the clusters grow and the system will be separated into two phases ultimately. However, we do not know the precise nature of the transition. It might be of first order. That is, the average concentration might jump discontinuously just below the transition. If this is true, the values of σ at which $\lim_{q\to 0}\lim_{\tau\to\infty} S(q,\tau)$ diverges should correspond to the limit of metastability, although these values have been regarded as the critical values in this Letter.

Finally it should be remarked that the results of this Letter are based on the LBM approximation and cannot be conclusive. Their verification (or modification) should be made in future theories or experiments.

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Second Zone in Ionic Solutions

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High-resolution incoherent neutron spectroscopy has, for the first time, been applied to aqueous solutions and has demonstrated unambiguously the existence of a second zone of weakly interacting water molecules around two divalent cations Ni^{2+} and Mg^{2+}.

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In an important paper published some 20 years ago, Frank and Wen[1] postulated that around ions in aqueous solutions two well-defined zones of water may exist. The first zone, the so-called primary hydration shell, is now established beyond any doubt.[2,3] The dynamical behavior of weakly interacting water molecules like those in the second zone, however, is not amenable to conventional spectroscopic investigations.[3] To use incoherent quasielastic neutron spectroscopy, for example, two stringent criteria must be met. First, k [(momentum transfer)/$\hbar$] values must be such that

$$Dk^2\tau_\theta \ll 1,$$

where D is the translational diffusion coefficient and τ_θ is the correlation time for rotational motion of the hydrated ion; for $\tau_\theta \sim 10^{-11}$ sec,[4] and $D\sim 10^{-9}$ m^2 sec^{-1}, $k \ll 1\ \mathrm{\AA}^{-1}$. Secondly, the required observation time of the experiment τ_m (10^{-9} sec) implies an instrumental energy resolution of 1 μeV. Under these conditions the observed self-scattering law $S(k,\omega)$ will be Lorentzian in character and will, for ionic solutions in light water, be dominated by the hydrogen term, $S_H{}^S(k,\omega)$ given by

$$S_H{}^S(k,\omega) = (1/\pi)Dk^2/[(Dk^2)^2+\omega^2], \qquad (1)$$

if on the time scale of the experiment there is just one population of water molecules (the so-called "fast-exchange" limit). The backscattering technique as exemplified by the instrument IN10 now available at the Institut Laue Langevin, Grenoble, allows data to be collected under the

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right experimental conditions.[3] The incident wavelength was 6.27 Å and the corrections due to multiple scattering need considerable care. However, the sample thickness was ~2 mm or less so that a Monte Carlo method could be used to make the appropriate correction. Several tests were carried out to check that the method was sufficiently accurate for the present purposes, the most stringent of which was a detailed investigation of a $5m$ solution of LiCl [Fig. 1(a)]. This is a complex liquid but is characterized by a proton population which is in the fast-exchange limit. We therefore expect that (i) $S_H{}^S(k,\omega)$ at each value of k will be a *single* Lorentzian, (ii) the half-width of Lorentzians should be strictly proportional to k^2, and (iii) the value of the mean diffusion coefficient $\bar{D}$ predicted by these data should agree exactly with that derived from NMR spin-echo techniques. This is because both sets of data refer to the fast-exchange limit. Inspection of Figs. 1(a) and 1(b) shows that (i) and (ii) are indeed satisfied. The slope of half-width versus k^2 yields a value for $\bar{D}$ of $(1.30 \pm 0.05) \times 10^{-9}$ m^2 sec^{-1} which agrees, within experimental error, with the spin-echo value of $(1.23 \pm 0.05) \times 10^{-9}$ m^2 sec^{-1}.

