

Movement of channel H₂O in cordierite observed with quasi-elastic neutron scattering

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ABSTRACT

Quasi-elastic neutron scattering experiments have been performed on natural and synthetic, hydrous and anhydrous, powder samples of cordierite to elucidate the dynamics of the H₂O molecules incorporated in the cavities of the cordierite structure. At room temperature, all protons are dynamically disordered. A simple jump model yields residence times at room temperature of about 6 ps. These measurements show that a static description of the orientation of the H₂O molecules is inappropriate, which is in agreement with earlier NMR measurements. A model is proposed in which the H₂O molecules in alkali-free cordierite, where ideally all the proton-proton vectors are aligned || [001], revolve around their center of gravity while maintaining their orientation. This model is based on the wave-vector dependence of the elastic incoherent structure factor, which leads to a very small radius of gyration (≈ 0.4 Å). The proposed model is compatible with earlier infrared experiments, in which no disorder of the orientation of the proton-proton vector was observed at room temperature. It is also consonant with the large anisotropic atomic displacement parameters observed for the O in H₂O in earlier structural studies. In agreement with a recent theoretical study, the model proposed here implies that it is not the O in H₂O that is located at the center of the cavity but rather the center of mass of the molecule. Within the resolution of the current experiments, the time scale of the dynamic behavior of the protons in natural or synthetic samples is similar.

INTRODUCTION

The dynamics of H₂O molecules in structural cavities of silicates is of great interest, as it is the manifestation of the generally poorly understood interaction between the incorporated "guest" and the framework. These interactions are not only responsible for a variety of fascinating crystallographic phenomena, such as the ordering of the guest molecules and structural phase transitions leading to pseudosymmetric structures, but they also contribute to the thermodynamic properties of these compounds. The dynamics of H₂O molecules can be investigated by a number of techniques, such as nuclear magnetic resonance spectroscopy (NMR), vibrational spectroscopy (infrared and Raman), and quasi-elastic neutron scattering. Although quasi-elastic neutron scattering is a unique technique for the investigation of dynamic and geometric aspects of the movement of protons on very short time scales (in the picosecond regime, 1 ps = 10⁻¹² s), it has only rarely been used in the investigation of the dynamics of H₂O molecules in minerals. Typical examples of such earlier studies are those on the zeolites, especially harmotome (Fuess and Stuckenschmidt, 1988; Stuckenschmidt et al., 1988) and clays (Olejnik and White, 1972; Poinson et al., 1989). As part of a continuing project in which the dynamics of H₂O molecules

in minerals are investigated by neutron scattering techniques, we have begun to study the dynamics of H₂O molecules in cordierite using incoherent quasi-elastic neutron scattering.

Cordierite, (Mg,Fe)₂[Al₄Si₃]O₁₈·nH₂O, has an orthorhombic framework structure (space group *Cccm*), with cavities (about 6 Å in diameter) that are linked to form channels parallel to [001] (Gibbs, 1966). A variety of atoms, ions, and molecules can be incorporated into the cavities, and in natural cordierite the channels are commonly occupied by H₂O, CO₂, and alkali ions (Armbruster and Bloss, 1982). The channels can be evacuated by heating and refilled under pressure (Johannes and Schreyer, 1981; Armbruster, 1985). Langer and Schreyer (1976) deduced from geometric considerations that, because of the relatively small size of the cavities, it is unlikely that more than one molecule can be incorporated into a single cavity, and that the H₂O-framework interaction was very weak. There have also been suggestions that there might be two H₂O molecules side by side in a single cavity (Mirwald, 1982), but no such double occupation has ever been detected in structural studies of either synthetic or natural cordierite, to the best of our knowledge. Structural studies based on diffraction experiments gave contradictory results. From diffraction experiments, Cohen

et al. (1977) concluded that in natural Mg-rich samples the H₂O was oriented with its molecular plane parallel to (001), and they inferred from their structure refinements that the H₂O molecule was strongly asymmetric [$d(\text{H1-O}) = 1.04 \text{ \AA}$, $d(\text{H2-O}) = 0.97 \text{ \AA}$], and that the H1-O-H2 angle was compressed to 102.4°. Cohen et al. (1977) assumed disorder over four positions. Hochella et al. (1979) proposed that the O in H₂O was located at $\pm 0.027, 0, \frac{1}{4}$, and the molecular plane was inclined by $\approx 29^\circ$ from (100), with the H-H vector inclined 19° from [001]. Hochella et al. (1979) also concluded that the H₂O molecule was asymmetric. These studies pose the question why a very loosely bonded H₂O molecule should be distorted. Also, in the work of Cohen et al. (1977), the weaker H bond leads to a lengthening of the O-H distance of the H₂O molecule, although increasing H bonding leads to a lengthening of the O-H distance (Nakamoto et al., 1955; Novak, 1974). Recent ab-initio calculations (Winkler et al., 1994) show that the H₂O molecule is undistorted, in agreement with spectroscopic experiments mentioned below.

