Dielectric ordering of water molecules arranged in a dipolar lattice

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Intermolecular hydrogen bonds impede long-range (anti-)ferroelectric order of water. We confine H₂O molecules in nanosized cages formed by ions of a dielectric crystal. Arranging them in channels at a distance of ~5 Å with an interchannel separation of ~10 Å prevents the formation of hydrogen networks while electric dipole-dipole interactions remain effective. Here, we present measurements of the temperature-dependent dielectric permittivity, pyrrocurent, electric polarization and specific heat that indicate an order-disorder ferroelectric phase transition at T₀ ≈ 3 K in the water dipolar lattice. Ab initio molecular dynamics and classical Monte Carlo simulations reveal that at low temperatures the water molecules form ferroelectric domains in the ab-plane that order antiferroelectrically along the channel direction. This way we achieve the long-standing goal of arranging water molecules in polar order. This is not only of high relevance in various natural systems but might open an avenue towards future applications in biocompatible nanoelectronics.

https://doi.org/10.1038/s41467-020-17832-y
For decades intense research activities tackle the question whether water molecules with their rather strong dipole moment of $p_0 = 1.85$ Debye can condense into a ferroelectrically or antiferroelectrically ordered state. In pure liquid water or in H$_2$O ice no such ordering occurs under ambient conditions or during experimentally available time scales because a complex time-dependent tetrahedral molecular hydrogen-bonded network emerges governed by Pauling’s ice rules$^{1-3}$. Proton ordered phases of water ice can be induced by defects introduced via doping with impurities or via irradiation$^{4,5}$. It is suggested that the so-called water ferroelectricity can exist in various natural systems where the role of H-bonds for intermolecular coupling is diminished due to a preferred orientation of water molecules imposed by the host frameworks, thus creating favorable conditions for mutual aligning of H$_2$O molecules. In practice, this can be realized when water molecules are adsorbed by two-dimensional interfaces or confined in nanosized channels or cages. Such kind of ferroelectricity of confined water molecules is discussed to be of central importance for a wide range of phenomena in geology, mineralogy, meteorology, soil chemistry, etc. Of special interest is the potential ordering of water molecules in biological systems, where the H$_2$O molecules are found in fully or partially confined states in cells, membrane channels, and proteins hydration shells$^{5-8}$, which can influence the functioning of living organisms substantially.

Various types of dipolar orderings and other exciting properties are predicted based on theoretical analyses or computer simulations of water molecules in nanometer-thick layers on substrates or at the interface$^{9-13}$, between two graphene layers$^{14-17}$, for H$_2$O chains within carbon nanotubes$^{18-23}$, for networks of H$_2$O molecules in nanovoids, e.g., in fullerences$^{24-26}$ or within protein hydration shells$^{27}$. Besides fundamental aspects, the interest in such systems is fueled by the perspective that ordered water dipoles can find practical applications in nanoelectronic devices$^{28-33}$. It turned out, however, that it is not so trivial to experimentally verify the predictions made by theory and modeling. Even to realize the dipolar ordering under laboratory conditions appears to be a challenging task. Corresponding reports in the literature are very rare$^{9,11,34,35}$, and either observe only a tiny fraction of ordered dipoles ($\leq 1\%$)$^{10}$, or raise questions and discussions concerning the reliability of the results$^{36-41}$.

An ideal workbench for studying collective effects in ensembles of dipole–dipole coupled water molecules is provided by hydrated dielectric crystals, such as the beryl family. Compared to zeolites and microporous silicates$^{42,43}$, the special appeal of these crystals is that they contain just separate H$_2$O molecules that are isolated within nanosized voids formed by the lattice ions. Being only weakly linked to the ions and separated by 5–10 Å, the water molecules do not experience hydrogen bonding (interaction length 1–2 Å); nevertheless, they interact via long-range dipole–dipole coupling (interaction length 10–100 Å). This kind of network of interacting water molecules is of broad interest and fundamental importance providing the opportunity to study electric-dipolar systems whose properties are expected to be qualitatively different from those occurring in systems with magnetic moments$^{44,45}$.

