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Li⁺ hydration in concentrated aqueous solution

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Abstract. Neutron diffraction experiments were carried out on aqueous solutions of lithium chloride in heavy water at three concentrations—14, 3.6 and 1 molal. The first-order isotopic difference method was applied to the lithium ions, and structural results were obtained for the Li⁺ hydration: the Li–O and Li–D near-neighbour distances in the first hydration shell remain the same at 1.95(3) and 2.5(5) Å over the concentration range studied. However, there is an increase in coordination number from 3.2 at 14 molal to ≈6.5 at 1 molal. There is also evidence for a relatively weak second hydration shell, which becomes displaced to larger distances at lower concentrations.

1. Introduction

The monovalent lithium ion, Li⁺, is a useful probe of the structural and thermodynamic properties of ionic liquids. From an experimental viewpoint lithium salt solutions have been the subject of many investigations, at both the macroscopic and microscopic levels [1]. Theoretically, the hydration properties of Li⁺ have been calculated from various model (usually pairwise additive) potentials [2], and also from *ab initio* quantum mechanical computations on Li⁺ [H₂O]₄ clusters [3]. All such studies usually constitute part of a series of experiments or calculations, the aims of which are to compare the properties of Li⁺ in solution with those of other cations in the alkali series. In particular, it remains a matter of interest to know the exact details of the Li⁺ hydration in terms of the distances between the Li⁺ and atoms of the water molecule and the number of water molecules in the first coordination shell at low concentration, ideally at ‘infinite dilution’. Such information is also useful in the study of Li⁺ in more complex systems, such as encountered in biology and geochemistry.

In this paper we present new results of a concentration dependent study of Li⁺ hydration in concentrated solutions of lithium chloride in heavy water, and compare them with previous results on similar systems. In particular, reference is made to the work of Newsome *et al* [4], who carried out the first detailed structural study of lithium chloride heavy-water solutions based on the method of neutron diffraction and isotopic substitution (NDIS), and were able to identify a change in hydration structure with concentration. At that time, the results were at the technological limit of the NDIS technique and subject to large statistical and systematic errors associated respectively with relatively low neutron count rates and insufficiently well characterized samples. Since that time major developments have occurred in neutron diffractometry, noticeably by the implementation of multidetector assemblies, and the increase by several orders of magnitude in count rates. Moreover,

improvements in sample characterization and more sophisticated computational techniques have enabled correction procedures to be carried out to a significantly higher accuracy. As a result more reliable information can now be obtained for ionic hydration structure at lower ionic concentrations.

In recent years the work of Powell *et al* [5], has clearly demonstrated that more detailed results can also be obtained in solutions of water–heavy-water mixtures. (Prior to that work, all NDIS experiments had been carried out in solutions of heavy water in order to overcome difficulties in data gathering and data treatment caused by the presence of ordinary water (H₂O), which has a prohibitively large incoherent scattering cross section [6] and its protons exhibit appreciable kinematic (Placzek) effects.)

2. Experimental details and data analysis

Neutron diffraction experiments were carried out on heavy-water solutions of isotopically enriched lithium (⁶Li/⁷Li) in lithium chloride at three concentrations: 14, 3.6 and 1 molal. The samples were prepared by standard procedures [7] which included direct dissolution of isotopically enriched lithium chloride in heavy water and repurification by preferentially boiling off any light-water contamination. Sample composition and purity were monitored by densitometry, colourimetry, infrared spectrometry and mass spectrometry (table 1). The samples were prepared under glove box conditions in a dry nitrogen atmosphere. Transfer to Ti/Zr sample containers was also carried out in a dry glove box. The neutron diffraction experiments were carried out on the D4 diffractometer of the Institut Laue Langevin (ILL). The neutron wavelength was 0.704 Å in the experiment on the 3.6 molal solution and 0.7055 Å for experiments on the 1 and 14 molal solutions. Because ⁶Li is a strongly absorbing isotope, transmission measurements were made to check literature values of absorption and scattering cross sections. Test experiments (the data of which are unpublished) indicated that the cross section of ⁶Li in aqueous solution may have been different from that quoted by Sears [6]. It was found that this was not the case, but that the deviation from isotopic purity of the Li was the main correction that had to be made in calculating the sample cross sections. When this was done, additional special correction procedures were not required for the samples containing ⁶Li. As a matter of fact, it was found that values computed from the tables of Sears [6] were within 5% of those determined experimentally (table 1). The data for each isotopically distinct set of two samples were analysed by standard procedures which included corrections for sample and container absorption, multiple scattering, incoherent scattering and normalization to give total structure factors, $F(k)$, in units of barns sr⁻¹ by reference to a vanadium rod [5] ($\hbar k$ is the momentum transfer in the neutron scattering process). Differences were calculated between the two structure factors at each concentration, and the first-order difference functions, $\Delta_{Li}(k)$ were calculated. These functions can be written as

