Structural independence of hydrogen-bond symmetrisation dynamics at extreme pressure conditions

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The experimental study of hydrogen-bonds and their symmetrization under extreme conditions is predominantly driven by diffraction methods, despite challenges of localising or probing the hydrogen subsystems directly. Until recently, H-bond symmetrization has been addressed in terms of either nuclear quantum effects, spin crossovers or direct structural transitions; often leading to contradictory interpretations when combined. Here, we present high-resolution in-situ 1H-NMR experiments in diamond anvil cells investigating a range of systems containing linear O-H⋯O units at pressure ranges of up to 90 GPa covering their respective H-bond symmetrization. We found pronounced minima in the pressure dependence of the NMR resonance line-widths associated with a maximum in hydrogen mobility, precursor to a localisation of hydrogen atoms. These minima, independent of the chemical environment of the O-H⋯O unit, can be found in a narrow range of oxygen oxygen distances between 2.44 and 2.45 Å, leading to an average critical oxygen-oxygen distance of \( r_{\text{crit}}^{\text{OO}} = 2.443(1) \) Å.
Understanding the stability and properties of hydrous minerals, possibly contributing to hydrogen transport to the lower mantle is crucial as key properties of the constituents of Earth’s mantle, e.g., melting temperatures, rheology, electrical conductivity and atomic diffusivity\(^3\)-\(^5\) can be strongly affected by the presence of even small amounts of hydrogen. In particular, the high-pressure (\(P\)) phases of \(H_2O\) ice, \((Al,Fe)OOH\) and dense hydrous magnesium silicates are important candidates for hosting large amounts of hydrogen\(^6\). These phases have a common O-H-O sequence, with an asymmetric hydrogen-bond (O-H⋯O) at low compression, which symmetrizes under increasing \(P\) (O-H-O).

During the symmetrization, compressional (e.g. bulk modulus) as well as transport properties undergo significant modifications, but although the common O-H-O sequence endorses the conclusion that the phases should show very similar behaviour, significantly distinct characteristics are observed, e.g. (i) the symmetrization \(P\) has a great variation, e.g. \(\pm120\) GPa in ice-VII\(^7\)-\(^9\) compared to \(\pm15\) GPa in \(\delta\)-\(AlOOH\)\(^10\)-\(^12\), (ii) proton tunnelling dominates the transition in ice-VII\(^7\),\(^8\),\(^13\)-\(^15\), but is absent in \(\delta\)-\(AlOOH\)\(^10\), (iii) The bulk modulus in ice-VII\(^8\),\(^16\),\(^17\) shows a noticeable softening, while only a minor effect is found in \(\delta\)-\(AlOOH\)\(^11\).

In order to shed light on the underlying mechanisms it is essential to gain a deeper understanding of the similarities and disparities between different oxide-hydroxide phases with respect to the hydrogen-bond symmetrization. Hydrogen atoms, however, have a very low X-ray cross-section and neutron techniques are typically unavailable at \(P \geq 25\) GPa, therefore knowledge about the hydrogen subsystem is widely limited to computational and optical studies (e.g. Raman or Infrared). Advances in high-\(P\) nuclear magnetic resonance spectroscopy in recent years\(^16\)-\(^20\) allow for a direct investigation of the hydrogen subsystem (Fig. 1) beyond the megabar-range and enables previously unattainable experimental insight.

Here, we present in-situ high-\(P\)\(^1\)\(H\)-NMR data on four hydrous mineral phases: (i) dense magnesium silicate phase-D with composition (\(Mg_{0.88},Fe_{0.12}\))(\(Si_{0.9},Al_{0.1})_2O_6H_2\), (ii) pure and (iii) iron-bearing aluminum oxide-hydroxide (\(\delta-(Al_{0.3},Fe_{0.7})OOH\)) as well as (iv) \(H_2O\) ice-VII/X. Under compression, we find a distinct maximum in hydrogen mobility in all sampled systems at the same critical O-H-O in-bond oxygen-oxygen distance (\(r_{\text{crit}}\)). Being a precursor for H-bond symmetrization and under further compression localisation, this minimum was found to solely depend on the short-range local structure, i.e. \(r_{\text{crit}}\) is independent of the nature of the further chemical surrounding, marking \(r_{\text{crit}}\) as an unifying parameter of pressure-induced hydrogen-bond symmetrization dynamics.

