressure. Many of these investigations have concentrated on the role of hydrogen bonding as a function of increasing pressure and several authors have presented arguments for and against pressure-induced H-bonding, based upon spectroscopic [39-42] theoretical [43, 44] and crystallographic studies [37, 38, 45-47]. The behavior of these hydroxides at high pressure is diverse. Brucite appears to remain fully crystalline beyond 50 GPa and appears not to undergo any reconstructive

phase transitions [37, 38]. This contrasts with the behavior of portlandite, $\text{Ca}(\text{OH})_2$, which undergoes amorphization [40, 41] above 10 GPa at room temperature and transforms to a new structure related to baddelyite (ZrO_2) if heated at 300°C at 10 GPa [48]. The behavior of $\text{Co}(\text{OD})_2$ also appears to be anomalous with reports of H-sublattice amorphization or "multi-staging" [41] and evidence for anomalous *c*-axis compressibility under pressure [37]. We have also recently noted the divergence in the behavior in the compressibilities of the closed shell and transition element containing hydroxides (Fig. 1).

Fig. 2. Perspective drawing of the structure of CdI_2 -type deuterioxides such as $\text{Mg}(\text{OD})_2$, $\text{Mn}(\text{OD})_2$, $\text{Ni}(\text{OD})_2$ and $\beta\text{-Co}(\text{OD})_2$ viewed along [001] with the unit cell indicated by dotted lines. Open circles represent metal atoms while dark and light gray circles represent oxygen and hydrogen (deuterium) respectively. The structure consists of layers of $\text{M}(\text{OD})_6$ octahedra with the O-D vector in approximately the [001] direction with possible hydrogen bonds (D...O) between the layers shown as dashed lines. In this representation the D sites (light gray) are shown, with exaggeration, displaced from the fully occupied ideal position ($1/3, 2/3, z \approx 0.43$) to position $6i$ ($x \approx 0.38, -x, z$) with occupancy $1/3$. This displacement can be successfully modeled using the same number of least squares parameters [38] either as the split sites represented here or with anisotropic displacement ellipsoids [49] centered at the ideal position. As pressure increases the displacement from the ideal site increases, thereby decreasing one of the D...O distances, increasing the strength of the D...O bond and decreasing D...D repulsion.

It is the geometry of the hydrogen bond which chiefly governs its stability [20, 50] and theoretical studies [50] suggest that electrostatic effects predominate, particularly for weak bonds, while covalency effects increase with the strength of the bond [19, 20]. The strength of the hydrogen bond formed will therefore

depend upon the geometric relationships in the $\text{X}^+-\text{A}^--\text{H}^+ \cdots \text{B}^--\text{Y}^+$ unit and on the interplay between the electron withdrawing power of the elements involved [51]. In minerals the electronegative "donor" (A^-) and "acceptor" (B^-) [20] are usually oxygen. The strength of the $\text{H} \cdots \text{O}$ bond will then depend on the configuration of the $\text{X}-\text{O}-\text{H}^+ \cdots \text{O}-\text{Y}$ unit, including the $\text{O}-\text{H} \cdots \text{O}$ angle and $\text{H} \cdots \text{O}$ distance, as well as the acidity of the metal atoms X and Y [19, 20, 50, 51].

The importance of structural studies in characterizing the nature of the hydrogen bond in solids and how these change with pressure has been recognized since the pioneering work of Hamilton and Ibers in molecular solids. Even in hydrous minerals as seemingly simple as brucite and portlandite the precise nature of the H-bond has only recently come to light [37-42, 45-47, 52]. These minerals were presumed by most workers to be Van der Waals solids [20, 34] and were confirmed as such by a number of theoretical studies [43, 44]. More recently however, suggestions by Kruger *et al.* [40] that spectroscopic observations indicated the presence of H-bonding in portlandite and brucite, were investigated in both room pressure and high-pressure [37, 38, 48] using neutron diffraction [53]. Our study [37, 38] found evidence for subtle structural rearrangements of the H-sublattice responsible for enhanced H-bonding between the layers at high pressures but suggested, in agreement with other spectroscopic results presented by Lutz *et al.* [54], that little hydrogen bonding exists at room pressure. Reported here is a summary of high pressure neutron diffraction experiments carried out to investigate the systematics of H-bonding in the CdI_2 -related alkaline earth and transition metal deuterioxides (Fig. 1) including recently completed work on the $\text{Ni}(\text{OD})_2$.