$$\Delta_{Li}(k) = A[S_{LiO}(k) - 1] + B[S_{LiD}(k) - 1] + C[S_{LiCl}(k) - 1] + D[S_{LiLi}(k) - 1] \quad (1)$$

where

$$A = 2c_{Li}c_O b_O \Delta b_{Li} \quad B = 2c_{Li}c_D b_D \Delta b_{Li} \quad C = 2c_{Li}c_{Cl} b_{Cl} \Delta b_{Li}$$

$$D = c_{Li}^2 ((b_{^6Li})^2 - (b_{^7Li})^2)$$

$$\Delta b_{Li} = (b_{^6Li} - b_{^7Li}).$$

c_α is the atomic concentrations of species ' α ', whose coherent neutron scattering length is b_α . Second-order corrections for slight imbalances in the H₂O/D₂O content were made by

fitting a fourth-order polynomial even in terms of 'k' following the method outlined in the appendix by Powell *et al* [5].

Table 1. The atomic fractions of the samples and the scattering and absorption cross-sections used in the correction procedures.

Solution	c_{6Li}	c_{7Li}	c_{nCl}	c_0	c_D	σ_s^a	σ_a^b	ρ (\AA^{-3})
14.0 m ⁶ Li ⁿ Cl	0.0752	0.0035	0.0787	0.2809	0.5618	4.52	73.30	0.091
14.0 m ⁷ Li ⁿ Cl	0.0029	0.0758	0.0787	0.2809	0.5618	4.55	5.36	
3.6 m ⁶ Li ⁿ Cl	0.0218	0.0011	0.0229	0.3181	0.6361	4.03	21.28	0.091
3.6 m ⁷ Li ⁿ Cl	0.0009	0.0220	0.0229	0.3181	0.6361	4.04	1.59	
1.0 m ⁶ Li ⁿ Cl	0.0063	0.0003	0.0066	0.3290	0.6590	6.11		0.097
1.0 m ⁷ Li ⁿ Cl	0.0003	0.0063	0.0066	0.3290	0.6579	3.89	0.46	

^a Calculated using measured total cross-sections for D₂O at the incident neutron wavelength (in [23]).

^b At an incident neutron wavelength of 1.8 \AA .

The pair radial distribution function, $g_{Li\alpha}(r)$ is related to the partial structure factor, $S_{Li\alpha}(k)$ through the Fourier transformation equation:

$$g_{Li\alpha}(r) - 1 = 1/(2\pi^2\rho r) \int dk \{S_{Li\alpha}(k) - 1\} k \sin(kr) \quad (2)$$

where ρ is the total number density, which for an aqueous solution is typically 0.1\AA^{-3} .

Consequently, Fourier transformation of (1) gives the total Li⁺ radial distribution function, $G_{Li}(r)$, in terms of a linear combination of functions $g_{Li\alpha}(r)$ i.e.

$$G_{Li}(r) = Ag_{LiO}(r) + Bg_{LiD}(r) + Cg_{LiCl}(r) + Dg_{LiLi}(r) + E \quad (3)$$

where $E = -(A + B + C + D)$.

The radial distribution functions $g_{Li\alpha}(r)$ contain the basic structural information of the solution from which properties such as nearest- and next-nearest-neighbour distances to Li⁺ can be determined. It is also possible to calculate coordination numbers \bar{n}_{Li}^α , which give the number of 'α' atoms within a certain range, $r_1 < r < r_2$, of the Li⁺ from the formula

$$\bar{n}_{Li}^\alpha = (4\pi\rho c_\alpha/A_\alpha) \int_{r_1}^{r_2} \{G_{Li}(r) - E\} r^2 dr \quad (4)$$

where $A_\alpha = A, B, C$ or D .