**Results and discussion**

We use the equation of state (EOS) parameters (Fig. 2a) for \(\delta\)-\(AlOOH\) (\(V_0 = 56\ \text{Å}^3, K_0 = 183\ \text{GPa}, K' = 3.7\)) from\(^21\), \(\delta-(Al_{0.3},Fe_{0.7})OOH\) (\(V_0 = 63.71\ \text{Å}^3, K_0 = 164.7\ \text{GPa}, K' = 4.04\)) and \(\delta\)-\(FeOOH\) (\(V_0 = 84.73\ \text{Å}^3, K_0 = 162\ \text{GPa}, K' = 4\)) are determined from synchrotron X-ray diffraction (XRD, see Methods section). For \(H_2O\) ice-VII/X we use the global EOS by\(^22\), based on DFT calculations, which was found to be in excellent agreement with recent dynamical diamond anvil cell XRD experiments\(^8\). The volume collapse in iron bearing oxide-hydroxide at \(P = 45\) GPa originates from the \(S = 5/2\) high spin to \(S = 1/2\) low spin transition of ferric iron\(^23\),\(^24\). Analogous transitions in dense magnesium silicate phase-D are not observable in our XRD data due to the low concentration of iron, but distinct transitions can be found in synchrotron Mössbauer spectroscopy (SMS) (see Methods section).

In order to quantify the evolution of hydrogen NMR signals with respect to the local symmetry under compression, we calculate oxygen-oxygen distances in the H-bonds (\(r_{\text{O-O}}\), using both diffraction data (for \(\delta-(Al,Fe)OOH\)\(^21\) and phase-D) as well as DFT calculations for high-\(P\) ice-VII/X\(^22\). As shown recently in ref.\(^20\), the hydrogen-bond manifold in \(\delta-(Al_{0.3},Fe_{0.7})OOH\) can be resolved and the observed signals assigned to different local environments, \(Q^i\) (\(i = 1-6\)) where the fraction \(i\) of 6 possible next-nearest-neighbour positions around the hydrogen-bond (Fig. 1) is occupied by ferric iron paramagnetic centres. We deduce the \(P\) dependence of \(r_{\text{O-O}}\) in \(\delta-(Al_{0.3},Fe_{0.7})OOH\) by interpolating between the endmember \(\delta\)-\(AlOOH\)\(^10\),\(^21\) and \(\epsilon\)-\(FeOOH\)\(^25\) with respect to the local iron content around the hydrogen nearest-neighbours (Fig. 1). We neglect the volume collapse due to the spin transition in iron bearing phases as is at significantly higher \(P\) than the hydrogen-bond symmetrization.

We performed high-resolution \(^1\)\(H\)-Lee Goldburg (LG) NMR measurements\(^26\) for \(\delta-(Al_{0.3},Fe_{0.7})OOH\) and \(Mg_{0.88},Fe_{0.12})(Si_{0.9},Al_{0.1})_2O_6H_2\) phase-D in order to investigate the influence of different next-nearest-neighbour configurations (Figure 1) and recorded \(^1\)\(H\)-NMR solid echo for pure \(\delta\)-\(AlOOH\) as well as \(H_2O\) ice-VII/X.

The electronic environment of the hydrogen nuclei should, to first approximation, be determined by their nearest-neighbours, i.e. the oxygen atoms involved in the hydrogen-bonds.\(^27\) Presence of paramagnetic centres among the next-nearest-neighbours, such as in phase-D or \(\delta-(Al_{0.3},Fe_{0.7})OOH\), induces additional contributions to NMR resonance shifts and relaxation times\(^28\). These should not significantly influence dynamical effects, but instead lead to a modulation of the energy landscape of H-bonds in these systems\(^29\) and therefore a separation of the signals in the indirect LG-projection frequency domain \(F_2\) is observable.

