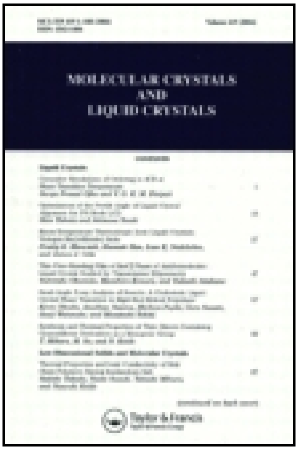

# Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

# Dynamics of Intercalated Water Molecules in Synthetic Layered Silicates

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# Dynamics of Intercalated Water Molecules in Synthetic Layered Silicates

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Diffusional motions of water molecules in a synthetic fluorinated layered silicate have been studied by neutron scattering. Motions in a one-water-layer hydration state are slower than in those in a two-water-layer hydration state. Good fits to the data were obtained with the Kohlrausch-Williams-Watt lineshape that is often applied to disordered systems.

*Keywords:* water dynamics; neutron scattering; clay; layered silicates; hydration

## INTRODUCTION

Many of the most fascinating and useful properties of clay minerals derive from the interaction of water with these ubiquitous materials. Questions regarding how and why water is taken up or expelled and how it moves within the material are of basic interest. Detailed investigations of water dynamics by modern techniques have included several neutron scattering studies [1-3]. The present study differs from previous ones in that a synthetic clay material is used, which has the advantages of superior neutron properties and well-defined, easily achieved hydration states.

The broadening of scattering near zero energy transfer in an inelastic neutron scattering experiment provides a powerful probe of the scattering system. Such quasielastic scattering is present only if some of the scattering atoms do not have well-defined time-average positions, i.e, it is indicative of diffusional motion as opposed to vibrational motion. The dependence of the quasielastic intensity and lineshape on the wave vector transfer Q is determined by the geometry and rapidity of the diffusional motion.

## THE SYSTEM UNDER STUDY

A synthetic fluormica obtained from Co-op Chemical Co., Ltd., in Japan, was used in our experiments. It consists of silicate layers separated by interlamellar spaces that contain $Na^+$ counterions. In this material, each silicate layer comprises a sandwich of two sheets of silica tetrahedra straddling an interior sheet of oxygen octahedra. It is instructive to compare structures and composition with Na-vermiculite, which may be represented as $Na_{0.67}Mg_3Si_{3.34}Al_{0.66}O_{10}(OH)_2$. All of the sites available to $Mg^{2+}$ ions within the octahedral layers are occupied. Hydroxyl groups occupy positions within the silicate sandwich, such that the OH line points toward the interlamellar site occupied by Na ions. In the synthetic fluormica, which may be represented as $Na_{0.67}Mg_{2.67}Si_4O_{10}F_2$, there are 0.33 vacancies per formula unit in the sites available to Mg, there are no Al atoms substituting for Si, and the OH groups are replaced by F atoms. Like Na-vermiculite, the fluormica is expandable, able to absorb one or two water layers which hydrate the Na ions in the interlamellar space. The dry material has a separation between silicate layers of 9.7 Å, expanding to 12.6 and 15.7 Å in the one- and two-water layers hydration states (1- and 2-WLHS) respectively. In the 1-WLHS, there are approximately three water molecules per Na ion, while there are about six in the 2-WLHS. Because H has a much larger incoherent scattering cross section than all the other atoms, and OH groups are absent in the synthetic material, one is able to observe quasielastic spectra from interlamellar water essentially free of other scattering contributions.

## EXPERIMENTAL DETAILS

The fluormica material as supplied is a fine white powder. By mixing the material with water and allowing sedimentation and drying over a period of about a day, a partially oriented material was produced. Flakes several cm in diameter, and a fraction of a mm in thickness, were obtained. Neutron diffraction scans revealed that the flakes had a strong texture, with a distribution of the crystallites such that the directions perpendicular to the layers had a Gaussian distribution with a full width at half maximum of approx. 50 degrees. The samples could be dehydrated by gentle heating, typically to 80 C for a few hours. By exposing the samples to a 100% relative humidity environment at ambient temperatures, while continuously measuring weight uptake, 1-WLHS and 2-WLHS samples could be readily formed in times ranging from a few hours to two days, depending on sample size and hydration state. The samples, each a stack of several flakes, were wrapped in flat Al foil envelopes, and enclosed in cylindrical Al containers sealed with rubber or indium gaskets. Neutron diffraction scans were taken to ensure that the samples were in pure 0-, 1-, and 2-WLHS.

The quasielastic neutron scattering (QENS) data were obtained on the Fermi-chopper time-of-flight spectrometer at the NIST Center for Neutron Research. Two incident neutron wavelengths were used, 4.8 Å and 6 Å. The former gave a FWHM resolution at the elastic position of 0.145 meV, while the latter gave a resolution of 0.062 meV. Data were collected on the 1-WLHS and 2-WLHS samples at both these resolution conditions at temperatures ranging from 150 K to 305 K. Since the crystallites in the samples have a preferred orientation, it was possible to take data mostly with the direction of the wave vector transfer **Q** in parallel to the silicate layers, so that in-plane diffusive water motions could selectively be observed.

