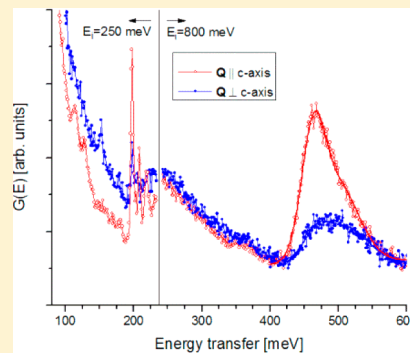


Strong Anisotropic Dynamics of Ultra-Confined Water

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ABSTRACT: Dynamics of water confined in ~ 5 Å diameter channels of beryl and cordierite single crystals were studied by using inelastic (INS) and quasielastic (QENS) neutron scattering. The INS spectra for both samples were similar and showed that there are no hydrogen bonds acting on water molecule, which experiences strong anisotropic potential, steep along the channels and very soft perpendicular to it. The high-resolution ($3.4 \mu\text{eV}$) QENS data revealed gradual freezing out of the water molecule dynamics for both minerals at temperatures below about 80 K when the scattering momentum transfer was parallel to the channels, but not when it was perpendicular to the channels. The QENS study with medium energy resolution (0.25 meV) of the beryl with the scattering momentum transfer along the channels showed gradual freezing out of water molecule dynamics at temperatures below about 200 K, whereas at higher temperatures the data could be described as 2-fold rotational jumps about the axis coinciding with the direction of the dipole moment (that is, perpendicular to the channels), with a residence time of 5.5 ps at 225 K. The energy resolution dependence of the apparent dynamics freezing temperature suggests gradual slowing down of the rotational jumps as the temperature is decreased, until the associated QENS broadening can no longer be detected, rather than actual freezing.



I. INTRODUCTION

The dynamical properties of water under confinement are significantly changed compared to those of the bulk water. Although there has been significant work on the properties of such materials, the dynamics of fluids under ultraconfinement, where the dimensions of the confining environment are similar to that of the confined molecule, have not been as thoroughly investigated. Recently, we have studied the dynamics of water in single crystals of beryl,¹ the structure of which contains 4.86 Å diameter channels parallel to the *c*-axis, by using inelastic (INS) and quasielastic (QENS) neutron scattering. In the current work we extend this study to water confined in single crystal of cordierite, which has a slightly larger diameter of the channels, 5.50 Å. In both minerals we used alkali-metal-free samples, where water has its H–H axis parallel to the *c*-axis of crystals (type-I water). Water molecules in the channels do not have direct water–water interaction due to large separation distance; therefore, it is interesting to understand the behavior of isolated confined water molecule, which also has a weak interaction with the confining material. The neutron scattering technique is one of the best to investigate the vibrational dynamics and diffusion of hydrogen containing materials due to anomalously large neutron scattering cross-section of hydrogen (~ 82 barns) compared to those of other elements (a few barns on average).

II. MATERIALS AND EXPERIMENTAL METHODS

The samples used for this study were gem-quality single crystals beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$)¹ and cordierite ($\text{Al}_4\text{Mg}_2\text{Si}_5\text{O}_{18}$), both containing about 2 wt % H_2O water. Beryl has hexagonal

structure, and its channels consist of six silica tetrahedra rings of approximately 4.86 Å diameter, with Al tetrahedra and Be octahedra lying between the rings (Figure 1, top). At room temperatures cordierite is orthorhombic, and water is confined in a six-ring channels made of four SiO_4 and two AlO_4 tetrahedra with a diameter of approximately 5.50 Å, although the rings are somewhat elongated (Figure 1, bottom). The samples were cut into flat slabs approximately 0.7 mm thick to reduce multiple neutron scattering.