Figure 3a shows a high-resolution \(^1\)\(H\)-LG NMR spectrum of \(\delta-(Al_{0.3},Fe_{0.7})OOH\) at 15.7 GPa. As recently shown\(^30\), the 2D-LG spectrum can be separated in six different regions. Under the

**Fig. 1 Structure of hydrogen-bond environments.** Schematic representation of the local hydrogen-bond environments with the hydrogen atom at the center. The energy potential of the H-bond (green graph) is determined predominantly by the nearest-neighbour atoms (e.g. oxygen atoms). Depending on initial O-O distances, hydrogen probability distributions, \(|\Psi(x)|^2\), (purple schematic graph) may exhibit uni- or bimodal characteristics. Shown here is a typical broad energy potential without barrier, leading to an uni-modal probability distribution and thermally activated hydrogen mobility. Next-nearest-neighbours may constitute metal anions, e.g., in hydrous minerals, or other hydrogen atoms in \(H_2O\) ice-VII/X.
Fig. 2 Structural data of investigated systems. a Equation of state (EOS) data of the different hydrogen-bonded phases. We use the EOS for H$_2$O ice-VII/X (gray graphs) of from$^{22}$, based on ab-initio computations and the XRD based EOS of$^{21}$ for δ-AlOOH (green graphs). The other curves are based on third order Birch-Murnaghan EOS fits to our diffraction data for iron-bearing δ-AlOOH (brown graphs) and phase-D (blue graphs). δ-(Al$_{0.3}$Fe$_{0.7}$)OOH exhibits a 7% volume collapse associated to the electron spin crossover of ferric iron (c.f. Fig. 4a). b Oxygen-oxygen distance ($r_{OO}$) as a function of $P$. Different pressure dependencies of the $Q_i$ ($i = 3, 5, 6$) (red, brown and yellow graphs respectively) H-bond environments in δ-(Al,Fe)OOH$_20$ were estimated through interpolation of $r_{OO}$ between endmembers δ-AlOOH$_{10, 21}$ and ϵ-FeOOH$_{25}$ with respect to the local iron content. We only consider the high spin state in iron bearing phases, as the spin transition occurs at significantly higher $P$ (~45 GPa) than the hydrogen-bond symmetrization (~15 GPa).

Fig. 3 $^1$H-NMR spectra of all sample systems. a High-resolution 2D-Lee Goldburg (LG) spectrum of δ-(Al$_{0.3}$Fe$_{0.7}$)OOH at 15.7 GPa showing up to six distinguishable hydrogen signals in the indirect LG projection $F_2$. Assuming a stochastic distribution of ferric iron in the sample, a comparison with signal intensities allows for the assignment of the H-bond species $Q_i$ ($i = 1$–$6$). Spectra at different pressures were recorded at reduced resolution due to experimental time restrictions and solely signals from $Q_3$, $Q_5$ and $Q_6$ species were recorded over the full pressure range. The integration limits for 2D signal intensity determination were defined by 35 kHz in the direct time domain $F_1$ and by the FWHM of each signal in the indirect LG-projection dimension $F_2$. The colored regions are guide to the eyes and do not correspond to the integration limits. $^1$H-NMR solid-echos of b δ-AlOOH and c H$_2$O ice-VII/X as a function of pressure. Measurements were conducted at a magnetic field of 1.2 T. Figures a and b are reproduced from ref.$^{20}$; licensed under a Creative Commons Attribution (CC BY) license.
assumption of a stochastic distribution of ferric iron, several different H-bond environments should be present in the sample due to a modulation of the local magnetic fields at the hydrogen atoms caused by the paramagnetic centers. We associated these different regions to the different next-nearest neighbour surroundings ($Q^3$), by matching the relative size of the regions, i.e. the 2D-signal intensities, with the probability distribution of finding a local surrounding with $i$ of 6 possible positions being occupied by iron atoms. For further details of the signal assignment in $\delta$-(Al$_{0.3}$Fe$_{0.7}$)OOH (c.f.20). Signals associated to fully Fe$^{3+}$ depleted H-bond environments ($Q^0$) lie below the detection limit of our experiments. Interestingly, the signal associated to four ferric iron paramagnetic centres occupying next-nearest neighbour positions ($Q^4$) was found to be much broader than to the other H-bond environments, possibly due to significant gradients in the local magnetic field stemming from an asymmetric distributions of paramagnetic centres, further hyperfine interactions or signal overlap28. The spectrum shown in Fig. 3a was recorded by oversampling in the indirect Lee-Goldburg dimension $F_2$, other spectra were recorded using faster $F_2$ sampling and therefore reduced resolution due to experimental time restrictions and solely intense signals $Q^3$, $Q^5$ and $Q^6$ were recorded over the full pressure (see Methods section).