## QENS RESULTS

Strongly broadened quasielastic spectra were observed for both the 1- and 2-WLHS. Fig. 1 shows data for the 2-WLHS at 293 K, with the direction of **Q** aligned parallel to the layers, using a neutron wavelength of 6 Å. Very good fits to the spectra were obtained by considering a lineshape of the Kohlrausch-Williams-Watt (KWW) form, which is the Fourier transform of a stretched-exponential function, $F(t) = A \exp(-[t/\tau]^{\beta})$. An example of such a fit to a typical spectrum is shown in Fig. 1. Data at the two resolution conditions gave consistent values of $\beta$ and $\tau$, with the values of $\beta$ tending to 1 as Q decreases to zero, and generally lying in the range 0.5 to 1.0 for the 2-WLHS, 293 K spectra. The Q = 0 limit, $\beta = 1$, implies that the lineshape tends to Lorentzian, as one would expect for the long-range diffusional motions. It is

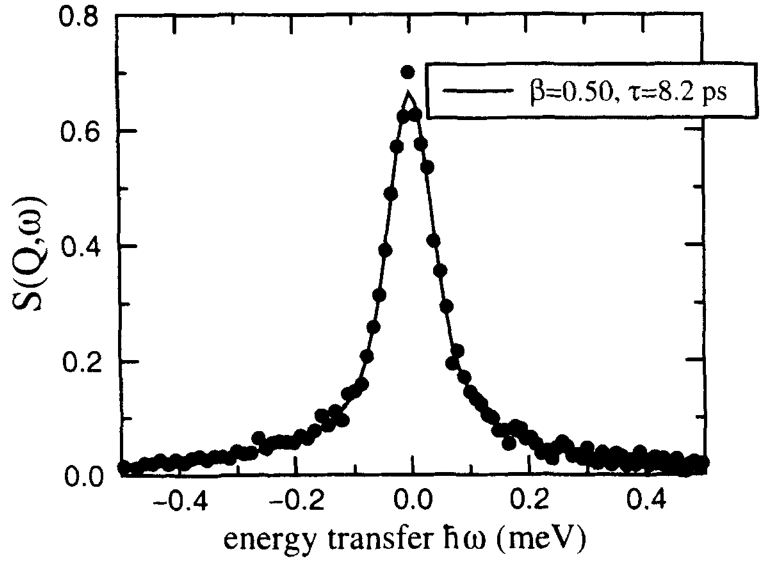

FIGURE 1. Quasielastic neutron scattering from water in the 2-WLHS at 293 K, Q = 1.0 Å$^{-1}$. The line is a fit to a KWW function, as described in the text.

noteworthy that similar fitting has been very successful in describing the water dynamics in various other systems, including water in confined geometries, such as the pores of silicate glass [4]. Such fits are also very common in describing quasielastic scattering from glasses. We observe no phase transitions in the water dynamics for either the 1-WLHS or the 2-WLHS samples as they are cooled. The water motions continuously become less rapid, becoming unobservably slow within the resolution of our spectrometer at temperatures below approximately 190 K. We believe that disorder in the environment of interlamellar water is an important aspect in describing the dynamics of hydrated clay minerals.

The small-Q behavior of the scattering function may be used to determine the diffusion coefficient for the interlamellar water. If KWW fits are used, then [4] one has $\langle\tau\rangle^{-1}=DQ^2$, where D is the diffusion coefficient, and $\langle\tau\rangle= \tau\beta^{-1}\Gamma(\beta^{-1})$. The fitted line in Fig. 2, where $\langle\tau\rangle^{-1}$ is plotted against $Q^2$, has a slope that gives a value for D that is approximately a third of that for bulk water at the same temperature. As shown in Table I, values of the diffusion coefficient D were also obtained for two lower temperatures for the 2-WLHS sample, but only at room temperature for the 1-WLHS sample, for

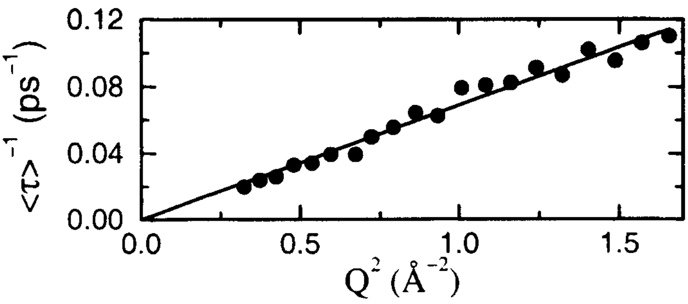

FIGURE 2 Inverse characteristic time $\langle\tau\rangle^{-1}$ vs $Q^2$ for the two-water-layer hydration state at 293 K.

which the broadening is an order of magnitude smaller. At lower temperatures, although quasielastic broadening is clearly visible in the spectra for high Q values, the low-Q data are not broadened enough to extract reliable values of the diffusion coefficient. Higher-resolution measurements are planned. Although there are only three values of D for the 2-WLHS sample, it is already apparent that the temperature dependence does not follow an Arrhenius law. Indeed, one should not expect it to do so, since it does not in bulk water [5] or other common liquids. The temperature dependence of D resembles what one would have in bulk water at temperatures about 25 K lower.

TABLE I Diffusion coefficients obtained from the QENS data, compared with bulk water [5].

| System | T (K) | D ($10^{-9}$ $m^2/s$) |
|---|---|---|
| bulk water | 293 | 2.26 ± 0.03 |
| 2-WLHS | 293 | 0.69 ± 0.06 |
| 2-WLHS | 273 | 0.32 ± 0.03 |
| 2-WLHS | 253 | 0.06 ± 0.02 |
| 1-WLHS | 298 | 0.06 ± 0.02 |

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