In addition, introducing dopants like Na and K ions at bottlenecks that separate nanovoids can lead to a polarization of H$_2$O molecules and the formation of statically polarized so-called water-II molecules. Having also the possibility to encapsulate heavy water molecules (D$_2$O, DHO), one gets a unique “laboratory” for studies of various excitations, phases and phase transitions in the water dipolar network. Very recently it was reported$^{46-51}$ that H$_2$O molecules in beryl exhibit the tendency towards a macroscopic alignment of their dipoles: a ferroelectric soft mode was observed with the temperature evolution of dielectric strength and frequency following the Curie–Weiss and Cochran laws, respectively. However, due to quantum tunneling of the dipoles in the symmetric six-well localizing potential of the hexagonal beryl lattice$^{52}$ no phase transition into a macroscopically ordered phase occurs.

In this communication, we present our studies of the dielectric response, pyrocurrent and specific heat of an array of separate H$_2$O molecules confined within ionic matrix of the orthorhombic cordierite crystal lattice, and supplement our experimental data with Density Functional Theory Molecular Dynamics and Monte Carlo simulations. We discover that at $T_0 \approx 3$ K the water dipolar network undergoes an order–disorder ferroelectric phase transition. In the ground state the water molecules form ferroelectric domains in the ab-plane that order antiferroelectrically along the channel direction.

## Results

### Material

In the present study, we explore the possibility to order water molecules macroscopically by dipole–dipole interaction. To that end, we consider hydrated crystals with a strongly asymmetric localizing potential; i.e. the presence of a certain crystallographic direction along which the molecular dipoles align and form an ordered phase. Crystalline cordierite (Mg,Fe)$_2$Al$_2$Si$_5$O$_{18}$ is ideally suited for these requirements as it is structurally similar to beryl, except for the lack of rotational symmetry. Beryl contains Si$_5$O$_{18}$ rings, while in cordierite two of six silicon atoms are replaced by aluminum, leading to (Si,Al)$_6$K$_8$ rings that are stacked along the c-axis and form channels with 2.5 Å diameter ionic “bottlenecks”, see Fig. 1. As a consequence, the cages in cordierite are anisotropic (5.4 Å along the b-direction and 6.0 Å along the a-axis) and the lattice exhibits orthorhombic symmetry space group Ccmm$^{53}$. There are indications that the H$_2$O dipole moments in cordierite are preferably oriented parallel to the b-axis$^{54}$. In the present study, slices of well characterized natural hydrous cordierite single crystal were cut along different crystallographic axes in order to measure the dielectric response in all three principal polarizations. We have investigated the electrodynamic properties in a broad frequency range, $\nu = 1$ Hz–3 THz, covering temperatures down to 0.3 K, supplemented by pyroelectric and heat capacity measurements. From the comparison with reference measurements on dehydrated samples, the characteristics of the water molecular subsystem can be extracted.

### Dielectric spectra

For the E $\parallel$ a polarization, we find a broad relaxation-like excitation whose peak frequency decreases when the temperature is lowered down to $T_0 \approx 3$ K and increases on further cooling. Around the same temperature, pronounced anomalies are observed in the dielectric strength of the excitation and of the H$_2$O contribution to the specific heat. We assign this behavior to an order–disorder phase transition within the water molecular network. Density functional theory molecular dynamics (DFT-MD) and Monte Carlo simulations of water molecules indicate that the low-temperature ordered phase contains domains lying in the ab-planes and composed of unidirectional H$_2$O dipoles polarized preferably along the b-axis but ordered antiferroelectrically along the c-axis.