The INS experiments were performed at the fine-resolution Fermi chopper spectrometer SEQUOIA at the Spallation Neutron Source (SNS) at the Oak Ridge National Laboratory.⁴ Measurements were made at temperature $T = 6$ K with three incident neutron energies $E_i = 160, 250$, and 800 meV, selected by the Fermi chopper, which provided good quality spectra at energy transfer in the range $50 \text{ meV} < E < 150 \text{ meV}$, $150 \text{ meV} < E < 240 \text{ meV}$, and $240 \text{ meV} < E < 750 \text{ meV}$, respectively, with energy resolution being about 2–4% of E_i . The samples were measured for two orientations with the *c*-axis vertical (which corresponds to *Q* being perpendicular to the *c*-axis) and the *c*-axis horizontal and having a 25° angle with the incoming neutrons (which for the large group of detectors corresponds to *Q* being parallel to the *c*-axis for energy transfer range between $1/2 E_i$ and $3/4 E_i$). To make correct direct comparison of the

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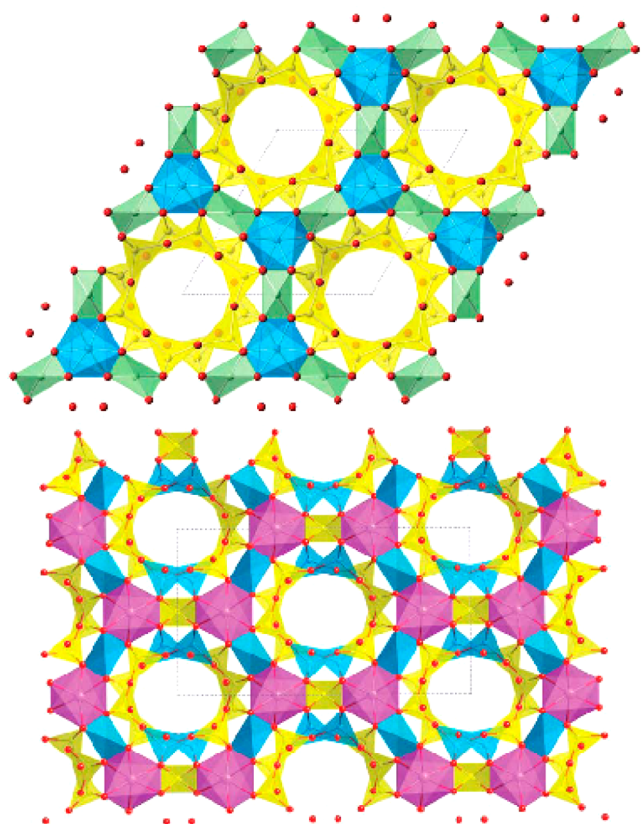


Figure 1. Structures of beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ (top) and cordierite $\text{Al}_4\text{Mg}_2\text{Si}_5\text{O}_{18}$ (bottom) showing large open channels running parallel to the crystallographic c -axis (out of the figures' plane). The channels consist of six SiO_4 tetrahedral rings in beryl and four SiO_4 and two AlO_4 tetrahedra in cordierite. Water molecules occupy positions in the center of the channels and have their H–H axis parallel to the c -axis of crystals. The dimensions of the unit cells are $a = 9.21 \text{ \AA}$ and $c = 9.19 \text{ \AA}$ for beryl² (space group $P6/mcc$) and $a = 17.08 \text{ \AA}$, $b = 9.72 \text{ \AA}$, and $c = 9.34 \text{ \AA}$ for cordierite³ (space group $Cccm$).

spectra in these two orientations, the samples in each orientation were placed in such a way that they occupied essentially the same space in the beam and had the same width, height, thickness, and angle between the sample surface and the neutron beam direction. Thus, all sample geometrical factors were almost identical for analyses carried out with the c -axis parallel and perpendicular to the momentum transfer. This permits the two sets of measured INS spectra to be compared directly. Observed spectral differences for the two orientations are therefore entirely due to the changes in the water vibrational properties along and perpendicular to the c -axis.

The elastic intensity scans that monitor the temperature dependence of the elastic (within the spectrometer resolution of 3.4 \mu eV , fwhm) scattering intensity were performed on the SNS backscattering spectrometer, BASIS,⁵ as the sample temperature was decreased at a rate of about 1 K/min . Quasielastic data were collected on the SNS cold chopper spectrometer, CNCS,⁶ at 225 K . The data collected at the baseline temperature of 1.7 K were used for the resolution function. With the incident neutron energy of 10 meV in the high-resolution mode, the resolution in the CNCS experiment was about 0.25 meV , fwhm.