3. Experimental techniques

Deuterated samples were prepared using established synthetic techniques [37, 55]. Neutron powder diffraction experiments were carried out in the Paris-Edinburgh (P-E) high pressure cell [56, 57] at the ISIS Pulsed neutron source at the Rutherford-Appleton Laboratory, UK. The opposed-anvil P-E cell maximizes scattering from the sample while minimizing scattering from the cell and routinely provides data to 10 GPa suitable for structural refinement using the Rietveld methodology [58, 59]. Of particular interest are the details of disorder [38-40, 45-47] in the site occupied by hydrogen (or deuterium) and the competition between H-bonding and repulsive interactions between layers in the structures (Fig. 2). For this reason attenuation corrections [60], good signal to noise discrimination and the availability of data below 0.7 Å resolution are important. Data were collected at the POLARIS beamline [61] of ISIS. Following each experiment, data from the individual detectors over the 14° range near 90° to the incident beam were combined (focused) to produce a single histogram of data suitable for Rietveld refinement [58, 59].

For most of the deuterioxides, data were first collected for the determination of the equation of state (EOS). The samples in these runs contained NaCl, to act as a pressure marker [62] and data were collected for 2 - 4 hours at proton currents of about 150 μA . For the collection of data for Rietveld refinement pure deuterioxide was loaded in the P-E cell and data were collected for at least 8 hours.

Preliminary results for $\text{Ni}(\text{OD})_2$ collected from ambient pressure to 7 GPa are presented here and will be compared with values for other high pressure studies of deuterioxides available in

Fig. 3. Calculated (continuous line) and observed X-ray powder diffraction profiles for $\text{Ni}(\text{OD})_2$ at 55T press load (an estimated 2.1 GPa). The difference between the observed and calculated profiles is plotted on the same scale below the tic-marks indicating the positions of allowed reflections for the phases contributing to the pattern. In this case the upper set of tic-marks indicate the positions of reflections from $\text{Ni}(\text{OD})_2$ and the lower set those from WC contamination arising from the opposed anvils in the Paris-Edinburgh cell in which the sample is contained. The fit to the data at low d-spacing is shown on an expanded scale (x10) above the full pattern.

the literature [37, 38]. Two structure models were tested at each pressure. In the first, all atoms occupy ideal positions with full occupancy and the anisotropic displacement parameters for the site occupied by deuterium were allowed to vary. For the second model deuterium was situated at site 6i ($x \sim 0.37$, $2x$, $z \sim 0.45$) with occupancy $1/3$ and isotropic displacement parameters (Fig. 2). Models assuming anisotropic displacement of a fully occupied D-site converged quickly with the ratio of the major axes of the anisotropic displacement ellipsoids, U_{11}/U_{33} , increasing from 2.5 to 4.4 for the pressure range studied (Table 1). This result is consistent with the situation noted in previous studies of the layered hydroxides and deuterioxides [37, 38, 45-47]. For data taken below 7 GPa, the isotropic split-atom model (Fig. 2, Table 1) gave either a statistically equivalent or slightly poorer fit, with no increase in the number of refined parameters. A summary of the results for the high pressure investigation of $\text{Ni}(\text{OD})_2$ are given in Table 1 and a typical fit is given in Fig. 3.

4. Results and Discussion

The bulk moduli, determined from least-squares fits to a second-order Birch-Murnaghan equation of state assuming $K' = 4.7$ [63] are summarized in Fig. 1. The value obtained for K from these and previous P-E [37, 64] and diamond anvil [63] powder

diffraction experiments will include the effects of deviatoric stress [65, 66] and will represent an overestimate of the true value. The general trends, and particularly the differences between the closed shell and transition metal-containing materials will not be affected. Indeed these trends are also noted in the hydrogen bonding of the hydroxides and this has been pointed out by Lutz *et al* [54] in their infrared studies at room pressure and in recent neutron powder diffraction studies at high pressure [37].

