

Single-crystal structure refinement of diaspore at 50 GPa

ALEXANDRA FRIEDRICH,^{1,*} EIKEN HAUSSÜHL,¹ REINHARD BOEHLER,² WOLFGANG MORGENROTH,³
ERICK A. JUAREZ-ARELLANO,¹ AND BJÖRN WINKLER¹

¹Institut für Geowissenschaften, Abt. Kristallographie, J.W. Goethe-Universität Frankfurt, D-60438 Frankfurt am Main, Germany

²Max-Planck-Institut für Chemie, D-55020 Mainz, Germany

³Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

ABSTRACT

The crystal structure of diaspore, AlO(OH), has been investigated by in situ single-crystal synchrotron X-ray diffraction at ~50 GPa using the diamond-anvil cell technique. Diaspore is found to retain its structure up to 51.5 GPa at room temperature, which is more than 30 GPa above the transition pressure to δ -AlO(OH) found in quenched high-temperature experiments and derived from density functional theory calculations. The compression is anisotropic and largest for the **a** axis. This can be explained by the fact that the structural response to pressure is mainly due to the shortening of the hydrogen bond, which is oriented nearly parallel to the **a** axis. The hydrogen bond becomes significantly more symmetric with pressure up to 50 GPa.

Keywords: Diaspore, high pressure, crystal structure, synchrotron radiation, single crystal

INTRODUCTION

Diaspore, α -AlO(OH), is an interesting model system for high-pressure studies of hydrogen bonds, as it possesses a relatively high symmetry (orthorhombic), a relatively small unit cell [unit-cell volume = 117.96(8) Å³, Busing and Levy 1958], and is chemically simple. The non-linear hydrogen bond is of intermediate strength (O-H stretching frequency ν is about 3000 cm⁻¹, Ryskin 1974). The crystal structure of diaspore (space group *Pbnm*, *Z* = 4) is built from “double rutile strings” (Ewing 1935) of edge-sharing AlO₃(OH)₃ octahedra (Fig. 1). These double strings are arranged parallel to the **c** axis and are connected via common oxygen corners. The OH groups form hydrogen bonds in the (001) plane across the channels formed by the coordination octahedra, with the O...O and O-H vectors tilted away from the **a** axis by about 31 and 20°, respectively. The oxygen atoms are arranged in a slightly distorted hexagonal close packing, with the Al atoms occupying part of the octahedral sites.

The high-pressure behavior of diaspore was studied initially by energy-dispersive powder X-ray diffraction. Experiments up to 25.5 GPa with a 4:1 methanol:ethanol mixture as the pressure medium gave a bulk modulus $B_0 = 167.5$ GPa (Mao et al. 1994). Experiments in a similar pressure range, but without the use of a pressure medium, gave $B_0 = 230$ GPa (Xu et al. 1994). No indications of a phase transition were observed in this pressure range. Another energy-dispersive X-ray diffraction study reported the (*P*, *V*, *T*)-equation of state of diaspore from data collected up to 7 GPa and 1073 K (Grevel et al. 2000). In that study, a significantly smaller value for $B_0 = 134$ GPa was found. The first theoretical study on the high-pressure behavior of diaspore predicted structural changes and elastic properties

up to 50 GPa (Winkler et al. 2001). The predictions of that study were subsequently confirmed by in situ single-crystal X-ray diffraction at pressures of up to 7 GPa (Friedrich et al. 2007). In the latter study, the theoretical investigations were extended to include predictions regarding the pressure dependence of the lattice dynamics. The main findings of these papers are (1) the bulk modulus determined from experiments and theory agrees well (B_0 is around 150 GPa); (2) the compression of the crystal structure proceeds mainly by bond shortening, and particularly by compression of the hydrogen bond; (3) the hydrogen bond strength increases with pressure; (4) the hydrogen bond becomes significantly more symmetric with increasing pressure; (5) a complete symmetrization is not reached in the investigated pressure range up to 40 GPa and does not seem likely to occur in diaspore even at higher pressures; and (6) the stretching frequencies of the O-H bond decrease approximately linearly with increasing pressure, and therefore also with increasing O-H bond length and decreasing hydrogen bond length.