It was Smith and Schreyer (1962) who first suggested that H₂O in cordierite is "not rigidly fixed in the centers of the cavities." Subsequently, the orientation and the dynamics of the H₂O molecules in cordierite have been the subject of several spectroscopic studies. Vibrational spectroscopic data (Farrell and Newnham, 1967; Goldman et al., 1977; Aines and Rossman, 1984) have been interpreted as showing that, for alkali-poor cordierite, the proton-proton vector is aligned parallel to [001], with the molecular plane lying in (010) in the crystal setting of Farrell and Newnham (1967), which has interchanged **a** and **b** axes relative to that of Goldman et al. (1977). In this paper, the former setting will be used. H₂O molecules with their proton-proton vector parallel to [001] have been termed type I; if the proton-proton vector is perpendicular to [001], the H₂O is said to be of type II. Aines and Rossman (1984) investigated the changes in the infrared spectrum of beryl and cordierite over a large temperature interval and deduced that above 473 K bound H₂O changes into an unbound state, that the temperature at which H₂O leaves the cordierite structure is 873 K, and that just below this temperature the ratio of bound to unbound H₂O is 3:1. Proton NMR measurements on natural alkali-bearing samples (Tsang and Ghose, 1972; Carson et al., 1982), however, showed that the H₂O molecules are dynamically disordered at room temperature. Carson et al. (1982) came to the conclusion that their NMR data were in agreement with infrared data of Goldman et al. (1977), who had observed type I and type II H₂O in their natural samples, under the assumption that, relative to the time scale of the NMR experiment (milliseconds), the H₂O changes its position rapidly, but that it changes position slowly with respect to the time scale of the infrared experiment (picoseconds).

In the present study, the time scale on which the H₂O molecules move has been investigated. Here, direct evidence of the motion of the H₂O in cordierite is presented,

obtained from quasi-elastic neutron scattering on a significantly shorter time scale than in the NMR experiments. Experimental aspects and methods for the evaluation of quasi-elastic neutron scattering studies have been summarized by Bee (1988). The principles and use of this method for mineralogical problems have been summarized by Line et al. (in preparation). Because of the very large incoherent scattering cross section of H, it is possible to observe the motion of H₂O molecules even at low concentration (on the order of 1 wt%), which is common in a variety of minerals. During the experiments using natural samples, we realized that we could not properly correct for elastic incoherent scattering by non-H elements. Because of the low H₂O concentration, the elastic incoherent scattering by other elements, especially Na in the channel, cannot be neglected; it prevents the determination of the elastic incoherent structure factor (EISF). Therefore, additional quasi-elastic neutron scattering experiments were performed with hydrous and anhydrous synthetic powder samples on a triple-axis spectrometer, albeit with a lower energy resolution. During the time-of-flight (t-o-f) experiments, we observed some unexpected low-frequency inelastic peaks. These were further investigated using single crystals, and a tentative assignment is presented.

EXPERIMENTAL METHODS

High-energy-resolution quasi-elastic neutron-scattering experiments using natural samples were performed on the six-chopper t-o-f spectrometer, Mibemol, situated at a cold neutron guide at the Orphee reactor of the Laboratoire Leon Brillouin at Saclay, France. One needs to appreciate that neutron beam time for high-resolution quasi-elastic experiments is at present in such short supply that only the minimum length of time necessary was made available for the experiments described here. The cordierite from Origaervi, Finland, was kindly provided by T. Armbruster (University of Bern, Switzerland). The sample was briefly ground, so that the largest grains were smaller than about 0.5 mm³. The sample was put in a Nb container with thin walls (0.1 mm), which was mounted in a radiation furnace. The tank in which the furnace was mounted was evacuated to 10^{-4} – 10^{-5} mbar. The sample was initially heated to 373 K, and during this period a noticeable degassing occurred, as could be observed by a sudden increase of pressure. After a few minutes, the degassing desisted; degassing also desisted after a few minutes when the sample was subsequently heated to 750 K or, at a later stage, when it was kept exposed to air for 1 d at room temperature and then reheated to 400 K. We therefore conclude, that H₂O that was adsorbed on the sample surface and on channel alkalis close to the surface had been driven off during the first heat treatment. The dehydration temperature of the sample used here is comparatively high, first, because the sample fragments were large, and hence, the diffusion distances very long, and second, because of the alkali ions, which are always pres-

ent in the natural samples, and which block the channels. For similar samples, Goldman et al. (1977) reported dehydration temperatures above 1000 K.