The behavior of the unit cells under compression for all the materials tested (Mg, Ca, Mn, Ni and $\text{Mn}(\text{OD})_2$) is similar [37], reports of anomalies in the behavior of the compressibility of the $\beta\text{-Co}(\text{OD})_2$ notwithstanding [37, 42]. The a -axes of these materials show a constant rate of decrease from 1 GPa, the c -axis is at least twice as compressible. The compressibility of the c -axis decreases with increasing pressure and approaches that of the a -axis at the highest pressures [37, 38, 47, 63]. Although the cause of the anomalous behavior for $\beta\text{-Co}(\text{OD})_2$ is as yet unknown, recent attempts to reproduce the anomalies in c -axis compressibilities [37] have not been successful and suggest they might be instrumental artifacts or due to differences in sample preparation leading to heterogeneities in the stress conditions within the P-E cell.

The behavior of the structures at high pressures is consistent with both the minimization of the increased repulsive forces as

Table 1. Refined atomic parameters* and selected interatomic distances (Å) for the split atom model* of deuterated synthetic theophrastite, Ni(OD)₂.

P (GPa) [§]	0.0	2.1	5.0	7.0
<i>a</i> (Å)	3.1316(1)	3.1020(1)	3.0715(1)	3.0525(1)
<i>c</i> (Å)	4.5970(2)	4.4537(2)	4.3668(3)	4.3249(5)
<i>V</i> (Å ³)	39.042(2)	37.114(2)	35.677(3)	34.900(4)
<i>z</i> (O)	0.2207(4)	0.2280(3)	0.2339(6)	0.2408(8)
<i>x</i> (D)	0.3665(9)	0.3679(8)	0.3732(8)	0.3716(11)
<i>z</i> (D)	0.4279(5)	0.4409(4)	0.4488(6)	0.4517(8)
<i>U</i> ₃₀ (Ni) [¶]	0.44(4)	0.71(5)	0.58(5)	0.34(4)
<i>U</i> ₃₀ (O) [¶]	0.93(6)	0.27(4)	0.30(5)	0.76(7)
<i>U</i> ₁₁ (D) [¶]	1.61(9)	1.81(8)	1.3(1)	1.5(1)
<i>U</i> ₃₃ (D) [¶]	1.61(9)	1.81(8)	1.3(1)	1.5(1)
<i>R</i> (F ²)	0.0643	0.0500	0.0344	0.0386
χ ²	0.4787	0.5811	0.5865	0.5974
O-D	0.969(3)	0.966(3)	0.962(5)	0.934(6)
D...O	2.294(4)	2.180(3)	2.087(4)	2.050(6)
D...O	2.497(3)	2.398(2)	2.342(3)	2.296(4)
Ni-O	2.073(1)	2.0587(7)	2.047(1)	2.047(2)

*P3m1 Ni at (0,0,0), O at (1/3,2/3,z), D moved from ideal position at (1/3,2/3,z) to 6i (x,x,z).

[§]Pressure determined from cell volume (*V*) of Ni(OD)₂ and equation of state determined from previous high pressure study using NaCl as internal pressure calibrant.

[¶]isotropic displacement parameter (Å² × 10³).