These findings are consistent with the results from Rietveld refinements of the structure of isostructural goethite from powder X-ray diffraction data up to 9 GPa (Nagai et al. 2003). However, the infrared spectra of goethite were interpreted in terms of a weakening of the hydrogen bond strength by bending of the O-H...O angle with pressure up to 10 GPa and successive strengthening at higher pressures up to 24 GPa, being mainly driven by the positions of the iron cations (Williams and Guenther 1996). The influence of the metal-hydrogen repulsion on the hydrogen-bond geometry was also derived from recent high-pressure powder neutron diffraction experiments on deuterated α -FeO(OD) up to pressures of about 7 GPa (Nagai et al. unpublished, in Parise 2006).

An extension of the experimental studies to significantly higher pressures would not only allow the further corroboration

* E-mail: friedrich@kristall.uni-frankfurt.de

of the predictions on the compression behavior, but would also contribute to our understanding of the high-pressure stability. This is relevant, as hydrous phases such as $\text{AlO}(\text{OH})$ are important hydrogen-containing components in subducting sedimentary rocks. Hence, knowledge of the stability conditions of hydrous minerals may lead to insight into the hydrogen-containing phases in the Earth's mantle. While diaspore was reported to be stable up to at least 15 GPa and 1123 K (Schmidt 1995), a high-pressure phase of diaspore, $\delta\text{-AlO}(\text{OH})$ (space group $P2_1nm$), was synthesized and found to be stable at pressures from 17 to at least 26 GPa at around 1273 to 1473 K (Suzuki et al. 2000; Ohtani et al. 2001; Sano et al. 2004). These (P,T) -stability fields have been determined from the analyses of quenched samples. It was deduced from first principles calculations that the α -to- δ phase transition occurs around 18 GPa at 0 K (Li et al. 2006).

In the present study, the crystal structure of diaspore was refined

at 50 GPa by in situ single-crystal synchrotron X-ray diffraction to elucidate the structure and compressibility of $\text{AlO}(\text{OH})$ at this high pressure and thus provide further constraints for the discussion of the results of ab-initio computations.

EXPERIMENTAL METHODS

We employ a new type of diamond anvil cell that has recently been developed (Boehler 2006). It is equipped with small conical diamond anvils (Boehler and de Hantsetters 2004) and hardened metal seats, which provide an opening angle of 85° . In this set-up, the absorption by the diamond anvil cell components is minimized, while the access to the reciprocal space is maximized. This is essential for single-crystal X-ray diffraction when using extremely small samples as is necessary in this pressure range (around 50 GPa).

The sample chamber was a hole of $130\ \mu\text{m}$ in diameter in a tungsten gasket, which had been pre-indented to a thickness of $43\ \mu\text{m}$. A single crystal of diaspore ($20 \times 30 \times 10\ \mu\text{m}$) was obtained from the same large gem-quality natural single crystal of unknown origin as the crystals used in Friedrich et al. (2007). Helium, which provides a nearly hydrostatic pressure even at 50 GPa, was used as the

FIGURE 1. Projection of the crystal structure of diaspore along the c axis. "Double rutile strings" of $\text{AlO}_3(\text{OH})_3$ octahedra are connected via common corners. The hydrogen bonds are formed across the channels. The assignment of the different Al-O distances is illustrated in two enlarged octahedra (right).