Several measurements at different temperatures were performed using incident neutrons with a wavelength of $\lambda = 7.5 \text{ \AA}$ and an elastic resolution (FWHM) of $50 \mu\text{eV}$. A measurement of an empty sample can for background subtraction and a measurement of a V standard for detector efficiency calibration and the determination of the instrumental resolution function were performed at room temperature. About 300 ³He detectors were grouped in banks at angular positions of $2\theta = 39.5, 45, 51.1, 57.4, 63.8, 72.3, 78.9, 98.5, 108.4, 117.3, 124.9, \text{ and } 137^\circ$.

During the high-resolution experiment, we realized that, because of the low concentration of H₂O, it was not possible to neglect the contribution of the other constituents to the elastic incoherent peak. This prohibited the evaluation of the elastic incoherent structure factor, as a subtraction of the unwanted incoherent scattering component seemed difficult; it was thought that a degassing might induce changes beyond the dehydration, which would falsify a subsequent interpretation. We were concerned about the loss of alkali ions located in the channel, especially Na, which has a relatively large incoherent scattering cross section. To ascertain that high-resolution experiments on synthetic samples are feasible, further quasi-elastic neutron scattering experiments were performed on the triple-axis spectrometer (TAS) 4F1, situated at a cold neutron beam tube of the Orphee reactor using hydrous and anhydrous synthetic samples. Also, for a comparison between the high-resolution and the TAS experiments, the same natural powder sample that had been used in the t-o-f experiment was employed. Furthermore, we investigated changes in that sample induced by degassing it at high temperatures.

The synthetic Mg end-member cordierite for the TAS experiment was synthesized by quenching a melt of a stoichiometric mix of the oxides to obtain a glass. The glass was ground and remelted several times at 1835 K, and electron microprobe analysis was used to ascertain its homogeneity. The glass was then crystallized at 1273 K, and the resulting hexagonal cordierite was converted into the orthorhombic polymorph by annealing the sample at 1673 K for 1 week. X-ray powder diffraction showed one very weak peak with a d value = 3.207 \AA , which could not be indexed. Ten grams of hydrous cordierite were synthesized by subjecting anhydrous cordierite to 3 kbar H₂O pressure at 853 K for about 1 week. At the end of the experiment, the vessels were cooled by blowing cold air on them; it took about 20 min to reach 373 K. Thermogravimetric analysis (TGA) confirmed that 2.6 wt% of H₂O had been incorporated (Fig. 1).

The TAS measurements using the synthetic powder samples were performed at room temperature. About 8 g of cordierite were loaded into a cylindrical Al container, with a height of 50 mm and an inner diameter of 10 mm. Energy transfers were between -1 and 1 meV , and mo-

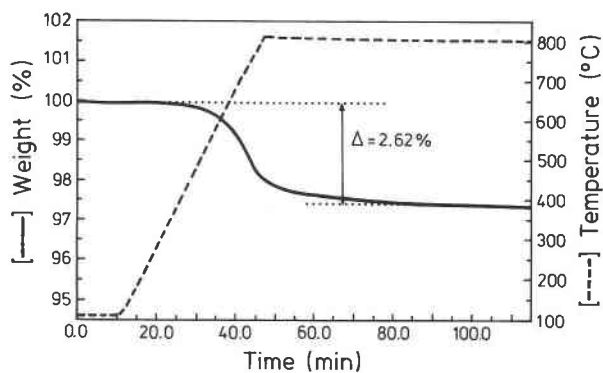


Fig. 1. Thermogravimetric analysis of the hydrous cordierite used in the TAS experiments. The continuous curve is the weight of the sample (%: left scale). The dashed line is the temperature of the sample (right scale).

mentum transfers were between 0.25 and 2.25 \AA^{-1} . Also, several measurements at larger energy transfers and several momentum transfers were performed at room temperature and 150 K during the search for the inelastic peaks seen in the t-o-f spectra on the natural sample. For all of these measurements, the instrumental conditions were similar to those described below for the single-crystal measurements.

Powder measurements on the same natural sample that had been used in the t-o-f experiments were also performed on the TAS to allow a comparison between the two techniques. The agreement was excellent. To investigate if the inelastic peaks were due to volatiles in the channels, the sample was heated under vacuum to 1123 K and kept there until no further degassing could be observed. Then the inelastic measurements were repeated.