Figure 2 presents the temperature-dependent radiofrequency (RF) spectra of the real $\varepsilon'(\nu)$ and imaginary $\varepsilon''(\nu)$ parts of the dielectric permittivity of water molecules in cordierite measured for the polarization E $\parallel$ a. Since the MHz–GHz reflectometry technique does not provide absolute values, the corresponding loss data are separately displayed in Supplementary Fig. 1. For the polarization E $\parallel$ b, the dielectric response is mostly governed by the higher frequency THz modes and does not reveal features that could be indicative of dipolar ordering. For that reason, in the following we focus on the E $\parallel$ a polarization, where strong...
variations in the spectra are observed on lowering the temperature. We find a pronounced maximum in $\varepsilon'(T)$ with a slope above $\approx 40$ K that follows the Curie–Weiss behavior:

$$\varepsilon'(T) = \varepsilon_\infty + C(T - T_c)^{-1}. \quad (1)$$

Here, $\varepsilon_\infty$ is the high-frequency dielectric constant, $C$ is the Curie constant and $T_c$ is the Curie temperature. The low-temperature wing of the maximum reveals a pronounced frequency dispersion that is caused by a relaxational band (Fig. 2b, c) signified by a typical relaxation step in $\varepsilon'(\nu)$ together with a broad peak in $\varepsilon''(\nu)$. The fact that this feature is completely absent in water-free crystals unambiguously links the relaxation process to the water subsystem in cordierite. Upon cooling down to $T_0 \approx 3$ K, the band shifts to lower frequencies, mirroring the usual slowing down of thermally activated dipolar dynamics for low temperatures. Surprisingly, a non-canonical increase of peak frequency is observed when cooling further, which implies an acceleration of the involved molecular dynamics. Such behavior is typical for order–disorder ferroelectrics below the phase transition\textsuperscript{55}.

It should be noted that the detected dielectric relaxation behavior (Fig. 2) in some respects resembles that of so-called relaxor ferroelectrics, which can be regarded as nano-ordered ferroelectrics with a smeared-out diffusive phase transition\textsuperscript{56}. There are model simulations predicting typical signatures of relaxors—dispersive maxima due to polar nanoregions in the temperature-dependent dielectric permittivity—in bulk water and in proteins hydration shells\textsuperscript{57,58}. Concerning the permittivity, the main distinction between a relaxor and an order–disorder ferroelectric phase transition observed in the present data is the critical behavior of the relaxation time $\tau$ (or critical slowing down of the peak frequency $\nu_p \propto 1/\tau$; Fig. 3), which is typical for order–disorder ferroelectrics. In a relaxor, it should exhibit glass–like freezing following the Vogel–Fulcher–Tamann law instead\textsuperscript{59,60}.

**Discussion**

The temperature evolution of the detected relaxation process is quantitatively summarized in Fig. 3 by presenting the peak frequency $\nu_p$ and the dielectric strength $\Delta \varepsilon$ of absorption band. At $3 \text{ K} < T < 8 \text{ K}$, the values of $\Delta \varepsilon$ were determined via fits of the RF spectra of Fig. 2b and c with the Havriliak–Negami function,

$$\varepsilon'(\nu) = \varepsilon_\infty + \Delta \varepsilon \left[ 1 + (\nu / \omega_R)^{1-\alpha} \right]^\beta, \quad (2)$$

where $\omega$ is the angular frequency, $\omega_R$ is the angular relaxation frequency and the exponents $\alpha$ and $\beta$ characterize the broadness and asymmetry of the relaxational band, respectively. Fitting results for three selected temperatures are shown in Fig. 2b, c by short-dashed lines. In the lowest temperature range, $0.3 \text{ K} < T_0 < 3 \text{ K}$, the values of $\Delta \varepsilon$ were determined by phenomenologically describing the RF spectra of Fig. 2a, b with the sum of two Havriliak–Negami relaxation terms with the dielectric contributions $\Delta \varepsilon_1$ and $\Delta \varepsilon_2$. Around $T_0 \approx 3$ K the peak frequency $\nu_p$ and the relaxation time $\tau = (2\pi \nu_p)^{-1}$ (inset in Fig. 3) exhibit a pronounced minimum and maximum, respectively, which are clear signatures of an order–disorder ferroelectric phase transition\textsuperscript{55}. The temperature dependence of the dielectric strength $\Delta \varepsilon$ exhibits a characteristic peak at the transition temperature, again typical for order–disorder ferroelectrics. In addition, the specific heat clearly reveals an anomaly around $T_c$.