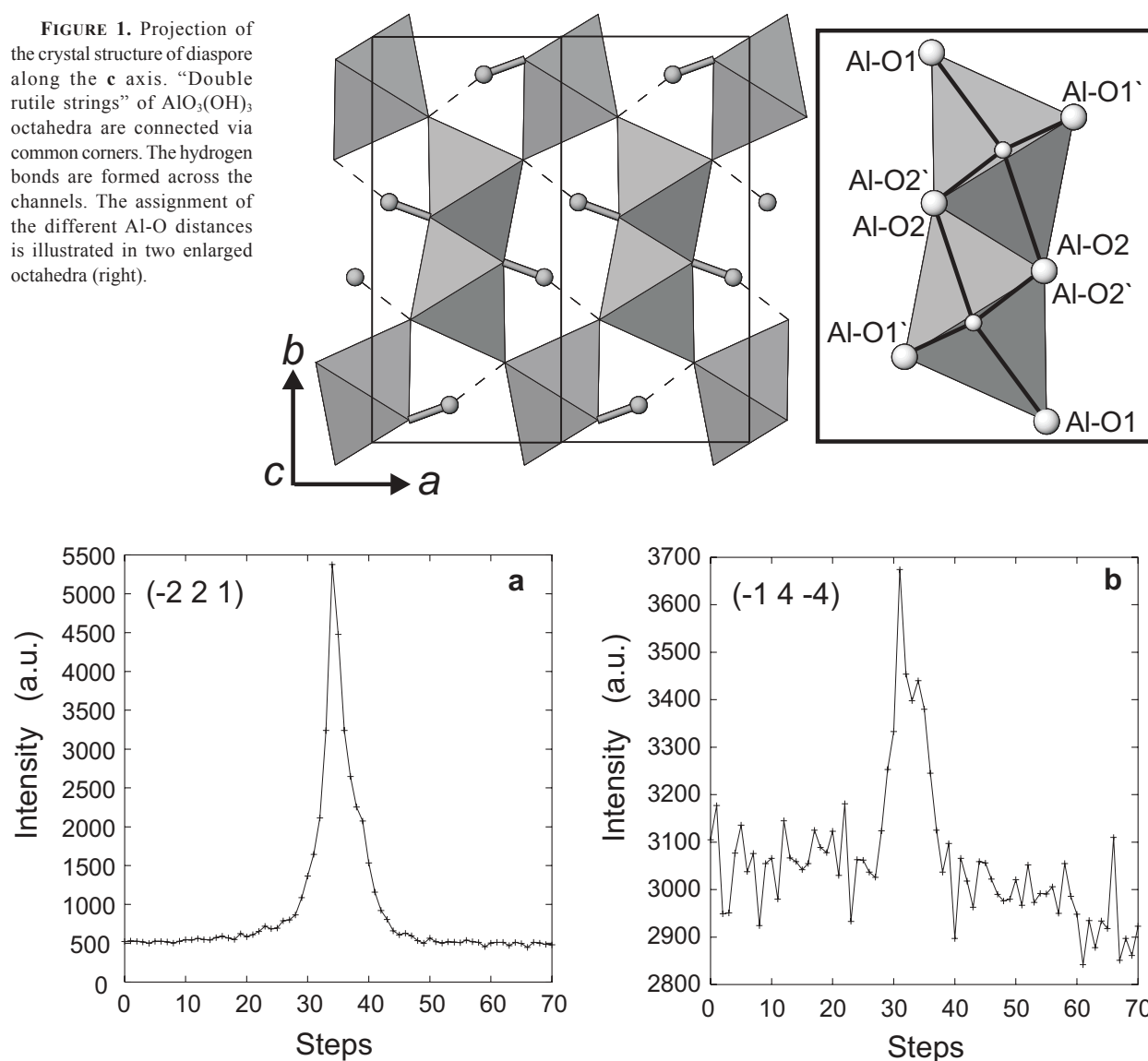


FIGURE 2. ω -scan profiles ($0.015^\circ/\text{step}$) of (a) a strong reflection (5 s/step scan time) and (b) a weak reflection (40 s/step scan time) of diaspore at 50 GPa.

pressure medium. Consequently, and due to the good quality of the crystal, we observed sharp single-crystal peak profiles (Fig. 2a). Based on the measurement of several ruby fragments distributed in the pressure chamber using the ruby fluorescence technique (Mao et al. 1978), we could demonstrate a constant pressure throughout the pressure chamber within experimental error of approximately 0.2 GPa. The pressure was measured several times before and after the data collection and relaxed continuously from the loading pressure of 51.5 GPa down to 48.3 GPa within several weeks.