To obtain a more complete description of the inelastic peaks observed in both the t-o-f and the TAS experiment on the natural sample, single-crystal measurements were performed. Natural, gem-quality crystals were kindly provided by T. Armbruster of the University of Bern and S. Herting-Agthe of the Technical University of Berlin. The Swiss sample was cut and had a size of about 400 mm^3 , the Berlin sample was uncut and had a size of about 800 mm^3 . Both samples were strongly pleochroic, with colors ranging from an intense purple-blue to a light brownish gray. Measurements were performed along all three basic reciprocal translation vectors for a variety of momentum transfers and temperatures. Typically, energy transfers ranged from about -1.4 to 3 meV . For some measurements, the incident wave vector, k_i , was fixed to 1.64 \AA^{-1} ($\lambda = 3.83 \text{ \AA}$), but, for the measurements aimed at determining the inelastic peaks at higher energy transfers, the measurements were performed with a fixed, final wave vector, k_f . Depending on the measurement conditions, either a pyrolytic graphite filter was used to suppress higher-order contaminations to $< \sim 3\%$, or a Be filter cooled by liquid N₂ was employed. No collimators were used, but, because of the horizontally curved ana-

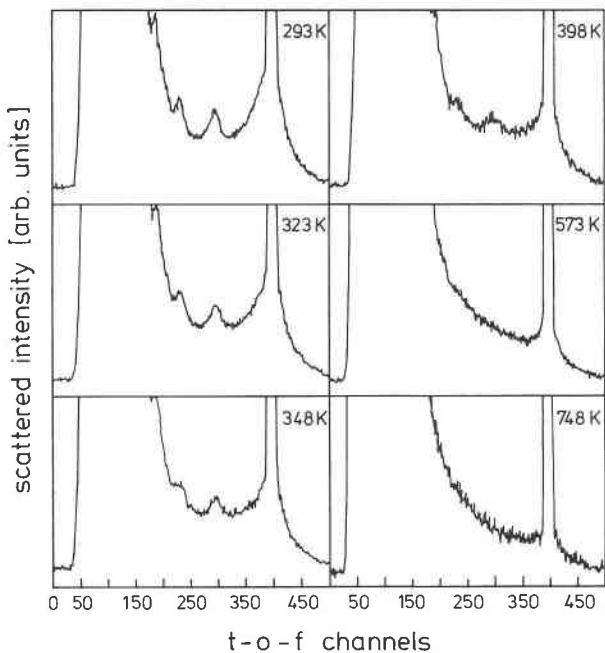


Fig. 2. Time-of-flight spectra of cordierite obtained at several temperatures. The elastic peak is near channel 400; the first inelastic peak mentioned in the text is at approximately channel 300.

lyzer, the equivalent collimation was $-/30/45/45$. For most measurements, the resolution (FWHM) was about $223 \mu\text{eV}$ for the elastic peak, and it varied from about $200 \mu\text{eV}$ for the energy gain measurements to about $340 \mu\text{eV}$ for the highest energy-loss measurements. The sample was cooled using a closed-cycle refrigerator, with the sample chamber filled with H as an exchange gas for some measurements, whereas for others no exchange gas was used. The temperature was measured with a standard Pt resistor, and temperature stability was approximately 0.1 K for the measurements with an exchange gas and about 2 K for those without.

RESULTS

The background-corrected and normalized t-o-f spectra, averaged over all scattering angles, are shown in Figure 2. Channel 0 corresponds to the arrival time of the neutrons at the sample. The maximum in the intensity, approximately t-o-f channel 390, is the elastic peak due to neutrons that were scattered by the sample without a change in energy. Its FWHM of $50 \mu\text{eV}$ is due to the convolution of a Dirac δ , with the triangular resolution function of the instrument. A second component, much broader and of less intensity, centered at the same t-o-f channel as the elastic peak, is the quasi-elastic contribution due to the motion of the protons. The very strong signal at t-o-f channels at short flight times and the sloping background around the elastic peak are due to phonons. Superimposed on this effective phonon density of

states are a number of peaks, which we call the inelastic peaks. The high-temperature experiments at 573 and 748 K were conducted first, followed by the room-temperature measurement and, finally, the experiments at intermediate temperatures. All observed changes in the spectra were reversible.