III. RESULTS AND DISCUSSION

A. Inelastic Neutron Scattering. The dynamical structure factors $S(Q, E)$ obtained from the INS spectra for beryl¹ and cordierite with the $E_i = 800 \text{ meV}$ exhibit strong anisotropy. The spectra show intense water intramolecular stretching O–H band (around 465 meV) for Q parallel to the c -axis, whereas for the Q -perpendicular orientation this band is much weaker and there is a strong background-like intensity below the stretching mode peak. Figure 2 shows the contour plots for beryl (a) and

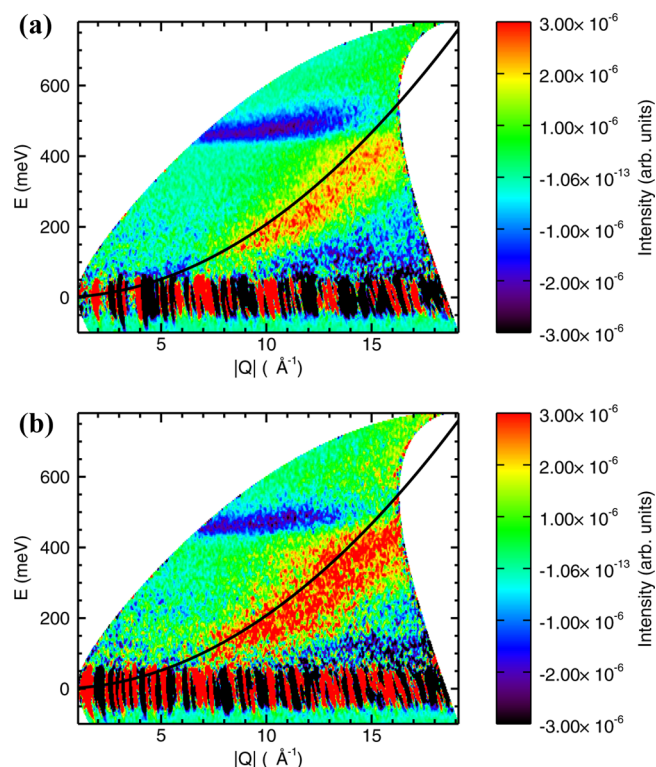


Figure 2. Contour plots for beryl (a) and cordierite (b) $S(Q, E)$ difference spectra between the neutron momentum transfer Q being perpendicular and parallel to the crystallographic c -axis. The INS data were collected at $T = 6 \text{ K}$ with $E_i = 800 \text{ meV}$. The black solid lines show the dependence of the neutron recoil scattering on free protons.

cordierite (b) $S(Q, E)$ difference spectra between the neutron momentum transfer Q being perpendicular and parallel to the crystallographic c -axis, which highlight the predominant vibrations of the water O–H stretching modes along the c -axis for both minerals. In addition, the difference spectra clearly show a strong excess of intensity in the Q -perpendicular orientation going very close to the dependence of the neutron recoil scattering⁷ on free protons (mass of m) $E_R = \hbar^2 Q^2 / 2m$, shown in Figure 2 as black solid lines. Actually, the maxima of the multiphonon neutron scattering for a single harmonic oscillator of mass m with ground state energy $\hbar\omega_0/2$ follow the same dependence, $n\hbar\omega_0 = \hbar^2 Q^2 / 2m$; therefore, if the energy value $\hbar\omega_0$ is comparable to the energy resolution of the spectrometer, the multiphonon neutron scattering will go close to the neutron recoil spectrum. Consequently, from the spectra shown in Figure 2 we can conclude that water molecules in beryl and cordierite behave very similarly on the energy scale $100\text{--}500 \text{ meV}$, they have a steep potential along the c -axis and very soft one across the channels.

Figures 3 and 4 show the projections of the generalized vibrational density of states $G(E)$ along and perpendicular to

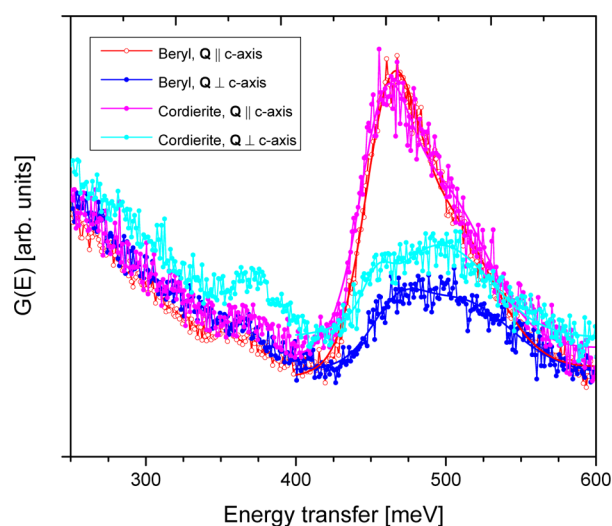


Figure 3. $G(E)$ spectra for beryl and cordierite measured with neutron momentum transfer Q parallel and perpendicular to the crystallographic c -axis; $E_i = 800$ meV.