the layers are forced closer and the formation of stronger hydrogen bonding (Fig. 2). The displacement of D from the ideal position in the disordered site model (Fig. 2) is also evidenced in the increasing anisotropy of the displacement ellipsoids for the model in which the D-site is constrained to position (1/3, 2/3, *z*). This has two consequences: 1) to increase the average distance between D-sites within and between the (001) layers (Fig. 2) thereby reducing repulsive forces as pressure increases and 2) to decrease the average D...O distance and to increase the O-D...O angle as pressure increases, favoring increased hydrogen bonding [38]. However, there is no obvious trend in the O-D distance with pressure, regardless of the model chosen to describe the displacement of the D-site (Fig. 2). With the exception of the highest pressures, the O-D bond length is constant within three estimated standard deviations from a mean, with the distance for the anisotropic model some 0.03 Å shorter at all pressures; this latter distance is not corrected for riding motion and so is an underestimate. For β-Co(OD)₂ for example this distance at 9.5 GPa [37] is unusually short (0.9 Å) for the anisotropic model, while the model in which D is split over three equivalent sites is more consistent with values in the literature, 0.94(1) Å [54, 67-72]; at the higher pressures this split-site model is a more appropriate description of the positions of deuterium atoms in these materials. To facilitate comparisons between the models and for the calculation of bond valence at the different pressures (Fig. 4), the isotropic split-atom models have been used rather than the model with incorporates an anisotropic displacement parameter for D (Table 1). Both models require the same number of least squares parameters and the fits to the data they provide are near equivalent;

Fig. 4. Bond valences, *s*, of the intramolecular OD bonds in CdI₂-type deuterioxides of Mg, Co, Ni and Mn; data were taken from reference [37] and from Table 1. The “cut-off” for H-bonding is taken from the work of Lutz et al. [70, 71]. For the accepted *v*_{OD} for free hydroxide (2623.3 cm⁻¹) and the O-H vs. *v*_{OD} correlation curves [70, 71], the bond valence corresponding to free deuterioxide is approximately 0.918 valence units (v.u.). The correlation suggests that at room pressure the degree of hydrogen bonding is less than in free deuterioxide, in agreement with IR results [54] and that the closed shell and half closed shell cations behave differently from the transition elements. This behavior at room pressure is attributed to the stronger M-O bonding (Fig. 2) for the transition elements [54].

the split atom model is superior at the highest pressures.

For brucite-like hydroxides, the strength of the hydrogen bond, H...O in the O-X...O moiety, has been interpreted in terms of the OH(D) bond length ([38, 47] and the OH(D) stretching frequency. The expectation is that the former will increase with pressure as H(D)...O are forced closer and that the latter will decrease with pressure as the O-H(D) bond is weakened by increased interaction in the O...H(D) bond. Unfortunately systematic and model-dependent errors, such as are introduced by thermal motion and static disorder, limit the accuracy of the experimentally available intramolecular O-H(D) distances. This problem with estimating the strength of hydrogen bonds in solid hydroxides and hydrates has recently been addressed and summarized in papers by Lutz and co-workers ([52, 70-72]. The bond valences for individual OD bonds can be given by:

$$s_{OD} = \exp[(R_1 - r)/b]$$

where *r* is the experimentally determined O-D (or D...O) distance,

and $R_1 = 0.914\text{\AA}$ and $b = 0.404\text{\AA}$ [70]. Reliable bond valences can be obtained by summing those associated with interlayer (Fig. 2) D...O distances, and subtracting them from the total valence for D (=1) using the formulation:

$$s = 1 - \sum s_{D...O}.$$

The error in the bond valence due to inaccurate O-D distances can also be minimized by a normalization procedure:

$$s' = s_{O-D} / (s_{O-D} + \sum s_{D...O}).$$

The value of s obtained from recent neutron diffraction experiments are compiled in Fig. 4. The "cut-off" for H-bonding shown in Fig. 4 is derived from the accepted v_{OD} for free hydroxide (2623.3 cm^{-1}) and the O-H vs. v_{OD} correlation curves are used to calculate the bond valence corresponding to free deuteroxide; it is approximately 0.918 valence units (v.u.). Pressure clearly increases hydrogen bonding in these solids. Its effects are consistent with the bond valence calculations and spectroscopic studies carried out by previous workers in a large variety of hydrates and hydroxides [68-72 and references therein]. In common with these observations there is a difference between the behavior of the closed shell or half closed shell cations and the transition elements. Similar trends have been noted in studies of the bulk modulus (Fig. 1) and spectroscopy of these materials.

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