Since the electric dipole–dipole interaction energy of water molecules along the channels is $U_{d-d} \approx 22 \text{ meV}$\textsuperscript{47}, at room temperature ($k_b T = 26 \text{ meV}$) the $\text{H}_2\text{O}$ molecules are mostly decoupled. The situation changes with cooling: the $\text{H}_2\text{O}$ dimers, trimers, etc., start to form in the channels\textsuperscript{47}, leading to the Curie–Weiss behavior of Eq. (1) with $C = 390 \text{ K}$ and $T_C = -15 \text{ K}$ (solid blue line in Fig.2a). The negative Curie temperature

**Fig. 1 Cordierite crystal structure with water molecules within ionic nanopores.** a Unit cell of cordierite crystal from X-ray analysis with thermal ellipsoids at 85 K. b The water molecules within cordierite nanopores form two-dimensional triangular lattice within the ab-plane. c One-dimensional chain of confined water molecules along the c-axis.
The temperature dependence of the dielectric permittivity \( \varepsilon' \) of a hydrous cordierite crystal for \( E \parallel a \) polarization at different frequencies as indicated. The blue solid line shows the result of a least-square fit with the Curie-Weiss expression, Eq. (1), with \( C = 390 \text{ K} \) and \( T_c = -15 \text{ K} \). b, c Hz-MHz and THz spectra of the real \( \varepsilon' \) and imaginary \( \varepsilon'' \) parts of the dielectric permittivity of the hydrous cordierite crystal measured at different temperatures as indicated. The short-dashed lines represent least-square fits with Eq. (2) of measured spectra shown by full dots. WF denotes the spectra obtained for a water-free crystal (squares). The dotted lines connecting the radiofrequency and terahertz spectra are guides to the eye.

Fig. 2 Temperature evolution of relaxational absorption band.

a Temperature dependences of the real part of the dielectric permittivity \( \varepsilon' \) of a hydrous cordierite crystal for \( E \parallel a \) polarization at different frequencies as indicated. In addition, \( \varepsilon'(T) \) data for a water-free cordierite crystal (WF, 1.2 kHz) are included. The blue solid line shows the result of a least-square fit with the Curie-Weiss expression, Eq. (1), with \( C = 390 \text{ K} \) and \( T_c = -15 \text{ K} \). b, c Hz-MHz and THz spectra of the real \( \varepsilon' \) and imaginary \( \varepsilon'' \) parts of the dielectric permittivity of the hydrous cordierite crystal measured at different temperatures as indicated. The short-dashed lines represent least-square fits with Eq. (2) of measured spectra shown by full dots. WF denotes the spectra obtained for a water-free crystal (squares). The dotted lines connecting the radiofrequency and terahertz spectra are guides to the eye.

The appearance of an ordered state of H\(_2\)O molecular dipoles below \( T_0 = 3 \text{ K} \) is conclusively demonstrated by the pyrocurrent that peaks at the same temperature, and the polarization appearing at \( T < T_0 \) see Fig. 4. The value of low-temperature polarization \( P = 3 \text{ nC cm}^{-2} \) allows us to estimate the number of dipoles that contribute to this polarization \( N = P/p_a = 1.4 \times 10^{19} \text{ cm}^{-3} \). (Here \( p_a \) is component of H\(_2\)O dipole along the a-axis). The obtained value is about two orders of magnitude smaller than the total concentration of water molecules in the crystal \( =1.9 \times 10^{21} \text{ cm}^{-3} \). The reason for this discrepancy lies in the fact that the H\(_2\)O dipoles form ferroelectric domains at temperatures below \( T_0 = 3 \text{ K} \) but also acquire antiferroelectric order along the c-axis. An estimate of the field binding two collinear dipoles separated by a distance \( \approx 10 \text{ Å} \) within domain provides a value of \( 750 \text{ kV cm}^{-1} \) that is comparable to crystalline internal fields. Then, the fields of 8 kV cm\(^{-1} \) used in our experiments will be able to polarize only small fraction of the dipoles (in the present case about 1%) that are located at the domains boundaries, close to the “defects” (empty cages) or isolated dipoles. We believe that for the same reasons we were not able to detect any meaningful signs of dielectric nonlinearity (hysteresis) in the fields up to 15 kV cm\(^{-1} \) because they are also not sufficient to affect the electric coupling between H\(_2\)O dipoles.