the c -axis for beryl and cordierite samples, where the $G(E)$ was obtained by using the expression $G(E) = S(Q,E)E/\{Q^2[n(E,T) + 1]\}$, where $n(E,T) = 1/[\exp(E/k_B T) - 1]$ is the population Bose factor. The energy position and the shape of the water intramolecular O–H stretching mode peak (the symmetrical, ν_1 , and asymmetrical, ν_3 , components of the peak are not resolved and appeared as one peak) for beryl and cordierite almost coincide ($E_{\text{stretch}} = 463$ and 458 meV for beryl and cordierite, Q parallel, Figure 3), and the intensity of the peak is strongly suppressed for the Q -perpendicular orientation. The high-energy components of the peak (at 496 and 490 meV, respectively) can be explained by two-phonon neutron scattering involving the fundamental optical mode (at 463 and 458 meV) and “intermolecular” low-energy vibrational band centered at ~ 33 meV. The coincidence of the stretching O–H peak at ~ 460 meV with that of a free water molecule rather than ice or liquid water suggests that there are no hydrogen bonds acting on this water molecule (in the case of a hydrogen bond acting on a water molecule, the O–H stretching modes getting softer, e.g., ~ 410 meV for ice-Ih, or 425 meV for water⁸).

At energies below 250 meV the $G(E)$ spectra for both minerals are also very similar (Figure 4a,b). The intramolecular water deformation H–O–H mode, ν_2 , is clearly seen at 197.5 meV for both samples, followed by two more peaks at 208.5 and 219.5 meV for beryl, and 203.5 and 208.5 meV for cordierite; these peaks are probably a combination of the ν_2 optical mode and the low-energy modes at 11 and 22 meV for beryl, and 6 and 11.5 meV for cordierite. Earlier, the INS spectrum for synthetic alkali metal free cordierite (type-I water) was measured at 3 K using TFXA spectrometer at ISIS⁹ and the two peaks observed at 6 and 11 meV were assigned to translational motions of water (which is in agreement with our assumption) and a broad band at 27 meV to a librational motion. There is also a peak in our INS spectrum for cordierite (Figure 4b) at 223.5 meV for the Q -parallel orientation, which can be explained as a combination of ν_2 mode and water librational band.