At ambient conditions, the resonance frequencies of these signals were found to be $\omega - \omega_0 = 80, 365$ and 506 ppm for $Q^3$, $Q^5$ and $Q^6$, respectively (Fig. 4a). The origin of such a pronounced proton resonance shift can reasonably be expected to be the effect of the hydrogen nuclei with localised electron moments of Fe$^{3+}$ ions, which should be modulated at the electron spin crossover around $V/V_0 \approx 0.85$ to 0.80. Indeed, we find a significant reduction in resonance frequency of all three signals at $V/V_0 \leq 0.78$, in excellent agreement with Mössbauer spectroscopy (see Methods section), evidencing the paramagnetic origin of these signals. Additionally, we observe a discontinuity in resonance shift at a relative compression of $V/V_0 = 0.94$ (Fig. 4a) in all $Q^i$ and therefore independent of the local iron content, which we associate with the sub- to super-group phase transition from $P_2_1 nm$ to $Pnm$ at $P \approx 10$ GPa10,21,30.

$^1$H-NMR signals of dense magnesium silicate phase-D (Fig. 3b) show a narrow resonance in the indirect LG-projection frequency domain $F_2$, indicating a well defined coordination of hydrogen atoms. The observed frequency shift of the signals (Fig. 4a) towards lower ppm values coincides with the electron spin crossover of ferric iron Fe$^{3+}$ in $\delta$-(Al$_{0.3}$Fe$_{0.7}$)OOH. Therefore, we assume the observed signals to stem from hydrogen atoms predominantly influenced by the presence of Fe$^{3+}$ ferric iron in phase-D. Signals shifted by the presence of Fe$^{2+}$ ferrous iron (see Methods section) were not observed in the chosen spectral range.

One-dimensional solid echo NMR spectra of pure $\delta$-AIOOH (Fig. 3c) at 1.2 T show a single signal at $\omega - \omega_0 = 0$ ppm close to the anticipated position of ferric iron depleted $Q^i$ species in the iron bearing oxide-hydroxide analogue, indicating a well defined hydrogen position in agreement with earlier NMR studies under.

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**Fig. 4 Resonance shift and FWHM line widths.**

a) Top panel: Resonance shift found in $^1$H-NMR solid echos of H$_2$O ice VII/X (gray). The resonance shift of the resonances follows the dependence previously reported at high magnetic fields13, after an initial decrease up to 20 GPa ($V/V_0 \approx 0.68$), the signals are shifted downfield corresponding to the transition from a high to low barrier hydroge- bond regime. The second jump at 73 GPa ($V/V_0 \approx 0.52$) signifies the onset of the ice-VII $\rightarrow$ X crossover. Lower panel: Resonance shift of $\delta$-AIOOH (green), $\delta$(Al,Fe)OOH (red, brown and yellow corresponding to $Q^i$ (i = 1...3) respectively) and phase-D (blue) as a function of the relative volume. Both $\delta$-AIOOH and $\delta$– (Al$_{0.3}$Fe$_{0.7}$)OOH undergo a super to subphase transition from $P2_1 nm$ to $Pnm$ which was observed at $V/V_0 \approx 0.94$ by a sudden increase of the shift by about 5–10 ppm. Between $V/V_0 \approx 0.83$ – 0.78, both iron bearing $\delta$– (Al$_{0.3}$Fe$_{0.7}$)OOH as well as phase-D undergo an electron spin crossover, resulting in a partial reduction of the paramagnetic shift interaction as well as a volume collapse observed in $Q^3$, $Q^5$ and $Q^6$. The red arrows mark the points of maximum hydrogen mobility. Error bars, center of gravity of resonance signals, are within symbol size.

b) Normalized FWHM line widths (same color code as in a), i.e. along $F_1$ for the 2D-LG NMR spectra and in the direct frequency domain for the one dimensional spectra, as a function of $Q_{OO}$. All investigated systems go through a maximum of proton mobility (shaded area in the graph), i.e. motional narrowing of resonance lines and a consequent minimum of FWHM line widths at critical oxygen-oxygen distances between $r_{OO}^{max} = 2.44$ and 2.45, with an average value of $r_{OO}^{max} = 2.443(1)$ Å. Error bars stem from fitting of FWHM linewidths using Voigtian lineshapes.
ambient conditions. Similar to $\delta(\text{Al}_{0.3},\text{Fe}_{0.7})\text{OOH}$, we associate the discontinuity at $V/V_0 = 0.94$ (Fig. 4a) to the aforementioned sub- to super-group phase transition.

