Supplementary Information
Emergent hydrogen bonding in dense LiOD

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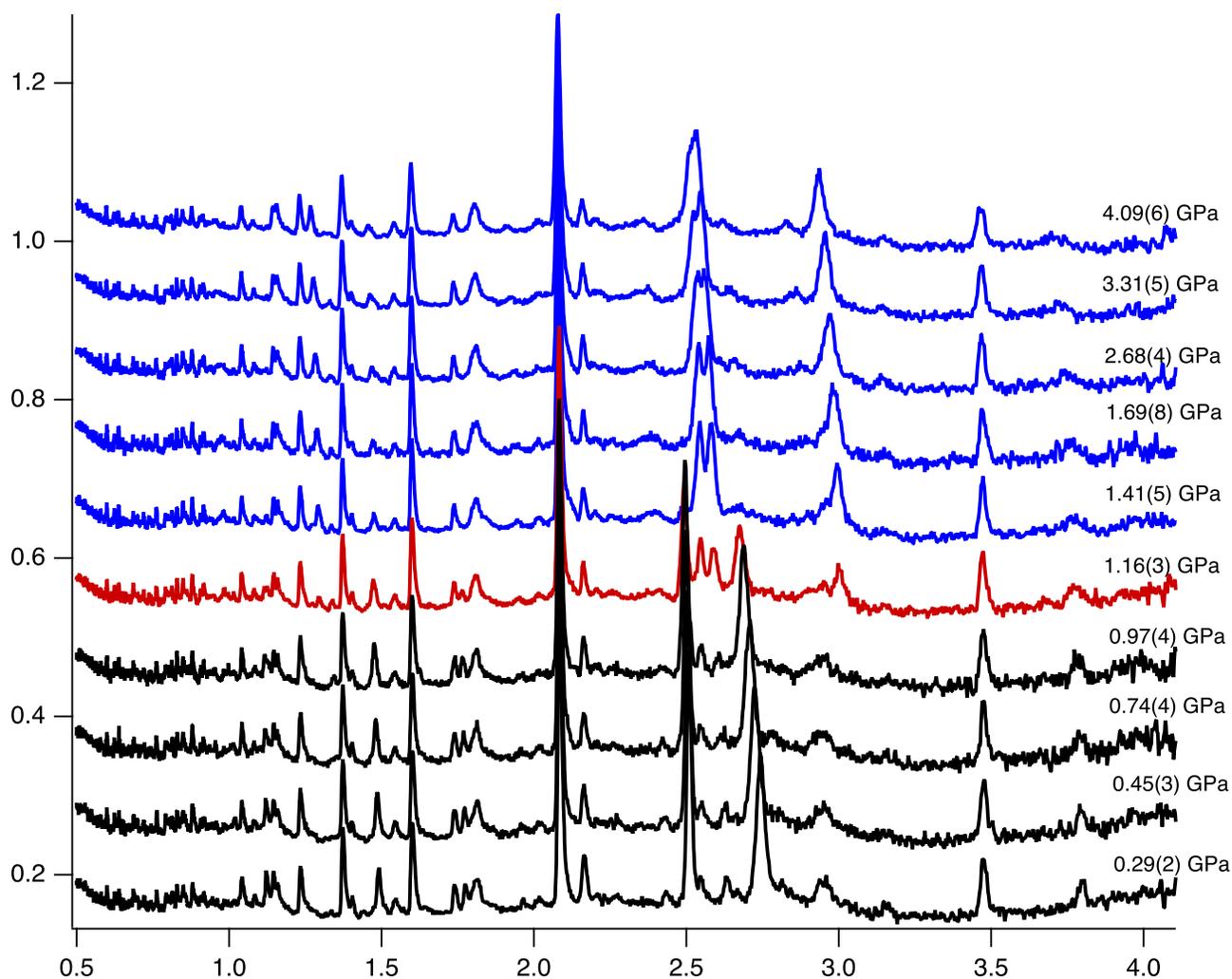
(Dated: December 2, 2021)