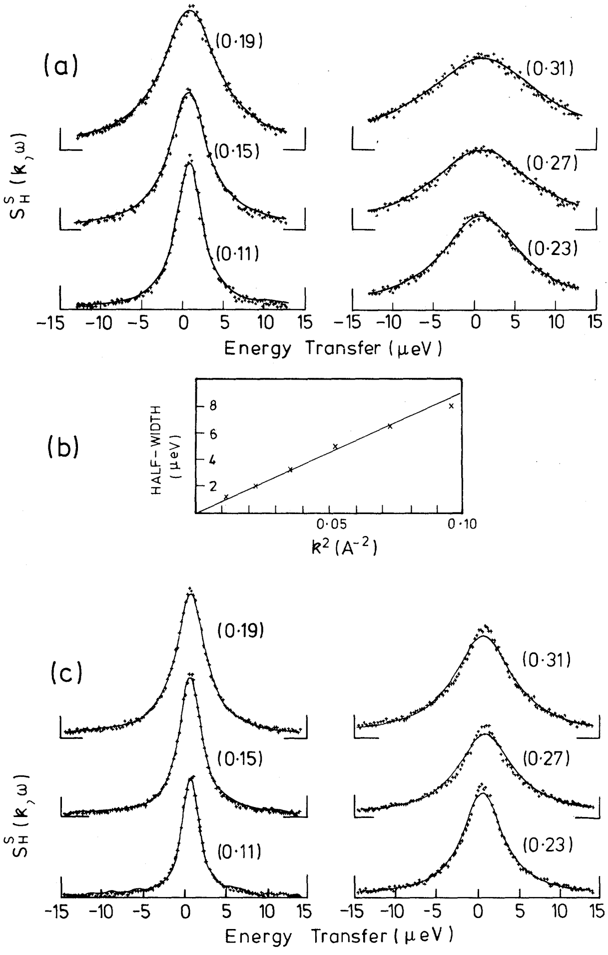

FIG. 1. (a) The neutron spectra for a $5m$ solution of LiCl in H_2O fitted by a single Lorentzian, with k values shown in brackets (in inverse angstroms). (b) The half-width of the Lorentzians in (a) as a function of k^2. The slope corresponds to an effective diffusion coefficient of $(1.30 \pm 0.05) \times 10^{-9}$ m^2 sec^{-1}. (c) An attempt to fit the neutron spectra for a $3m$ solution of $NiCl_2$ in H_2O by a single Lorentzian. The data were treated in exactly the same way as those shown in (a).

Consider now the situation in which i types of water molecule can be distinguished on the time scale of the experiment. For this case, $S_H{}^S(k,\omega)$ can be written as

$$S_H{}^S(k,\omega) = \sum (c_i/\pi) D_i k^2 / [(D_i k^2)^2 + \omega^2], \qquad (2)$$

where D_i and c_i are the diffusion coefficients and the atomic fraction, respectively, of the ith type. Specifically, for two types of water,

$$S_H{}^S(k,\omega) = \frac{1}{\pi}\left[\frac{c_1 D_1 k^2}{(D_1 k^2)^2 + \omega^2} + \frac{c_2 D_2 k^2}{(D_2 k^2)^2 + \omega^2}\right. . \qquad (3)$$

We focus attention on Fig. 1(c), which shows $S_H{}^S(k,\omega)$ at various k values for $3m$ solution of $NiCl_2$. These data were corrected for multiple scattering *in the same way* as those for the LiCl solutions referred to above. However, in this case a single Lorentzian [Fig. 1(c)] does not reproduce the experimental data (note especially the deviation for $k = 0.31$ Å^{-1}) and this result shows that there are at least two relevant diffusion coefficients (D_1 and D_2). For the first shell of Ni^{2+} we know, from a variety of studies,[4] that the IN10 experiment refers to the "slow-exchange" limit, i.e., the time scale of the measurement (~10^{-9} sec) is much shorter than the binding time of water molecules τ_b (~10^{-6} sec). Moreover, since for binding times greater than 10^{-11} sec the diffusion coefficients of the ion and the attached water molecules are essentially equal, we can set $D_1 = D_{ion}$, a quantity accessible independently through tracer measurements. Reliable values of D_{ion} as a function of concentration are available for both Ni^{2+} and Mg^{2+} in chloride solution and are shown in Fig. 2. The first-order difference method[3] has shown that for Ni^{2+} there are six water molecules in the first hydration shell.[5] We can therefore calculate, *without adjustable parameters*, the first term in Eq. (3).