In situ high-pressure single-crystal synchrotron X-ray diffraction was performed at the bending-magnet beamline D3 at HASYLAB (Hamburg, Germany). Unit-cell parameters and intensity data were collected on a HUBER four-circle diffractometer using a NaI point detector and a wavelength of 0.4 Å, provided by a Si(111) double-crystal monochromator. The intensity measurements were carried out with ω -scans according to the fixed- ϕ technique (Finger and King 1978), to select the beam path of least attenuation through the pressure cell. All accessible reflections within half a Ewald sphere and at $\phi = 0^\circ$ were collected in ω -scan-mode up to $2\theta \approx 37.8^\circ$. Due to the small single-crystal size and the weak X-ray scattering power of the elements present the scan time of a reflection was up to 47 min (Fig. 2b). As we measured only few symmetry-forbidden reflections with relatively short scan time (6 min), the confidence with which we can rule out the change of reflection conditions, e.g., due to the formation of a superstructure, is limited. Experimental details, scan parameters, and crystal data are summarized in Table 1.

Intensity data were obtained from the scan data by the Lehmann-Larsen algorithm and corrected for Lorentz and polarization effects using the beamline-adopted software REDUCE (Eichhorn 1987). The absorption of the X-ray beam by the sample and the diamond anvils was corrected with the program ABSORB, version 6.0 (Angel 2004). Structure refinements were carried out with SHELXL97-2 (Sheldrick 1997). The starting parameters for the refinements were taken from the high-pressure refinement at 7 GPa published by Friedrich et al. (2007). The final refinements of the high-pressure data sets were carried out with isotropic displacement parameters for Al and O, while H was excluded from the refinement.

TABLE 1. Crystal data, details of the data collection, and agreement factors for diaspoire, AlO(OH) at 49.3(7) GPa

Crystal data	
<i>a</i> (Å)	4.020(1)
<i>b</i> (Å)	8.896(6)
<i>c</i> (Å)	2.6653(7)
<i>V</i> (Å ³)	95.32(8)
Z (formula units)	4
Molecular weight (g/mol)	59.99
F(000) (e ⁻)	120
Density (g·cm ⁻³)	4.169
Linear abs. coeff. (mm ⁻¹)	0.18
Data collection	
Facility, beamline	HASYLAB, D3
Instrument	HUBER four-circle diffractometer
Monitor	Polarimeter
E (keV); λ (Å)	30.9954; 0.4
$\sin\theta/\lambda_{\max}$ (Å ⁻¹)	0.8102
Scan mode	ω scan (continuous)
Steps	71
$\Delta\omega$ (°); Time per step (s)	0.015; 5–40
Standards	$\bar{2} \bar{2} 1, 0 0 2$ every 60–600 min
<i>h</i>	$\bar{6}; 6$
<i>k</i>	$\bar{3}; 6$
<i>l</i>	$\bar{4}; 3$
Refinement results	
R_{int} (F ²)	0.08(6)
Observed reflections	231
Unique reflections	76
Reflections with $I > 4\sigma(I)$	60
Parameters	10
R_1 ; $ I > 4\sigma(I)$	0.0476
wR_2	0.0862
Goof	1.197
$\Delta\rho_{\max}$	0.54
$\Delta\rho_{\min}$	-0.54

Notes: For comparison, the cell parameters at ambient pressure are $a = 4.401(1)$ Å, $b = 9.421(4)$ Å, and $c = 2.845(1)$ Å (Busing and Levy 1958). Space group: *Pbnm* (no. 62).

TABLE 2. Results from fits of Birch-Murnaghan equations of state to the experimental (exp.) data including those from Busing and Levy (1958) and Friedrich et al. (2007) in comparison with previously calculated values (DFT) from Friedrich et al. (2007)