To provide a more detailed picture of the dipolar ordering, we performed density functional theory molecular dynamics simulations of two H\(_2\)O molecules located next to each other along the channel c-axis and within the ab-plane. The simulations were performed for various temperatures and yield averaged snapshots of the dipolar configurations.
of the oxygen and two protons of the corresponding two molecules in 1 fs steps during a period of 15 ps (see Supplementary Movie 1–6). Figure 5 displays the ab-projection of the positions of oxygen and two protons in two adjacent cages along the channel and in neighboring channels, respectively. At room temperature, hardly any correlations between the sites can be identified, the molecules are nearly independent. Upon cooling, however, the disorder due to thermal motion weakens and the molecules become progressively more confined. The important observation is that the molecules prefer to orient their dipole moments antiparallel within the channels while the dipoles align parallel within the ab-planes. Analogous simulations performed for the larger system of four adjacent H2O molecules in a channel, in plane and occupying all four cages of cordierite crystal unit cell, see Supplementary Figs. 2–4, do not qualitatively change the preferred configurations of dipoles. Only the potentials experienced by the molecules acquire a slightly more complex shape with local minima for oxygen and protons. The Monte Carlo analysis of the dynamics of N = 3072 interacting water molecules (see Monte Carlo simulations methods section) are in full agreement with the conclusions drawn from the DFT-MD simulations. As demonstrated in Fig. 6, the additional finding from the Monte Carlo analysis is that in order to minimize the energy of dipolar system, the molecules tend to form in-plane ferroelectric domains with a polarization predominantly along the b-axis and alternating its sign along the c-direction. We calculated the distribution of domains sizes as a function of their lengths at temperature $T = 0.001$ K (see Supplementary Fig. 5). Domains are considered as arrays of collinear (along the b-axis) dipoles with their boundaries given by dipoles of different directions, by defects (empty cages) or by boundaries of the sample. The obtained mean size of the domains is 1.75 and 2.28 Å in the $a$- and $b$-axis, respectively; after multiplication by the translation lattice vectors the average domains size is $1.496 \text{ nm} \times 2.220 \text{ nm} = 3.32 \text{ nm}^2$. Figure 7 displays the temperature dependences of the antiferroelectric order parameter along the a-axis and c-axis dielectric susceptibility, both clearly demonstrating a phase transition at $T_{\text{c}} = 3$ K. In other words, our DFT-MD and Monte Carlo results confirm a three-dimensional low-temperature order of the H2O molecular network. The water molecules in cordierite form a dipolar lattice with ferroelectric domains in ab-planes staggered antiferroelectrically along the channels c-axis, as shown in Fig. 8.

Based on our comprehensive experimental and numerical investigations of hydrous cordierite crystals we firmly conclude that H2O molecules form a highly ordered dipolar lattice at low temperatures. When confining water molecules to the anisotropic nanosized channels composed by the ionic lattice of the crystal, they undergo a ferroelectric order–disorder type phase transition near $T_{\text{f}} = 3$ K with characteristic features in the temperature dependence of dielectric permittivity, specific heat, pyroelectric current and polarization. Density functional theory molecular dynamics and Monte Carlo simulations indicate the antiferroelectric coupling of H2O molecular dipoles along the nanochannel c-axis and their ferroelectric coupling within the ab-planes. As a result, the low-temperature phase is characterized by in-plane ferroelectric domains ordered antiferroelectrically along the nanochannels direction. This long-sought polar phase transition in a system of coupled dipolar water molecules demonstrates that hydrous crystals provide an ideal workbench for studies of different phases and phase transitions in the electric counterpart of magnetic spin systems.