Water molecules in the second zone are in the "fast-exchange" limit with bulk water so that the total contribution to the scattering law will be a single Lorentzian characterized by a mean diffusion coefficient $\overline{D}_2$, given by

$$\overline{D}_2 = (c_{\rm sec}D_{\rm sec} + c_0 D_0)/c_2,$$

where $D_{\rm sec}$ and $c_{\rm sec}$ are the diffusion coefficient and the atomic fraction of water molecules in the second zone and D_0 and c_0 are the corresponding quantities for the bulk water molecules. The first-order difference method yields a value of 15 ± 2 water molecules in the second zone[5] so that $c_{\rm sec}$ and c_0 are known, and experiments on pure water yield D_0. Once again, therefore, we can, without adjustable parameters, find $D_{\rm sec}$ by fitting the observed $S_{\rm H}{}^{S}(k,\omega)$ with two Lorentzians [Fig. 3(a)]. The results for $D_{\rm sec}$ are shown in Fig. 2 for the case of $NiCl_2$ solutions. Similar results were obtained for $MgCl_2$ solutions (Fig. 2). We have carried out a number of checks on these data to confirm the basis of our analysis. In Fig. 3(b) we show that two Lorentzians with $D_1 = D_{\rm ion}$ and $D_2 = D_0$ fail to fit the experiment results. This failure to fit with D_1 and D_0 is a *direct* demonstration that there are water molecules, other than those in the first shell, whose dynamical properties are affected by the presence of the cations. In this respect our results contradict those of Sakuma, Hishino, and Fujii[6] which, in our view, were obtained in the wrong region of (k,ω) space.

The value of D_0 [$(2.30 \pm 0.03)\times 10^{-9}$ m^2 sec^{-1}] used for the fits was taken from our own measurements on samples of pure water for a range of thicknesses between 1.3 and 2.4 mm; this value agrees exactly with the accepted value of $(2.30 \pm 0.05)\times 10^{-9}$ m^2 sec^{-1} derived from the work of Mills.[7] This agreement constitutes a further proof that the multiple scattering effects are being properly allowed for. The value of $D_{\rm ion}$ was taken from Mills *et al.*[8] The accuracy of $D_{\rm ion}$ is $\sim\pm\frac{1}{2}\%$ but we have shown [Fig. 3(b)] that even if

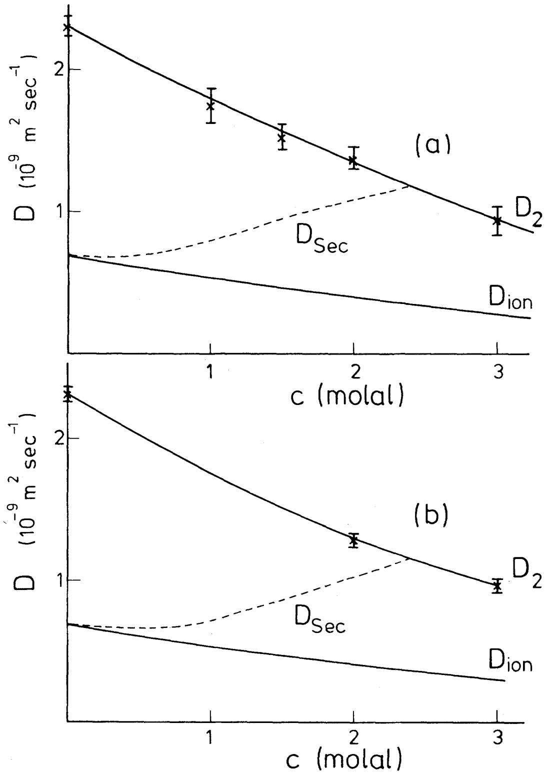

FIG. 2. The cationic diffusion coefficient $D_{\rm ion}$, together with the fitted values for D_2 and calculated values for $D_{\rm sec}$ for the two solutions studied. (a) $NiCl_2$ solutions. (b) $MgCl_2$ solutions. Data from NMR measurements were used in addition to the neutron results to produce the curve for D_2.