	V_0 (Å ³)	B_0 (GPa)	B'
exp. (2 nd order)	117.95(5)	151(2)	4 (fixed)
exp. (3 rd order)	117.97(7)	149(4)	4.1(2)
DFT (2 nd order)	121.06(7)	150.4(9)	4 (fixed)
DFT (3 rd order)	121.20(3)	143.7(9)	4.44(6)
	a_0 (Å)	B_0 (GPa)	B'
exp. (2 nd order)	4.4002(8)	104(2)	4 (fixed)
exp. (3 rd order)	4.401(1)	102(2)	4.2(2)
DFT (3 rd order)	4.4332(5)	107.8(7)	4.14(5)
	b_0 (Å)	B_0 (GPa)	B'
exp. (2 nd order)	9.424(3)	180(6)	6 (fixed)
exp. (3 rd order)	9.421(4)	194(16)	5(1)
DFT (3 rd order)	9.5108(9)	166(2)	6.1(1)
	c_0 (Å)	B_0 (GPa)	B'
exp. (2 nd order)	2.8451(6)	184(3)	3.44 (fixed)
exp. (3 rd order)	2.8448(9)	189(11)	3.2(5)
DFT (3 rd order)	2.8749(1)	174.2(5)	3.44(2)

RESULTS AND DISCUSSION

Stability of diaspoire

The measured unit-cell parameters at 50 GPa unambiguously show that diaspoire does not transform to δ -AlO(OH) under the conditions of our experiment as the unit-cell volume of δ -AlO(OH) is smaller by a factor of two in comparison to diaspoire. Compared to earlier experiments on the high-(*P,T*)-stability, it is now evident that the diaspoire structure can be retained to significantly higher pressures at room temperature.

Our observation can be compared with the results from the quench experiments at elevated temperatures (17 GPa at 1273 K; Suzuki et al. 2000; Ohtani et al. 2001; Sano et al. 2004) and the results from first principles calculations of Li et al. (2006), who proposed the α -to- δ phase transition to occur at much lower pressure of around 18 GPa at 0 K, by assuming that the transition is kinetically hindered at ambient temperature.

This points to a significant influence of temperature, but in the absence of further data obtained in situ at various temperatures, this cannot be quantified. However, it is remarkable that a relatively “open” structure can be pressurized by more than 30 GPa above the transition pressure without showing peak broadening or other indications of the onset of amorphization.

Unit-cell parameters and compressibility

The results of a fit of the present and earlier experimental data (including those from Friedrich et al. 2007 and from Busing and Levy 1958) with second- and third-order Birch-Murnaghan equations of state (BM-EOS) to the pressure-volume data and the pressure dependencies of the individual cell axes are summarized in Table 2. Similar bulk moduli are obtained from fits with a second-order BM-EOS [$B_0 = 151(2)$ GPa] and a third-order BM-EOS [$B_0 = 149(4)$ GPa, $B' = 4.1(2)$], respectively. These values are equal to the previously determined bulk modulus obtained from experimental data up to 7 GPa within one standard deviation [$B_0 = 150(3)$ GPa; Friedrich et al. 2007], and similar to those obtained from computed data up to 40 GPa (Table 2; Friedrich et al. 2007). These results again confirm that diaspoire is much more compressible than its high-pressure phase δ -AlO(OH) [$B_0 = 252(3)$ GPa; Vanpeteghem et al. 2002] and significantly less