**Methods**

**Sample preparation and characterization.** Natural cordierite crystal from India (the detailed location is unknown) have been carefully selected and studied. According to visual inspection with an optical microscope at low magnification (×10), the crystal was free of impurities or foreign phases. 10 independent measurements via microprobe analysis (JEOL JXA-8100, Analytical Center for multi-elemental and isotope research SB RAS) provided with the following chemical composition in mass %: Na2O—0.204; MgO—13.350; MnO—0.017; K2O—0.008; CaO—0.021; SiO2—49.296; Al2O3—33.140; FeO—1.584; Loss on ignition—2.200 (total—99.821). Recalculation of this chemical analysis on the basis of 18 oxygen atoms per formula gives the following chemical formula: $(\text{Mg}_{0.941}\text{Na}_{0.041}\text{K}_{0.001})_{3}\text{Si}_{1.953}\text{Al}_{0.027}\text{Fe}_{0.027}\text{Ca}_{1.002}\text{H}_{2.147} \approx 18 \text{O}$.

Our refinement of the cordierite structure provided with the following results. Space group is $Cccm$, $Z = 4$. Maximum angle of scattering of reflections is $\theta = 74.3^\circ$. Unit cell parameters are $a = 17.1004(3)$ Å, $b = 9.3739(2)$ Å, $c = 9.3286(2)$ Å. The residuals that describe the differences between the experimental and modeled electron density are $R = 0.017$ and $wR = 0.042$.

This recalculation assumes that the total weight loss on ignition is due to water loss, which is generally not the case, since some unknown amount of CO2 is also present in cordierite. Thus, the water content specified in the formula is an estimate from above. From the formula, the filling factors of water-I and water-II can be estimated as ~75.6% and ~4.2%, respectively.

To solve the complex problem of identification of water molecules in the studied cordierite crystal, an accurate X-ray diffraction analysis was carried out. The sets of diffraction reflection intensities at different temperatures were collected on a Rigaku Oxford Diffraction Xcalibur diffractometer equipped with an EOS S2 detector. Our refinement of the cordierite structure provided with the following results. Space group is $Cccm$, $Z = 4$. Maximum angle of scattering of reflections is $\theta = 74.3^\circ$. Unit cell parameters are $a = 17.1004(3)$ Å, $b = 9.3739(2)$ Å, $c = 9.3286(2)$ Å. The residuals that describe the differences between the experimental and modeled electron density are $R = 0.017$ and $wR = 0.042$ electrons per $\text{Å}^3$ for 5693 symmetry-independent reflections. Structural results are presented in Supplementary Table 1.
on dehydrated samples (annealing at a temperature 1000 °C for 8 h according to ref. 67) allowed us to extract the characteristics determined exclusively by water molecules. Complete dehydration was monitored by the weight loss of the specimen and by disappearance of internal vibrations of the H2O molecule in the infrared spectra.

**Density functional theory molecular dynamics simulation.** Ab initio DFT calculations were carried out using the Vienna Ab initio Simulation Package (VASP)68 with plane wave basis sets cut off at 400 eV, PAW pseudopotentials70, and Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional71. The Brillouin zone integration was carried out using a 1x2x2 k-point sampling and Gaussian smearing. One unit cell of cordierite of 116 atoms was simulated with initial geometry taken from X-ray diffraction (Supplementary Table 1). For all calculations lattice parameters were fixed to the experimentally observed values (see section Sample preparation and characterization above) and periodic boundary conditions were applied. One unit cell of cordierite forms four nanocages, and several types of nanocage filling were simulated. At the first stage, one water molecule and two water molecules within nanocages arranged along the c-axis and within the ab-plane were studied. For each geometry, molecular dynamics simulations were performed at 10 K, 50 K, 75 K, 100 K, 150 K, 300 K for 15 ps or 20 ps with 1 fs time step using Nose–Hoover thermostat. Additionally, molecular analysis was performed for four molecules occupying all four cages of the unit cell and for large system of 1x1x2 and 1x2x1 super cell with four water molecules arranged next to each other along the channel c-axis and within the ab-plane, respectively. In each procedure, the first 1.5 ps of simulation were considered as thermalization and