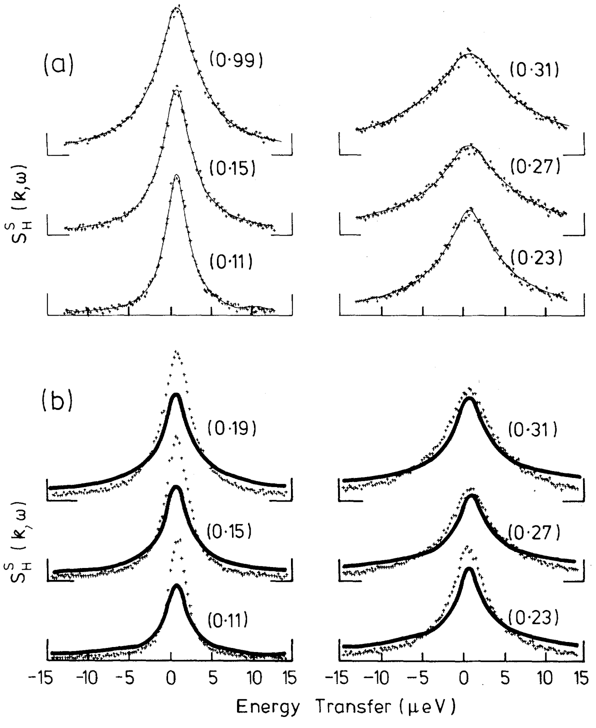

FIG. 3. Attempts to fit a theoretical curve to the neutron spectra for various values of k for $NiCl_2$ solutions. The fitted functions were (a) two Lorentzian peaks, the narrow peak width determined by $D_{\rm ion}$ (concentration: $2m$); (b) two Lorentzian peaks, with both widths fixed to correspond to D_0 and $D_{\rm ion}$ and with six water molecules bound to Ni^{2+}, the rest considered free. A range of $D_{\rm ion}$ values from $(0.21$ to $0.26)\times 10^{-9}$ m^2 sec^{-1} were tried and the resulting curves are all contained within the band shown (concentration: $3m$).

D_{ion} is allowed to change by ± 10%, two Lorentzians with one of them having $D_2 = D_0$ cannot fit the experimental data. Another test of the data can be made by considering Mg^{2+}. A mean proton diffusion coefficient $(\bar{D} = c_1 D_1 + c_{\mathrm{sec}} D_{\mathrm{sec}} + c_0 D_0)$ is available from NMR measurements[7] which were made in the fast-exchange limit. We have derived the individual D's in our analysis and knowing c_1, c_{sec}, and c_0 from the structural work we are able to predict the NMR value for $\bar{D}$. The agreement is, within error, exact. For example, at $3m$, our predicted value is $(0.76 \pm 0.05) \times 10^{-9}\ \mathrm{m}^2\ \mathrm{sec}^{-1}$ and the measured value is $(0.81 \pm 0.05) \times 10^{-9}\ \mathrm{m}^2\ \mathrm{sec}^{-1}$. At $2m$ the values are $(1.10 \pm 0.05) \times 10^{-9}\ \mathrm{m}^2\ \mathrm{sec}^{-1}$ and $(1.17 \pm 0.05) \times 10^{-9}\ \mathrm{m}^2\ \mathrm{sec}^{-1}$, respectively.

We believe this work to be the first unambiguous structural and dynamical evidence for the Frank-Wen model of solutions and it opens up the possibility of a microscopic interpretation of solution properties; it is particularly significant to note that $D_{\mathrm{sec}} \rightarrow D_{\mathrm{ion}}$ as we approach infinite dilution. Up to the present, the evidence for the original model was based almost entirely on macroscopic measurements like viscosity, thermal diffusivity, and partial molar volumes.

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Thermalization of a Phonon Spectrum Observed by Frequency Crossing

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Measurements of the size of holes burned in the frequency spectrum of a heat current in $\mathrm{Al_2O_3}$ by resonant phonon scattering show that the holes decay when they leave the region containing the scattering centers in distances which indicate that the crystal surface scattering is largely inelastic at 200 GHz and 2 K. The hole is monitored by observation of the scattering produced by a second ionic species tuned to the same frequency.

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When a heat current passes through an insulating solid doped with scattering centers, the centers burn holes in the frequency spectrum of the phonon current at their resonant scattering frequencies. If now the current enters an undoped region these holes should start to decay and the spectrum should approach the equilibrium spectrum for the pure crystal. A hole at frequency ν_i should decay in a distance $\sim l_I(\nu_i)$, the inelastic scattering length, to its remanent value determined by the trace impurity concentration in the undoped region.

Experiments to examine this have been made using an $\mathrm{Al_2O_3}$ bicrystal: a crystal doped with V in one half and Fe in the other. A heat current passing from the V half, say, to the Fe half has holes burned in its spectrum at three frequencies which can be varied with a magnetic field. The holes are due to transitions within the split ${}^3A_2$ ground state of V^{3+}. The size of the holes at points in the Fe-doped end can be determined from the size of the minima in the temperature

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