FIG. S1. High pressure data from LiOD collected on the PEARL diffractometer. Pressures, determined from the equation of state of the Li_2CO_3, are indicated above each profile. From bottom to top, pure phase-II data are shown in black (up to 0.97 GPa), mixed phase in red (1.16 GPa), and pure phase-III in blue (up to 4.09 GPa) (colour online).
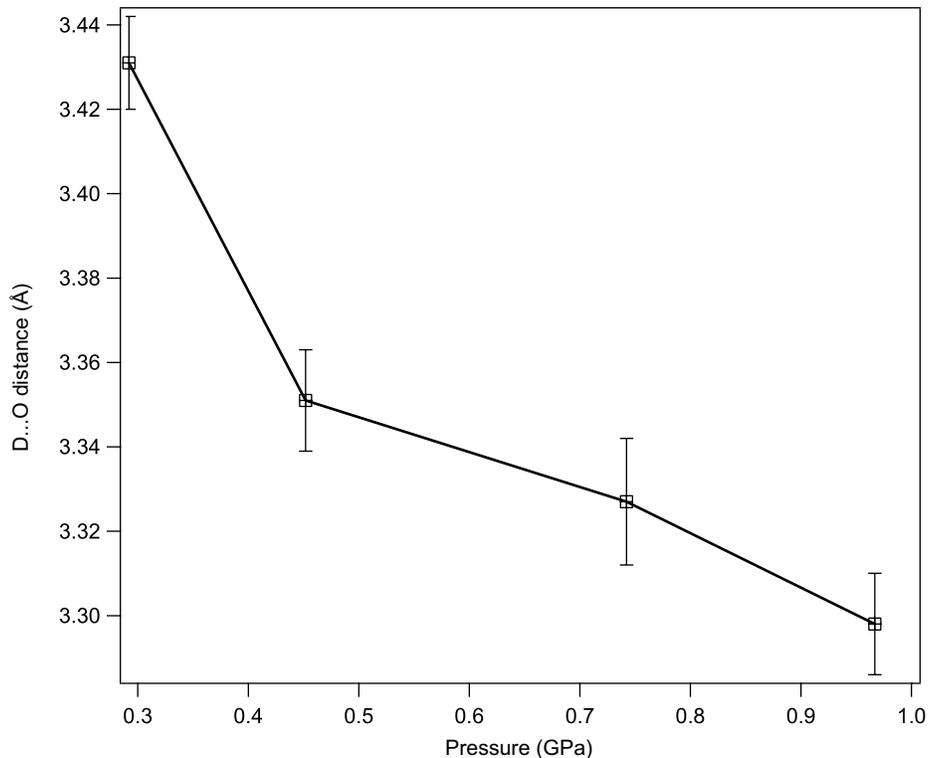
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FIG. S2. Variation in D⋯O separation as a function of pressure in phase-II of LiOD.

Strain calculation

The pseudo cubic axis length can be defined as $a_o = \sqrt[3]{a^2 c}$, from the tetragonal lattice parameters (a, c) in each phase. Where the axes between the pseudo-cubic and tetragonal cells are defined to be orthogonal, the two principal strains are then defined as, $\epsilon_1 = {}^a/a_o - 1$ and $\epsilon_3 = {}^c/a_o - 1$, and the total spontaneous strain can then be calculated as, $\epsilon_s = \sqrt{\epsilon_1^2 + \epsilon_3^2}$. The volumetric strain may be calculated similarly as ${}^V/a_o^3 - 1$.

Crystallographic data

TABLE S1. Crystallographic data for the 300 K compression of phase-II of LiOD determined from Rietveld analysis of the PEARL neutron powder diffraction data. All refinements are performed using the $P4/nmm$ tetragonal space-group with Li: Wyckoff 2a ($^3/_4$, $^1/_4$, 0), O and D: Wyckoff 2c ($^1/_4$, $^1/_4$, z). The atomic coordinates were not refined for the 1.16(3) GPa mixed phase pressure point, due to instability, and are therefore omitted.