The normalized and background-corrected data around the elastic peak were analyzed by fitting them with the convolution product:

$$\left[A_0(Q)\delta(\omega) + A_1(Q)\frac{\Gamma}{\pi(\omega^2 + \Gamma^2)} + C_1(Q)\omega + C_2(Q) \right] \otimes R(\omega, Q).$$

The first term within the bracket describes the elastic, and the second term the quasi-elastic scattering originating from the motion of the protons. The third and fourth terms describe the background. R is the instrumental resolution function obtained from a V experiment. Details of the numerical treatment of quasi-elastic spectra may be found in Bee (1988) or Line et al. (in preparation).

Although a quasi-elastic component was observed at all temperatures, at temperatures above room temperature, the quasi-elastic contribution gets too broad to be distinguished unambiguously from the background. At room temperature, an extrapolation to a zero wave-vector transfer gives an HWHM, Γ , $\approx 0.1 \text{ meV}$. The extrapolation is necessary, as the quasi-elastic signal vanishes as $Q \rightarrow 0$. To a first approximation, the residence time, t , of the protons can be obtained from $t = \hbar/\Gamma \approx 6 \text{ ps}$. There is no long-range translational diffusion, as this would, according to Fick's law, lead to $\Gamma \rightarrow 0$ for $Q \rightarrow 0$.

For a further analysis of quasi-elastic neutron scattering data, the ratio of the incoherently elastically scattered intensity to the total incoherently scattered intensity as a function of momentum transfer, $A(Q)$, is calculated to obtain the elastic incoherent structure factor (EISF), whose wave-vector dependence can give insight into the microscopic aspect of the motion of the proton (Bee, 1988, 1992):

$$A(Q) = \frac{I^{\text{el}}(Q)}{I^{\text{el}}(Q) + I^{\text{qe}}(Q)}$$

where el is an abbreviation for incoherent elastic and qe stands for incoherent quasi-elastic. The elastic incoherent peak is due to the localization of the incoherent scatterer, and the quasi-elastic component is due to the characteristic time of the motion of the incoherent scatterer (Bee, 1988, 1992). Hence, in a solid (e.g., V, which has a large incoherent cross section and is therefore used to determine the resolution function of the spectrometer, as has been mentioned above), only the elastic incoherent component can be observed, as all the atoms are fixed at their sites. In contrast to this, the absence of the incoherent elastic peak and the presence of only incoherent quasi-elastic scattering are characteristic for liquids, e.g., water (Bellisent-Funel and Teixeira, 1991; Salmon, 1989). In cordierite, both components have been observed, and

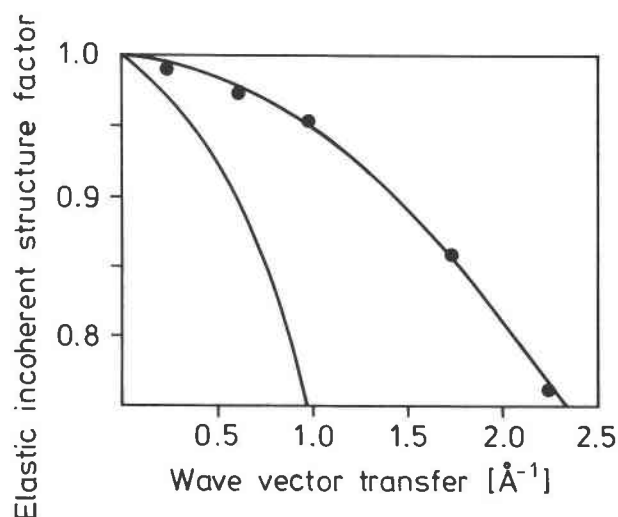


Fig. 3. Observed elastic incoherent structure factor (circles). A jump model based on a radius of gyration of 0.4 Å describes the data well. For comparison, the EISF for a jump model with a radius of 1 Å is indicated as well.

hence the protons are dynamically disordered, but they are confined to a small volume.

As has been mentioned above, we could not correct for the incoherent scattering by non-H elements in the initial high-resolution experiments. In the TAS experiments, with the synthetic samples, results obtained with the anhydrous sample were used for a background correction. After the subtraction, the data obtained with the hydrous sample were evaluated using a procedure similar to the one employed in the analysis of the t-o-f data. The EISF is shown in Figure 3. The extrapolation of the EISF to $Q = 0$ shows that $A(Q = 0) \approx 1$. This is the expected value for the EISF, as the time correlation of a position vector associated with the incoherent scatterer at the time origin, $r(0)$, and at time t , $r(t)$, is investigated in the limit of $t \rightarrow 0$. This confirms that our observations are not influenced by multiple scattering, as this leads to a decrease in the EISF at $Q = 0$ (Bee, 1988, 1992).