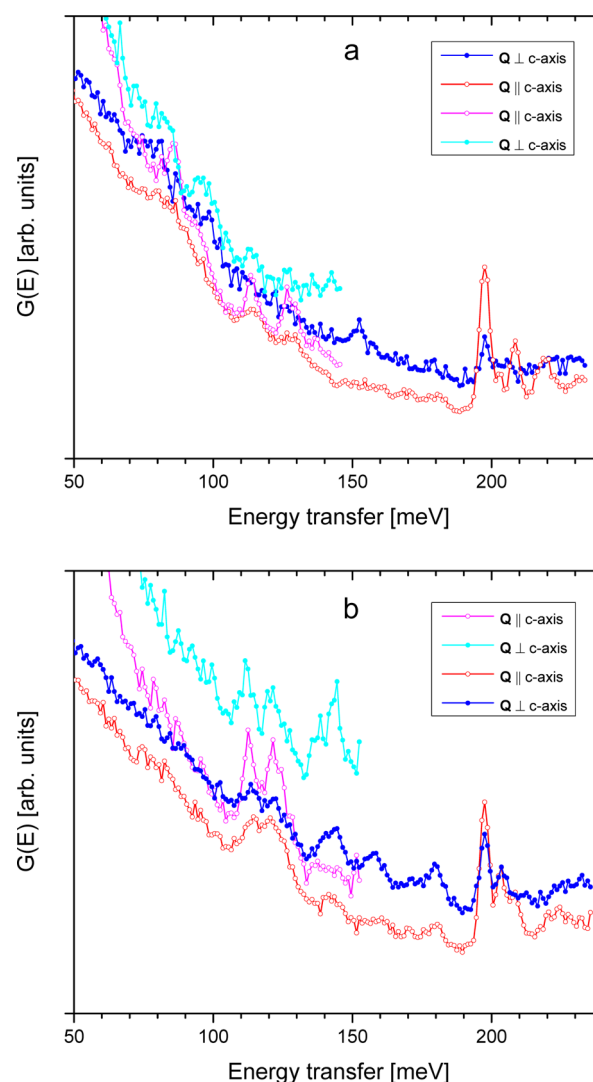


Figure 4. $G(E)$ spectra for beryl (a) and cordierite (b) measured with neutron momentum transfer Q parallel and perpendicular to the crystallographic c -axis; $E_i = 160$ and 250 meV.

According to the empirical relation between the energies for bending and stretching modes of water,¹⁰ $E_{\text{bend}} = 197.3 + 0.26(459.7 - E_{\text{stretch}})$, the observed smallest possible value for the water bending mode (197.5 meV) corresponds to a water molecule having no hydrogen bonds. Other observed modes are at energies 86.0, 114, 128, and 152.5 meV for beryl, and at 112.5, 121.5, 142.5, 157.5, and 179.5 meV for cordierite. The close positions for the peaks at 114 and 128 meV for beryl and 112.5 and 121.5 meV for cordierite indicate their similar origins, which can be related to water librational modes, whereas other listed peaks probably have the multiphonon origin. Note that almost all these modes (except for 152.5 meV for beryl, and 142.5, 157.5, and 179.5 for cordierite) are much stronger for Q -parallel orientation compared to Q -perpendicular one, but the intensity of the spectra between the peaks is more intense for Q -perpendicular orientation. This is probably due to a greater intensity of the low-energy modes of water molecules in the direction perpendicular to the c -axis, which produces the larger $\langle u_{\text{perp}}^2 \rangle$ values for water protons and as a result a larger multiphonon contribution at higher energies. This conclusion is in agreement with the optical spectroscopic measurements,¹¹ where the authors also observe intense

translational and librational vibrations of water in beryl in the direction perpendicular to the c -axis and suggested water tunneling between the equivalent positions in the plane across the channel.

B. Quasielastic Neutron Scattering. Figure 5 shows the temperature dependence of the elastic intensities measured on

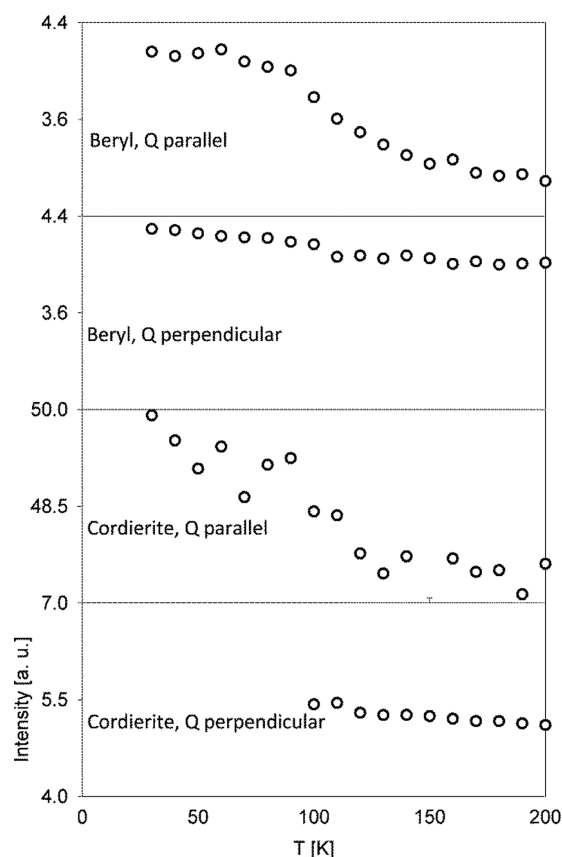


Figure 5. Temperature dependence of the elastic ($3.4 \mu\text{eV}$, fwhm) scattering intensity for beryl and cordierite with the samples oriented in such a way that the scattering vector, Q , was either parallel or perpendicular to the direction of the channels in the sample. Because the data were averaged over $0.2 \text{ \AA}^{-1} < Q < 1.8 \text{ \AA}^{-1}$, the scattering vectors were exactly perpendicular to the channels in the Q -perpendicular orientation, but only approximately parallel to the channels in the Q -parallel orientation. The data were obtained using BASIS.