Earlier high-resolution $^1$H-LG NMR experiments on $\delta$-AlOOH at similar magnetic fields and pressures indicated that the observed signals are comprised of only a single spectral contribution influenced by a minor chemical shift anisotropy. Influences of smaller pressure gradients might influence the shape of the presented spectra, but are expected to be marginal due to the Argon pressure transmitting medium used to ensure quasi-hydrostatic conditions. Figure 3d shows representative $^1$H-NMR spectra of $\text{H}_2\text{O}$ ice-VII/X recorded at 1.2 T. We observe two distinct transitions in the $P$ dependence of the resonance frequencies (Fig. 4a): (i) At $V/V_0 = 0.66$ (20 GPa), after a continuous shift of about $40$ ppm up-field, the proton signals showed a sudden discontinuity of $\approx$55 ppm, indicating the transition from the high to low barrier hydrogen-bond regime in ice-VII, where the number of tunnelling protons is increasing and (ii) at $V/V_0 = 0.51$ (73 Gpa) a discontinuity of $\approx$20 ppm associated with the beginning of the continuous transition from ice-VII to ice-X. This behaviour is in excellent agreement with our previous study.

In order to find a common parameter indicating the onset of the hydrogen-bond symmetrization, we calculate the full width at half maximum (FWHM) line-widths as a function of $P$ as well as relative compression ($V/V_0$). We analyse the change in line-width as an indicator for changes in proton mobility. The small sample sizes (10 pl) are required for our high-pressure experiments, very long data acquisition times are necessary which prohibits an analysis of other NMR parameters, such as spin-spin or spin-lattice relaxation times which would provide an even more detailed picture of hydrogen dynamics. We find a minimum in the $^1$H-NMR FWHM line-widths in all signals. These minima occur within a wide compression range, i.e. $V/V_0 \approx 0.92$ to 0.55 (red arrows in Fig. 4a), corresponding to $P$ between 11 to 50 GPa. We furthermore calculate the FWHM as a function of the respective oxygen-oxygen distances ($r_{OO}$) for all four compounds, resolving different local environments ($Q^i$) in $\delta-(\text{Al}_{0.3},\text{Fe}_{0.7})\text{OOH}$ (Fig. 4b). Surprisingly, all signals were found to have a continuous transition through this pronounced minimum at almost identical O-O distances $r_{crit}^{Q^i} = 2.44$ and 2.45, with an mean value of $r_{crit}^{Q^i}$ of $2.443(1)$ Å. Several possible error sources might lead to a minor modulation of this value, such as insufficient diffraction data above 40 GPa in the electronic low spin state or the interpolation of the $r_{OO}$ evolution of the $Q^i$ species in $\delta-(\text{Al}_{0.3},\text{Fe}_{0.7})\text{OOH}$. Nevertheless, estimating errors based on these effects was found to not significantly alter the position of the observed minima but only the respective width and thus the spread of $r_{crit}^{Q^i}$ (c.f. inset in Fig. 4b). In absence of magic angle spinning or Lee-Goldburg derived experiments, line narrowing in NMR mainly originates from two distinct mechanisms: (i) local structural symmetrization, leading to sharper resonance line distributions (structural narrowing) and (ii) local diffusive motion of the probed nuclei leading to an averaging of short range electromagnetic interactions (dynamic narrowing).