The interpretation of the EISF is model-dependent. In analcime (Line et al., in preparation), similar measurements and results indicated that only a fraction of the H₂O molecules were reorientating. Hence the measured EISF was smaller than the EISF corresponding to the motion of the protons. This could, in principle, also be the case in the present measurements. However, the NMR measurements of Carson et al. (1982) indicate that at room temperature there is only one kind of H₂O which is undergoing a reorientational anisotropic motion. A qualitative analysis of our high-temperature data supports the conclusions of Carson et al. (1982), as no additional quasi-elastic signal has been observed. Therefore, although the jump geometry and characteristic time of the motion at high temperatures may be very different (which is likely to be the case, as is indicated by the high-temperature data of Aines and Rossman, 1984, and an

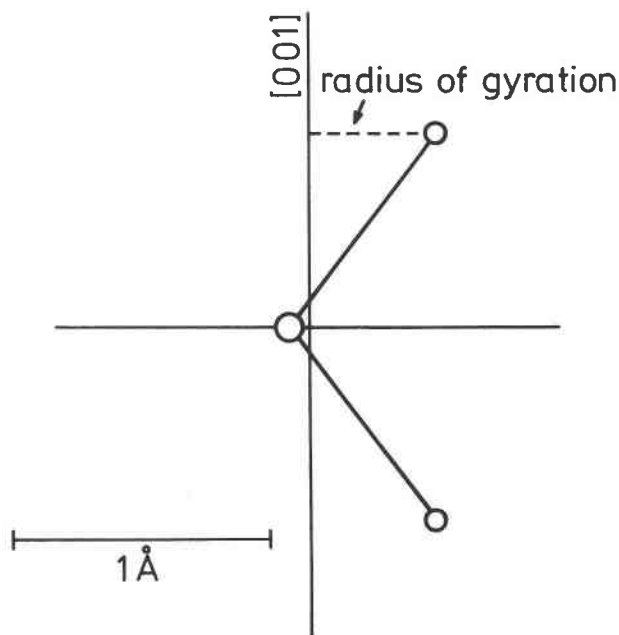


Fig. 4. Schematic representation of the model proposed in the present study. A rigid H₂O molecule with its center of mass located near the center of the cavity revolves around [001] while maintaining the orientation of the H-H vector. A two-orientation model is proposed, where the second orientation of the H₂O molecule is obtained by a 180° rotation around [001]. The protons move on a circle that has a radius of gyration of about 0.5 Å.

extrapolation of the data of Carson et al., 1982), the number of protons moving does not seem to increase.

The model proposed by Carson et al. (1982) implies the localization of the protons on a sphere or an ellipsoid around the center of the cavity with a radius of ≈ 1 Å. Our measurements yielded a wave-vector dependence of the EISF that could not be fitted to such a model (Fig. 3). Hence, here we propose an alternative model based on a rigid H₂O molecule with a fixed orientation of the proton-proton vector (Fig. 4). The dynamics of this H₂O molecule can be derived from the revolution around its center of mass. A fixed orientation of the proton-proton vector implies that the protons would move on a circle, as has been indicated in Figure 4. This may be either a hopping motion between distinct sites or a continuous, diffusive motion. The EISF for a powder average of such a model has been calculated by Bee (1988). Figure 3 shows that a model based on a radius of gyration of 0.4 Å describes the wave-vector dependence of the EISF well. However, the restricted data set obtained in the present study does not allow a more detailed interpretation. The simplest model would be a two-orientations model, where for each proton two positions, related to each other by a mirror plane in (100), would be energetically most favorable. A rigid H₂O molecule would then revolve around its center of mass, and the protons would each move on a circle that is characterized by its radius of gyration. In this model, the proton-proton vector is always parallel to [001].

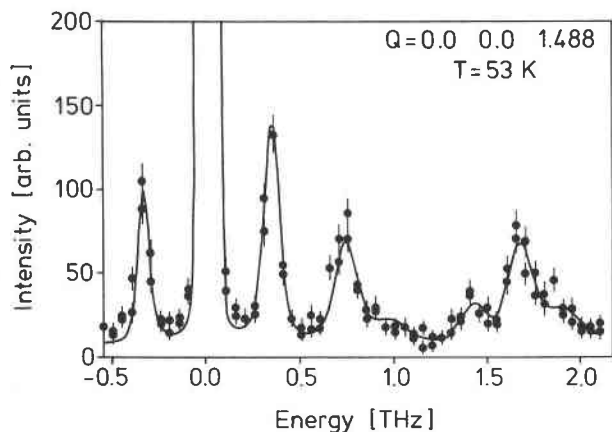


Fig. 5. Typical inelastic scan obtained during a TAS experiment. The incoherent elastic peak is at 0 energy transfer; the weak peaks at approximately 1 THz (4.1 meV) and 1.7 THz (6.9 meV) are contaminations.