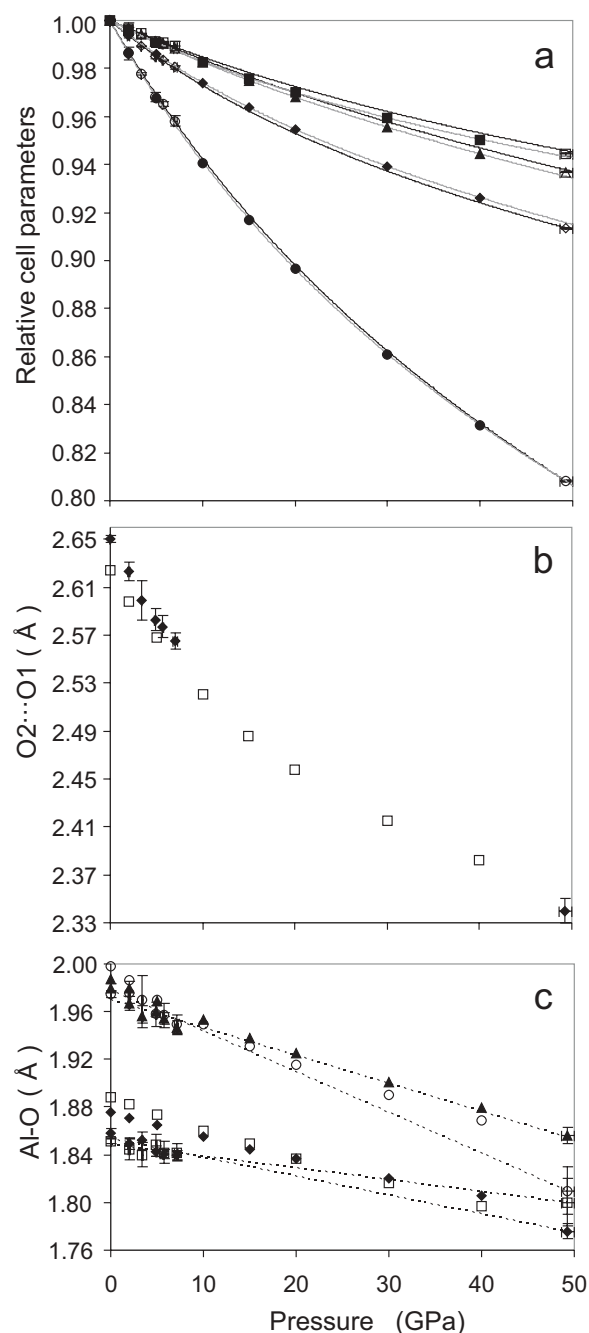


FIGURE 3. (a) Pressure-dependencies of the normalized unit-cell parameters (symbols = V/V_0 : circles; a/a_0 : diamonds; b/b_0 : squares; c/c_0 : triangles) up to 50 GPa. Open symbols with error bars represent experimental data from Friedrich et al. (2007) and this experiment (50 GPa), filled symbols theoretical data (Friedrich et al. 2007). Fits of third-order Birch-Murnaghan equations of state to the experimental and theoretical data are plotted by black and gray lines, respectively. (b) Pressure-dependencies of the donor-acceptor O1...O2 distance of the hydrogen bond from experimental (filled diamonds with error bars) and theoretical data (open squares) and (c) of the Al-O bond distances from experiment (symbols with error bars) and theory. Data were taken from Friedrich et al. (2007) and this study. Symbols = Al-O1: filled diamonds; Al-O1': open squares; Al-O2': filled triangles; Al-O2: open circles. Linear fits to the experimental data are shown as guide to the eyes.

TABLE 3. Atom positions and isotropic displacement parameters (\AA^2) for diaspoire, AlO(OH) at 49.3(7) GPa; $z = 0.25$ for all atoms

Atom	x	y	U_{iso}
Al	0.0293(5)	0.8645(7)	0.0033(5)
O1	0.709(1)	0.194(2)	0.003(1)
O2	0.225(1)	0.047(2)	0.003(1)

TABLE 4. Selected interatomic distances (\AA) and polyhedral volume V (\AA^3) from experimental and theoretical data of diaspoire

P (GPa)	0*	0.0001†	7.1(2)‡	40*	50
Al-O1' $\times 2$	1.876	1.851(2)	1.840(4)	1.806	1.776(6)
Al-O1	1.888	1.858(4)	1.842(7)	1.797	1.80(2)
Al-O2' $\times 2$	1.987	1.975(3)	1.947(5)	1.880	1.856(7)
Al-O2	1.998	1.980(3)	1.949(8)	1.869	1.81(2)
OQE§	1.020	1.020(4)	1.018(6)	1.009	1.008(12)
V	9.392	9.10(1)	8.83(2)	8.189	7.84(4)
O1...O2	2.624	2.650(3)	2.565(7)	2.382	2.34(1)

* Theoretical data as obtained from density functional theory based model calculations.

† Ambient pressure; data were taken from Busing and Levy (1958).

‡ Experimental high-pressure data taken from Friedrich et al. (2007).