BASIS for the two different orientations of the samples. The data were averaged over $0.2 \text{ \AA}^{-1} < Q < 1.8 \text{ \AA}^{-1}$. Because the sample orientation remained fixed in both the Q -perpendicular and Q -parallel measurements, the scattering vectors were exactly perpendicular to the channels in the Q -perpendicular orientation, but only approximately parallel to the channels in the Q -parallel orientation. The temperature-dependent spectra in Figure 5 are indicative of the evolution of the dynamics of the water molecules, which at lower temperatures become too slow to be resolved and contribute only to the elastic intensity, leading to the apparent freezing out of the water molecules dynamics. In beryl, the freezing out is pronounced only when Q is aligned parallel to the channels, in agreement with earlier observations.¹ Similar freezing out when Q is aligned parallel to the channels is also observed in cordierite. The anisotropy of the freezing out (that is, lack of this effect when Q is aligned perpendicular to the channels), is evident for beryl, as is likely

the case for cordierite too, even though the elastic intensity scan in the Q -perpendicular orientation for cordierite could not be completed within the allocated experiment time. Nevertheless, the elastic intensity in cordierite in the Q -perpendicular orientation shows no significant increase down to 100 K, whereas such an increase already becomes apparent in cordierite in the Q -parallel orientation, suggesting the same anisotropy in freezing out of the water dynamics in cordierite as in beryl.

To elucidate the nature of the anisotropic dynamic process that exhibits freezing out in beryl (and likely in cordierite too), quasielastic neutron intensity spectra were collected on CNCS for beryl in the Q -parallel orientation at 225 K. This choice of the measurement temperature was made following the quick elastic intensity scan on CNCS that yielded the temperature dependence of the intensity of the elastic peak as presented in the inset of Figure 6. As expected for a dynamic process that

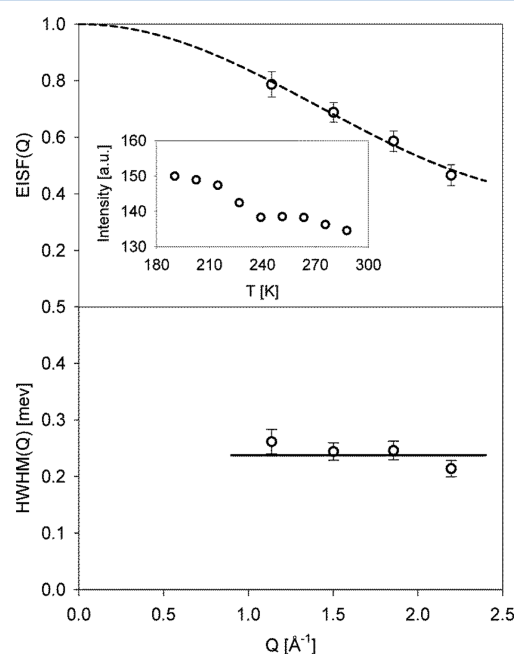


Figure 6. Parameters of the QENS signal obtained from beryl at 225 K in the Q -parallel orientation (exact for every Q value) fitted with eq 1. Top: elastic incoherent structure factor, EISF. Bottom: HWHM of the Lorentzian broadening. Inset: the temperature dependence of the elastic (0.25 meV, FWHM) scattering intensity. The data were obtained using CNCS.

gradually disappears into the resolution line as the temperature is decreased, in the CNCS experiment with its much coarser energy resolution compared to that in the BASIS experiment, the freezing out is shifted to a higher temperature compared to the freezing out seen in the topmost panel of Figure 5. Thus, 225 K is a suitable temperature for studies using CNCS of the dynamic process in beryl that manifests itself with the Q -parallel, but not Q -perpendicular, orientation of the sample. One of the advantages of CNCS measurements is the capability of adjusting the orientation of a sample readily; therefore, for each analyzed Q value in the Q -parallel orientation, the sample was oriented in such a way that the elastic Q was exactly parallel to the channels.