The time taken for the reorientation is assumed to be negligible; this is virtually always assumed in the interpretation of quasi-elastic neutron scattering data. Experiments on time scales longer than the picosecond regime therefore always give a constant orientation of the molecular plane, which, in the setting used here, is parallel to (010).

Other features in the *t*-*o*-*f* spectra (Fig. 2) are low-energy inelastic peaks. There was no significant change in the intensity or position of the inelastic peaks of the degassed natural sample relative to the same sample before the degassing. No such peaks could be observed under any measuring condition in the synthetic samples. The single-crystal experiments obtained between room temperature and 20 K for several wave vectors along the three basic directions of the reciprocal lattice allowed a more thorough description of the inelastic peaks. A typical result is shown in Figure 5. The peaks at approximately 0.99 (very small) and 1.6 THz (Fig. 5) are contaminations caused by elastic scattering ($3\mathbf{k}_i = 4\mathbf{k}_r$, and $2\mathbf{k}_i = 3\mathbf{k}_r$ contamination). At all temperatures, the ratios of the intensities of the inelastic peaks observed in energy gain to those observed in energy loss are related by the detailed balance principle. These excitations are anisotropic and are most probably due to transitions between ground states split by the crystalline electric field experienced by $^{56}\text{Fe}^{2+}$. We are currently investigating if the excitations can be used as a local probe for the Fe environment, and a full discussion will be given in another study.

DISCUSSION

A model that attempts to explain the motion of the H₂O molecules must consider previous X-ray, NMR, infrared, and optical data. Here we discuss whether the model derived above, in which a rigid H₂O molecule with a fixed orientation of the proton-proton vector relative to [001] revolves around its center of mass, is consistent

with all the earlier and present data. In the absence of further data, the discussion is restricted to the simplest model, which is the two orientation model described above.

First, we consider only the case in which there are no alkalis in the channel. The infrared spectroscopic measurements do not necessarily imply that the molecule is bound, as has been inferred by Aines and Rossman (1984), but only show that there is no significant disorder of the orientation of the proton-proton vector relative to [001] on the time scale of the IR experiment and that the molecular plane is parallel to (010) virtually all the time. Hence the two-orientation model proposed here is consistent with these measurements. In their temperature-dependent, infrared spectroscopic study (Aines and Rossman, 1984), the appearance of a broad band at 473 K indicated the free reorientational motion of the H₂O molecules. The temperature for the appearance of freely rotating H₂O molecules obtained by Aines and Rossman (1984) is in good agreement with an extrapolation of the NMR data of Carson et al. (1982), which implies that all H₂O molecules rotate isotropically at about 450 K. However, these two results show that there is a distinct difference between the high-temperature motion and the dynamics at room temperature, which have been investigated in the present study.

From structure refinements of hydrous cordierite it is well known that the O is localized near or at the center of the cavities. The atomic displacement parameters of the O in H₂O show a distinct anisotropy, with $U_{11} \approx U_{22} \approx 2 \times U_{33}$ (Armbruster, 1985). These U_{ij} are one order of magnitude larger than the atomic displacement parameters of the framework atoms, and hence the X-ray data imply that the O in H₂O is either statically or dynamically disordered. Both NMR and our quasi-elastic experiments show that the H₂O is dynamically disordered; the quasi-elastic neutron scattering experiments indicate that this disorder is on the picosecond time scale. Hence the X-ray data can be interpreted by assuming that the O in H₂O is moving in (001) around the center of the cavity at 0,0,1/4. If one assumes a rigid H₂O molecule, with its proton-proton vector parallel to [001], an O-H distance of 1 Å, and an H-O-H angle of 104.5°, revolving around its center of mass, the protons would move on circles with radii of ≈ 0.54 Å (Fig. 4). The observed radius of gyration (≈ 0.4 Å) is smaller than the value obtained from this simple model. However, the deformation of the H₂O molecule due to the host-guest interactions and the actual dynamics of the H₂O molecule, which have been approximated only roughly, may explain this relatively small difference. A recent theoretical study by Winkler et al. (1994) also showed unambiguously that an orientation of the proton-proton vector parallel to [001] was energetically most favorable, and that the O in H₂O of the undistorted molecule was slightly displaced within (001) from the center of the cavity. The orientation of the molecule obtained in the theoretical study is different from that in the model presented here, as the center of mass

in the ab-initio calculations did not coincide with the center of the cage. However, because of computational limitations, the influence of the dynamics of the molecule on its orientation have not been studied. Also, for the same reason, Winkler et al. (1994) could not study the effect of different orientations of the molecular plane.