§ The octahedral quadratic elongation (OQE) values were calculated using the VOLCAL program (Finger 1971), following the method of Robinson et al. (1971).

compressible than isostructural goethite, FeO(OH) [$B_0 = 111(2)$ GPa; Nagai et al. 2003]. The new data reported here should therefore end the controversial discussion of the bulk modulus of diaspoire (see Winkler et al. 2001 and Friedrich et al. 2007).

In Figure 3a, the unit-cell parameters obtained at 50 GPa are included with the data reported by Friedrich et al. (2007). Our data at 50 GPa show that the anisotropy of the linear compressibilities of diaspoire extends to this pressure, with the a axis being much more compressible than the b and c axes (Fig. 3a). While the compressibilities of the b and c axes are nearly equal in the low-pressure range (Fig. 3a) as confirmed by the similar values of B_0 , the pressure derivatives of B are significantly different when including the 50 GPa data. This is consistent with previous DFT computations (Friedrich et al. 2007), which had predicted that the b axis becomes increasingly more incompressible than the c axis between 10 and 50 GPa.

Compression of the crystal structure

Experimentally determined atom positions and isotropic displacement factors are given in Table 3, while interatomic distances and polyhedral volumes are listed in Table 4. As discussed in Friedrich et al. (2007) the compression of the crystal structure proceeds mainly by bond shortening and particularly by compression of the hydrogen bond. While at low pressures two longer Al-O2 distances (with O2 being the hydrogen bond donor) are distinguished from two shorter Al-O1 distances (with O1 being the hydrogen bond acceptor) in the $\text{AlO}_3(\text{OH})_2$ octahedron, the crystal structure refinement at 50 GPa shows that the Al-O2 distance becomes similar to the Al-O1 and Al-O1' distances, and only the Al-O2' bonds remain longer. There are some slight differences between the experimental and theoretical results, in that the theoretical value for the Al-O2 bond is larger than the experimental value by about 0.06 Å (Table 4, Fig. 3c). However, further experimental data at intermediate pressures are required before the significance of this discrepancy can be evaluated. Not all of the hydrogenated and non-hydrogenated Al-O distances become similar with increasing pressure and therefore a complete symmetrization of the hydrogen bond does not occur. While it

is experimentally very challenging to determine the hydrogen position unambiguously, the refined O···O distance of 2.34(1) Å (Table 4, Fig. 3b) is in reasonable agreement with the trend from the theoretical data, where the compressibility of the hydrogen bond derived from the experiment is slightly larger than that obtained from theory (Winkler et al. 2001; Friedrich et al. 2007). An extrapolation of the experimental O···O distances to higher pressures implies that a symmetrization of the hydrogen bond is unlikely to occur below 110 GPa.

The observed pressure-dependent behavior of the intra- and inter-octahedral angles of the $\text{AlO}_3(\text{OH})_2$ octahedron confirms the structural compression computed using DFT (Friedrich et al. 2007). We also found a straightening of the O1-Al-O2 octahedral-axis angle from 162.2(2)° (Busing and Levy 1958) to 171.9(9)° at 50 GPa, which is in agreement with the low compressibility of the **b** axis.

The fit of a third-order Birch-Murnaghan equation of state to the pressure-dependence of the octahedral volume results in the octahedral bulk modulus $B_0(\text{AlO}_6) = 222(21)$ GPa and its pressure derivative $B' = 5.3(1.5)$ at $V_0 = 9.10(1)$ Å³. This value is equal to that obtained from computed data [$B_0 = 213.1(9)$ GPa, Friedrich et al. 2007] within error, and much higher than the overall bulk modulus of $B_0 = 143.7(9)$ GPa (Table 2). This confirms the conclusions drawn earlier (Xu et al. 1994; Winkler et al. 2001; Nagai et al. 2003; Friedrich et al. 2007) namely that the structural compression is mainly due to the compression of the hydrogen-containing channels, as derived from the strong decrease of the O1···O2 donor-acceptor distance (Fig. 3b, Table 4). This in turn causes the high compressibility of the **a** axis.

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