Pressure (GPa)	0.29(2)	0.45(3)	0.74(4)	0.97(4)	1.16(3)
a–axis (Å)	3.5435(3)	3.53731(12)	3.53097(14)	3.5245(2)	3.5207(2)
c–axis (Å)	4.3211(7)	4.2578(8)	4.2011(9)	4.1437(9)	4.10204
V_{cell} (Å^3)	54.257(11)	53.276(10)	52.378(12)	51.472(12)	50.845(14)
Oz	0.191(2)	0.184(2)	0.201(3)	0.206(2)	-
Dz	0.397(2)	0.397(2)	0.409(2)	0.410(2)	-

TABLE S2. Crystallographic data for the 300 K compression of phase-III of LiOD determined from Rietveld analysis of the PEARL neutron powder diffraction data. All refinements performed using the $I4/_1acd$ tetragonal space-group with Li: Wyckoff 8a (0, $^1/_4$, $^3/_8$), and Wyckoff 8b (0, $^1/_4$, $^1/_8$), O and D: Wyckoff 16e (x, 0, $^1/_4$). The atomic coordinates were not refined for the 1.16(3) GPa mixed phase pressure point, due to instability, and are therefore omitted.

Pressure (GPa)	1.16(3)	1.41(5)	1.69(8)	2.68(4)	3.31(5)	4.09(6)
a–axis (Å)	5.9988(9)	5.9831(7)	5.9616(7)	5.9334(6)	5.9011(6)	5.8547(6)
c–axis (Å)	10.161(2)	10.14925(13)	10.13193(14)	10.09916(13)	10.06056(12)	10.0161(2)
V_{cell} (Å^3)	365.65(11)	363.32(8)	360.09(8)	355.54(7)	350.33(6)	343.32(7)
Ox	-	0.508(2)	0.510(2)	0.5109(13)	0.5102(12)	0.5131(12)
Dx	-	0.8209(12)	0.821(2)	0.8274(12)	0.8254(12)	0.8218(14)

Equation of state

A second order Birch-Murnaghan equation of state was fitted to the pressure-volume data for phase-II and -III, where V_0 is the unit-cell volume at zero pressure, and K$_0$ is the bulk modulus:

$$P = \frac{3}{2}K_0\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]$$
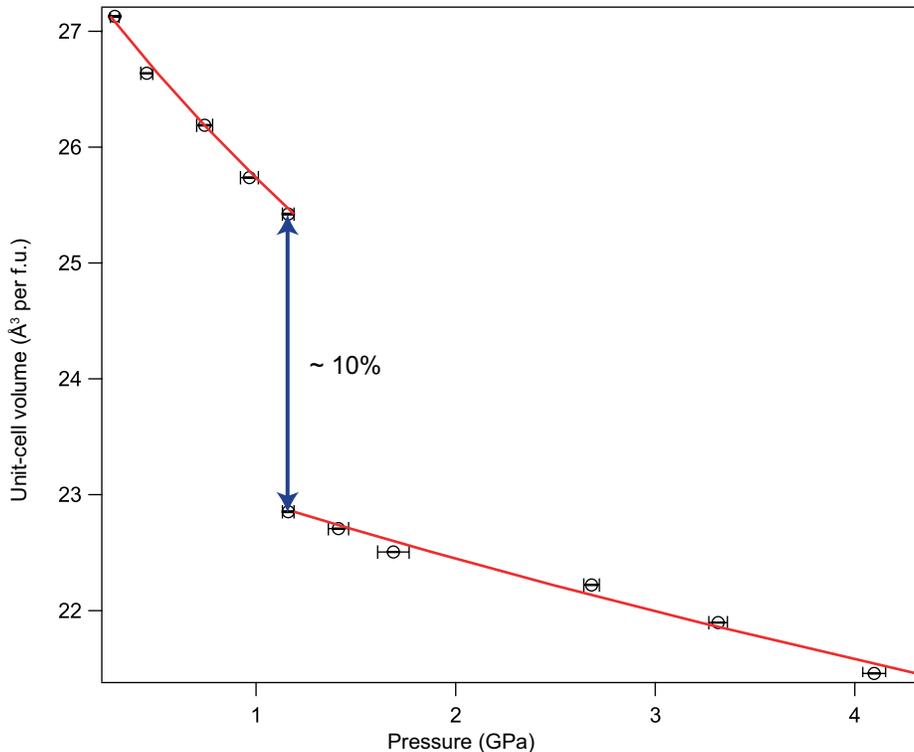

FIG. S3. Unit-cell volume (per formula-unit) vs. pressure for phase-II and phase-III of LiOD. A second-order Birch-Murnaghan equation of state was fitted to each phase, the parameters of which are provided in the main manuscript, and are shown as red lines over the data points.