While the first effect is particularly pronounced in quadrupolar NMR as the electric nuclear quadrupole moment of any $I > 1/2$ nucleus is a sensitive probe of the local electronic environment and charge distribution; such an effect might not be very pronounced for $I = 1/2$ (e.g. $^1$H) nuclei. Contrary, moderate dynamic averaging of hydrogen NMR resonances is a well established diagnostic tool to identify locally restricted low amplitude motions and has even been employed to determine hydrogen diffusivities in diamond anvil cell based research. This minimum indicates the point of maximum hydrogen diffusivity within the H-bond, leading to a striking conclusion. At low pressures and long $r_{OO} \approx 2.60 - 2.50$ Å, hydrogen mobility continuously increases. At $r_{crit}^{Q^i}$, hydrogen mobility reaches a maximum, i.e. minimum in the FWHM line width, as the majority of protons de-localise.

Even more interesting is the fact that the point of maximum hydrogen de-localisation in the oxide-hydroxides and phase-D, possessing a single-well H-bond energy potential is nearly identical to the maximum found in $\text{H}_2\text{O}$ ice-VII/X characterised by a pronounced double-well character and correlated proton tunnelling. This indicates that the observed effect is in a region of $r_{crit}$ where the barrier of the double-well potential is already negligible compared to the protons energy and therefore that the high-$P$ regime is independent of the low-$P$ symmetry of the H-bond potential and associated tunnelling.

Being a primer for hydrogen-bond symmetrization or, more accurately, for hydrogen localisation as the diffusive motion of protons diminishes at $r_{crit}^{Q^i}$, this hydrogen mobility maximum is spread over a surprisingly wide range of over 40 GPa, ranging from 11 GPa in $\delta$-AlOOH to about 50 GPa in $\text{H}_2\text{O}$ ice-VII/X. Since the FWHM linewidth dependencies are comparable in all observed samples, despite significantly different charge distributions of the respective environment (ratio of Al and Fe in $Q^i$, O, etc.) as well as 3D (e. g. $\text{H}_2\text{O}$ ice-VII/X) and 2D (e. g. $\delta$-AlOOH) hydrogen-bond networks, it is reasonable to assume that this effect is universal for all linear O-H···O hydrogen-bonded materials regardless of their long range atomic structure.

Furthermore, it has been argued that H-bond symmetrization or hydrogen localisation might be a primer to electron spin crossovers in iron bearing hydrous minerals like oxide-hydroxides. Contrary, our NMR data clearly demonstrates that electron spin transitions and pressure induced hydrogen localisation are independent physical phenomena.

In this study, we have shown that the onset of hydrogen-bond symmetrization and therefore proton localisation as a consequence of the modulation of the H-bond energy potential is a phenomenon inherent to a wide variety of materials ranging from high-$P$ $\text{H}_2\text{O}$ ices to (iron-bearing) oxide-hydroxides. The observed samples were found to follow identical scaling behaviour in the O-H···O oxygen-oxygen distance $r_{OO}$, solely dependent on the short range atomic and electronic structure. We identified an average critical oxygen-oxygen distance of $r_{crit}^{Q^i} = 2.443(1)$ Å, where the delocalisation of hydrogen atoms in H-bonds shows a pronounced maximum.

### Methods

#### Sample preparation and characterisation

$\text{H}_2\text{O}$ ice-VII/X $\delta$-AlOOH: The sample preparation and measurement of the $\text{H}_2\text{O}$ ice-VII/X and $\delta$-AlOOH data is in detail described in refs. 36 and 10, 21.

#### $\delta-(\text{Al}_{0.3},\text{Fe}_{0.7})\text{OOH}$

A mixture of regent grade FeOOH and Al(OH)$_3$ with a molar ratio of 7:3 was used as starting material. Single crystals of $\epsilon_-(\text{Fe},\text{Al})\text{OOH}$ were synthesized using a 1000-ton Kawai-type multi-arril high-pressure apparatus at the University of Bayreuth, Germany. Undefaced carbide (WC) anvils with 4-mm truncated edge lengths were used to compress the sample in combination with a 5 wt% Cr$_2$O$_3$-doped MgO octahedral pressure medium with a 10 mm edge length. A cylindrical LaCrO$_3$ heater was set at the center of the pressure medium. The starting material was packed in a platinum capsule, which was welded shut. The capsule was inserted in an MgO capsule and put at the central part of the heater. Sample temperature was monitored at the central part of the outer surface of the Pr capsule using a W – 3%Re/W – 25%Re thermocouple, neglecting pressure effects on electromotive force of the thermocouple.