The spectra were analyzed using a sum of the elastic line and a Lorentzian convolved with the resolution function, $R(E)$

(represented by the low-temperature data set), plus a linear background:

$$I(Q, E) = \left[\text{EISF}(Q) \delta(E) + (1 - \text{EISF}(Q)) \frac{1}{\pi} \frac{\text{HWHM}(Q)}{\text{HWHM}(Q)^2 + E^2} \right] \otimes R(E) + B(E) \quad (1)$$

where $\delta(E)$ is a delta function centered at zero energy transfer ($E = 0$), $\text{EISF}(Q)$ represents the elastic incoherent structure factor, $B(E)$ is the linear background term, $B(E) = C_1 E + C_2$, and $\text{HWHM}(Q)$ is the Lorentzian half-width at half-maximum. The parameters of interest, $\text{EISF}(Q)$ and $\text{HWHM}(Q)$, are plotted in Figure 6. The Q -independent HWHM clearly indicates a localized, likely rotational character of the dynamic process. In view of the structural orientation of the water molecules with the dipole moment perpendicular to the channels, it is natural to assume that they can perform 2-fold jumps about the axis coinciding with the direction of the dipole moment. Such jumps would yield QENS broadening in the Q -parallel, but not the Q -perpendicular orientation of the sample,¹² in agreement with the observed anisotropy of the elastic intensity scans (that is, the dynamic process, eventually freezing out, visible only in the Q -parallel orientation). The $\text{EISF}(Q)$ indeed could be fitted with an expression for the 2-fold jump on a circle of a radius r ,¹² $\text{EISF}(Q) = (1 + j_0(2Qr))/2$, where j_0 is the spherical Bessel function of the zeroth order. The fit (short-dashed line in the upper panel of Figure 6) yields $r = (0.74 \pm 0.02) \text{ \AA}$, in good agreement with the value of 0.76 \AA , the expected half-distance between the protons in a water molecule. Such close agreement is, perhaps, fortuitous, given that the functional form of the $\text{EISF}(Q)$ used in the fit was derived for the powder-averaged, not single-crystal scattering geometry.¹² Nevertheless, the anisotropy of the scattering process that yields the QENS signal freezing out at low temperatures strongly suggests that the associated motions of the water molecules do not have a component perpendicular to the channels. Besides, these motions are localized, not translational. For such motions, the 2-fold rotational jump about the axis coinciding with the direction of the dipole moment is a distinct possibility. The characteristic time between the water molecule jumps at 225 K can be estimated as (ref 12) $\tau = 2\hbar/\text{HWHM} = 5.5 \text{ ps}$. We can conclude that the dynamic process visible in the Q -parallel orientation that exhibits freezing out on cooling down is associated with localized jumps, not translational motions. Indeed, the latter motions were previously observed to be much slower, yielding QENS broadening on the scale of several μeV ($\sim 100 \text{ ps}$) at 300–370 K.¹

The cordierite sample with type-I water was previously studied with QENS (with 0.5 meV resolution) at room temperature and above,¹³ and it was shown that water molecule exhibits rotational diffusion with the residence time at room temperature is $\tau = 6 \text{ ps}$ (which is comparable to that in beryl at 225 K), and the EISF was best fitted with the model based on a radius of gyration of 0.4 \AA , which corresponds to water molecule jumps around the c -axis.

IV. CONCLUSIONS

Strong anisotropy was observed for dynamics of water confined in narrow ($\sim 5 \text{ \AA}$) channels of single crystals of beryl and cordierite by using inelastic and quasielastic neutron scattering. The INS spectra showed that vibrations parallel to the channels are significantly more hindered than that perpendicular to them

and that water in beryl and cordierite experiences steep potential along the channels and a very soft one across them. The QENS study of the beryl showed that water molecules perform rotational jumps, which can be described by a model of the 2-fold rotational jumps about the axis coinciding with the direction of the dipole moment (that is, perpendicular to the channels), with a residence time at 225 K of 5.5 ps. The rate of these rotational jumps gradually slows down as the temperature is decreased, until their dynamics becomes too slow for a given energy resolution of the QENS experiment, resulting in the apparent resolution-dependent freezing out of the water molecules dynamics.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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