Hydrogen bonding networks

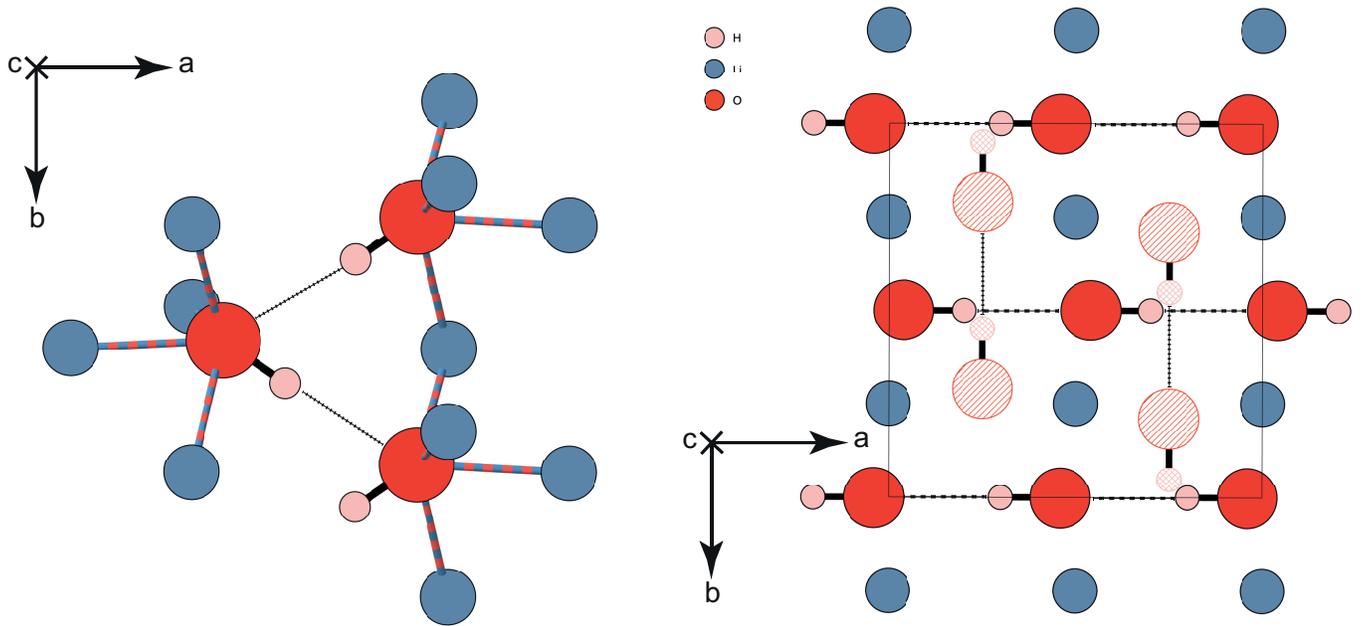FIG. S4. Hydrogen bonding networks for (left) the monoclinic ($P2_1/c$) structure of LiOD based on the low temperature structure of NaOD and (right) the tetragonal ($I4_1/acd$) structure, with the Li-O bonds omitted for clarity. Dashed lines represent hydrogen bonds in each case. The monoclinic structure forms zig-zag chains along the b-axis, forming a canted antiferroelectric-type arrangement between lines of oxygen atoms. The tetragonal ($I4_1/acd$) structure forms linear hydrogen bonds along the a- and b-axes, alternating between planes along the c-axis. The ordering is antiferroelectric like.