The sample was compressed to a desired press load at room temperature and then heated to a target temperature of 1200 °C at a rate of 100 °C/min. After keeping this temperature for 180 min, the sample was quenched by turning off electrical power and slowly decompressing to ambient pressure for 15 h.

Recovered single crystals with dimensions up to 200 μm were selected based on the absence of twinning and sharp optical extinction using a polarizing microscope. The crystals were mounted on a glass fibre and X-ray diffraction (XRD) data collected using a Huber Eulerian cradle single-crystal diffractometer driven by the SINGLE software. The diffractometer was equipped with a Mo Ka X-ray source.
and operated at 50 kV and 40 mA. Crystals with a half-width of the diffraction peaks less than 0.1° were further analysed in terms of their cell parameters with the vector least-squares method. The effect of crystal offsets and diffractometer aberrations for each crystal was eliminated using the eight-position centring method. The crystal had the space group of $P2_1/n$ and lattice parameters of $a = 2.9573(1) \ Å$, $b = 4.3884(1) \ Å$, $c = 4.8873(2) \ Å$, $V = 63.42(6) \ Å^3$. Chemical composition of the samples were measured using an electron microprobe analyzer (EPMA) with wavelength-dispersive spectrometers (JEOI, JXA-8200) operated at 15 kV and 10 nA, for 20 s on the peaks of Al and Fe and 10 s on the background. Synthetic hematite and corundum were used as standard material for Fe and Al, respectively. The composition of the dark-red crystals was expressed as $\text{Fe}_x\text{O}_{2-y}$, assuming that the cation number of oxide is one.

Next, powdered mixtures of regent grade chemicals of Mg(OH)$_2$ (45.11 wt.%), SiO$_2$ (38.02 wt%), Al$_2$O$_3$ (16.87 wt%), and Mg$_3$Si$_2$O$_5$ (Seybold et al. 1973) were coated by a thin layer of a Columbian-type anvil with pressure medium. The starting material was packed in a welded platinum capsule. The sample capsule was inserted in an MgO capsule and put at the central part of the heater. Sample temperature was monitored at the central part of the outer surface of the Pt capsule using a W-3%Re/W-25%Re thermocouple. Pressure effect on electromotive force of the thermocouple was ignored.

Above 36 GPa, SMS signatures of HS ferric iron are lost and new sub-spectra are lower than in the high-spin state and quadrupole splitting is found. The high quadrupole splitting is due to the enhanced electric field gradients, characteristic to a Mg substitution in the phase-D crystal lattice. Upon compression, SMS spectra change drastically: above 25 GPa, SMS spectra can no longer be described by only two doublets. Additional sub-spectra correspond to low-spin ferrous iron, indicating the onset of a HS – LS spin crossover. The ferric to ferrous iron ratio was constant throughout the whole compression range.

Above 36 GPa, SMS signatures of HS ferric iron are lost and new sub-spectra with characteristic hyperfine parameters of LS Fe$^{2+}$ appear indicating another long range spin crossover. Isomer shifts LS Fe$^{2+}$ are lower than in the high-spin state and quadrupole splitting is found. The high quadrupole splitting is due to the enhanced electric field gradients, associated with the non-uniform distribution of uncompensated $\delta d_{xy}$ valence electrons. The pressure dependence of hyperfine parameters show no anomalous changes in the local environment of the iron ions.

Before the final cell assembly, radio frequency resonators were prepared accordingly to their desired operation frequency: A pair of high inductance, skewed pogo coils ($\approx 100$ nH) for low frequency experiments of below 100 MHz or a pair of single turn printed circuit board (PCB) plated copper resonators for $\text{^1H-NMR}$ frequencies at high fields were used as driving coil arrangements for the Lenz lens resonators’ structure and were placed around each diamond anvil. After sample loading and initial pressurisation, the driving coils were connected to form a Helmholtz coil-like arrangement.

Pressure calibration was performed using the shift of the first derivative of the first order Raman signal of the diamond edge in the center of the cuvet. All DACs were fixed and connected to home built NMR probes equipped with customised cylindrical trimmer capacitors (dynamic range of $\approx 150$ pF) for frequency tuning to the desired resonance frequencies and impedance matching to the spectrometer electronics (50Ω).

Data availability

The data supporting the findings of this study are publicly available from the corresponding author upon request.

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