The model proposed here is different from that proposed by Carson et al. (1982), as in the latter the H₂O molecules flip between the two distinct positions corresponding to H₂O of type I and type II, i.e., with the proton-proton vector parallel or perpendicular to [001], respectively. The data presented here are not consonant with the time-scale argument invoked by Carson et al. (1982), as the motion of the protons is without any doubt on the picosecond time scale. Furthermore, the observed radius of gyration is only half as large as would be expected if the model based on the NMR data were correct. The infrared spectroscopic data also indicate that there is no flipping between the two orientations of the proton-proton vector at room temperature in alkali-free samples, as the intensity of infrared absorption bands characteristic for H₂O type II can be directly correlated to the presence of alkalis. The combination of the earlier and the present data can also be used to exclude a rotation around the diad of the H₂O molecule, as this would lead to a radius of gyration of ≈ 0.8 Å. It is, therefore, not compatible with the observed value.

Could the differences between the model proposed by Carson et al. (1982), who used alkali-bearing samples, and the model proposed here be due to the channel cations? It has long been recognized that, because of electrostatic interactions, the H₂O molecule could rotate so that the proton-proton vector is perpendicular to [001]. This actually seems not to influence the time scale of the dynamics of the protons, as the width of the quasi-elastic component observed in synthetic and natural (alkali-bearing) samples are indistinguishable. However, the potential in which an H₂O molecule close to an alkali ion moves is different from that experienced by an H₂O molecule in Mg end-member cordierite. As the orientation of the H₂O molecule is not due to H bonding, electrostatic interactions, probably between the O in H₂O and the framework O atoms, determine the potential in which the molecule moves. It is currently thought that, similar to beryl (Sherriff et al., 1991), in an idealized case each alkali ion located in the center of the six-membered ring is coordinated by two H₂O molecules in the two adjacent cavities. The possibility of a flipping motion between the two orientations of the H₂O molecule, which has not been observed directly yet, would then depend on the strength of the attractive interaction between the alkali ion and the O in H₂O. A model such as described by Sherriff et al. (1991) implies a relatively strong bonding, as there is virtually no shielding between the alkali and the O in H₂O. The model proposed here would then lead to the suggestion that, in this case, the orientation of the proton-proton vector is fixed perpendicular to [001], and that

therefore the H atoms would move in (001), thus having a radius of gyration of 0.8 Å. However, as noted above, the presence of Na in the channel must be taken into account when measuring the EISF, which greatly complicates the experiments.

The present data set is too limited to allow an unambiguous determination of the geometry of the movement of the H₂O molecules. The experiments necessary to confirm the present model and to determine the jump model are very demanding but may become feasible with the advent of new, more powerful neutron sources. The quasi-elastic scattering has to be measured up to wave-vector transfers of 10 \AA^{-1} . The resolution (FWHM) for elastic scattering must be better than about $150 \mu\text{eV}$. The minimum of the EISF should be at a wave vector transfer of about 5 \AA^{-1} ; this would confirm a jump over two sites on a circle with a radius of 0.4 Å. If the EISF only drops down to a low value of ≈ 0.1 without increasing at larger wave-vector transfers, that would indicate the protons hop over more than four sites. At higher temperatures, the radius of gyration should get larger until it reaches a value of ≈ 1.2 Å, which would indicate free rotation of the H₂O molecules.

In summary, the quasi-elastic neutron scattering experiments here have confirmed that the H₂O molecules are dynamically disordered at room temperature. This excludes a static description, such as has been proposed by Hochella et al. (1979). It also implies that the H₂O is not bound in a conventional sense, as has been deduced by Aines and Rossman (1984), but rather that the H₂O is fixed in a certain orientation because of short-range interactions with the framework and that these interactions do not prohibit a revolving motion. This has been deduced from the observed small radius of gyration, which has led to a model with a fixed orientation of the proton-proton vector. This model is therefore consonant with atomic displacement parameters derived from earlier X-ray studies (Armbruster, 1985) and the orientation of the proton-proton vector and the molecular plane obtained from infrared studies (Farrell and Newnham, 1967; Goldman et al., 1977; Aines and Rossman, 1984) and a theoretical study (Winkler et al., 1994). The present study also confirms some of the findings of a previous NMR study (Carson et al., 1982), namely, that the dynamics are indeed faster than what can typically be resolved with NMR measurements.

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