**Fig. 5 Temperature-dependent dynamics of nanoconfined water molecules.** Density functional theory molecular dynamics simulation during 15 ps and at five temperatures of two water molecules within two nanocages of cordierite crystal lattice, located next to each other along the channel c-axis (left) and within the ab-plane (right). The panels display projections of oxygen ions (O) and two protons (H1, H2) of the H2O molecules on the ab-plane; the c-axis is perpendicular to the figure plane. Red arrows represent the dipole moments of the molecules that show antiferroelectric alignment for molecules located along the channel and ferroelectric alignment for molecules in the ab-plane. Numbers correspond to the coordinates of atoms within the cages in fractions of translation vectors of cordierite unit cell.
The antiferroelectric order parameter is calculated via the expression for dielectric susceptibility via $N$ with the electric-dipolar system of water molecules in hydrous cordierite crystal. The dependences were obtained by Monte Carlo simulations for the antiferroelectric order parameter (blue) of nanocon.

removed from the subsequent analysis. To find out whether van der Waals (vdW) forces play any significant role in interaction between the water molecules and the ions of nanocage, we performed test calculations using the non-local dispersion corrected vdW-DF2 functional (Supplementary Fig. 6, Supplementary Note 1).

Monte Carlo simulations. Metropolis algorithm was used to simulate at different temperatures the behavior of the dipole system governed by the dipole–dipole interaction Hamiltonian $H = (8\pi\epsilon_0\epsilon_r) \cdot \sum_{ij} r_{ij}^{-3} \left( \mathbf{p}_i \cdot \mathbf{p}_j \right)$, where $\mathbf{p}_i$ is the dipole of water, $\epsilon_0$ is the dielectric constant, $\epsilon_r = 5$ is the relative dielectric permittivity due to other degrees of freedom than the water dipoles, $r_{ij}$ is the distance between two dipoles $\mathbf{p}_i$ and $\mathbf{p}_j$, and $\mathbf{n}_i$ is the unit vector between them. The presented results were obtained for a sample with 16 lattice sites along each axis ($a$, $b$, and $c$) with a filling factor of 75%.

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Acknowledgements
The authors acknowledge fruitful discussions with A. Bokov, A. Bush, H. P. Büchler, M.
Fyta, V. S. Gorelik, V. Gudkov, J. Hlinka, S. Kamba, G. Shakurov, V. Torgashev. We
acknowledge financial support of the Russian Foundation of Basic Research via RFBR
grants 18-32-00286 (sample preparation, room temperature experiments) and 18-32-
20186 (low-temperature experiments), 20-02-00314 and 18-02-00399 (Monte Carlo
grants 18-32-00286 (sample preparation, room temperature experiments) and 18-32-
simulations), Program 5

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carried out the radiofrequency experiments; J.K.H.F., P.L. carried out the radiofrequency
and microwave experiments; M.A.B., Z.Y.B., E.S.Z. carried out the infrared experiments;
R.K.K. carried out the heat capacity experiments; M.A.B., M.S., M.D., B.G., Z.V.B.,
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prepared the samples; V.G.T., A.D. carried out the samples characterization; M.A.B.,
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the work; all authors contributed to the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-
020-17832-y.

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Peer review information Nature Communications thanks Marivi Fernandez-Serra and
the other, anonymous, reviewer(s) for their contribution to the peer review of this work.
Peer reviewer reports are available.

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