Table 2. The weighting factors (mb sr⁻¹) of the different terms contributing to the difference functions $\Delta_{Li}(Q)$ and $G_{Li}(r)$ ((1), (3)).

Molality of LiCl solution	A	B	C	D
14.0	8.763	20.149	1.650	0.037
3.6	3.265	7.507	0.388	-0.005
1.0	0.970	2.231	0.032	-0.000

Clearly, the coefficients A–D of (1) and (3) are functions of ionic concentration (table 2). Consequently, for $G_{Li}(r)$ for the 3.6 m and 1 m solutions $A, B \gg C, D$ and $G_{Li}(r)$ is dominated by $g_{LiO}(r)$ and $g_{LiD}(r)$. For the 14 m solution the C term is 8% B and a

contribution from $g_{LiCl}(r)$ is evident in $G_{Li}(r)$ at 2.5 Å (figure 2). This observation can be demonstrated more formally by the determination of $g_{LiCl}(r)$ from a second-order NDIS study which will be the subject of another paper on the solute structure in a 14 m lithium chloride solution [8].

3. Results and discussion

The $\Delta_{Li}(k)$ curves (figure 1) show that an appreciable difference is obtained for ${}^6\text{Li}/{}^7\text{Li}$ substitution at concentrations as low as 1 molal, and based on the statistical accuracy of the data it is likely that NDIS experiments could be extended to concentrations as low as 0.2 molal. The general features in $\Delta_{Li}(i)$ remain essentially the same over the concentration range studied, albeit the data at 1 molal are proportionally noisier than those at 14 molal. The correction of the 1 molal data was also complicated by the presence of a larger $\text{H}_2\text{O}/\text{D}_2\text{O}$ imbalance between the two samples used to generate the difference function. Consequently the empirical correction used to generate $\Delta_{Li}(k)$ was significantly less well defined than those at the higher concentrations, and accounts for the large termination errors and the appreciable discrepancy between the $\Delta_{Li}(k)$ calculated directly from the $F(k)$ and that calculated ‘back’ Fourier transformation of the full curve shown in figure 2(iii). Indeed, the scatter on all three $\Delta_{Li}(k)$ (figure 1) between the ‘back’ transformed full $G_{Li}(r)$ (figure 2) curves and the ‘directly’ calculated $\Delta_{Li}(k)$ represents the statistical error of the experiment. Deviations between the dotted and solid lines in figure 1 are due to systematic errors, primarily caused by imbalances in $\text{H}_2\text{O}/\text{D}_2\text{O}$ content between pairs of samples.

Inspection of the functions $G_{Li}(r)$ (figure 2) shows that the hydration shell around Li^+ remains clearly resolved down to the lowest concentration. At 14 molal there is clear evidence that the first coordination shell contains both water molecules and Cl^- ions [8]. Integration over the first peak between 17 and 2.2 Å and application of (4) gives a hydration number \bar{n}_{Li}^O of 3.2. As the concentration is reduced \bar{n}_{Li}^O rises to a value of ≈ 6.5 at 1 molal (table 3); given that the radius of Li^+ is 0.6 Å it is likely that this is the limiting value for \bar{n}_{Li}^O .

Table 3. Li^+ hydration structural properties for a range of aqueous solutions.

Lithium salt	Concentration (molality; molarity)	r_{LiO} (Å)	r_{LiD} (Å)	$\bar{n}_{Li}^{D_2O}$	Reference
LiCl	14.0	1.96(2)	2.52(2)	3.2 ± 0.2	this work
	3.6	1.95(2)	2.52(2)	6.0 ± 0.4	this work
	1.0	1.96(2)	2.52(2)	6.5 ± 1	this work
	3.57	1.95(2)	2.55(3)	5.5 ± 0.3	[4]
	9.95	1.95(2)	2.50(3)	3.3 ± 0.5	[4]
	24.8 (130 °C)	1.95	2.31	2.3	[11]
	12.5	2.22	2.68	4 ± 1	[12]
	6.25	1.95	2.43	4 ± 1	[12]
9.32	2.01	2.61	4 ± 1	[13]	
LiBr	1.88 M	1.94	2.58	4.2(5)	[14]
LiOD	1.2	1.98(2)	2.53(3)	4.2(4)	[15]
LiPAA	1.2	1.97(2)	2.50(3)	4.0(4)	[15]

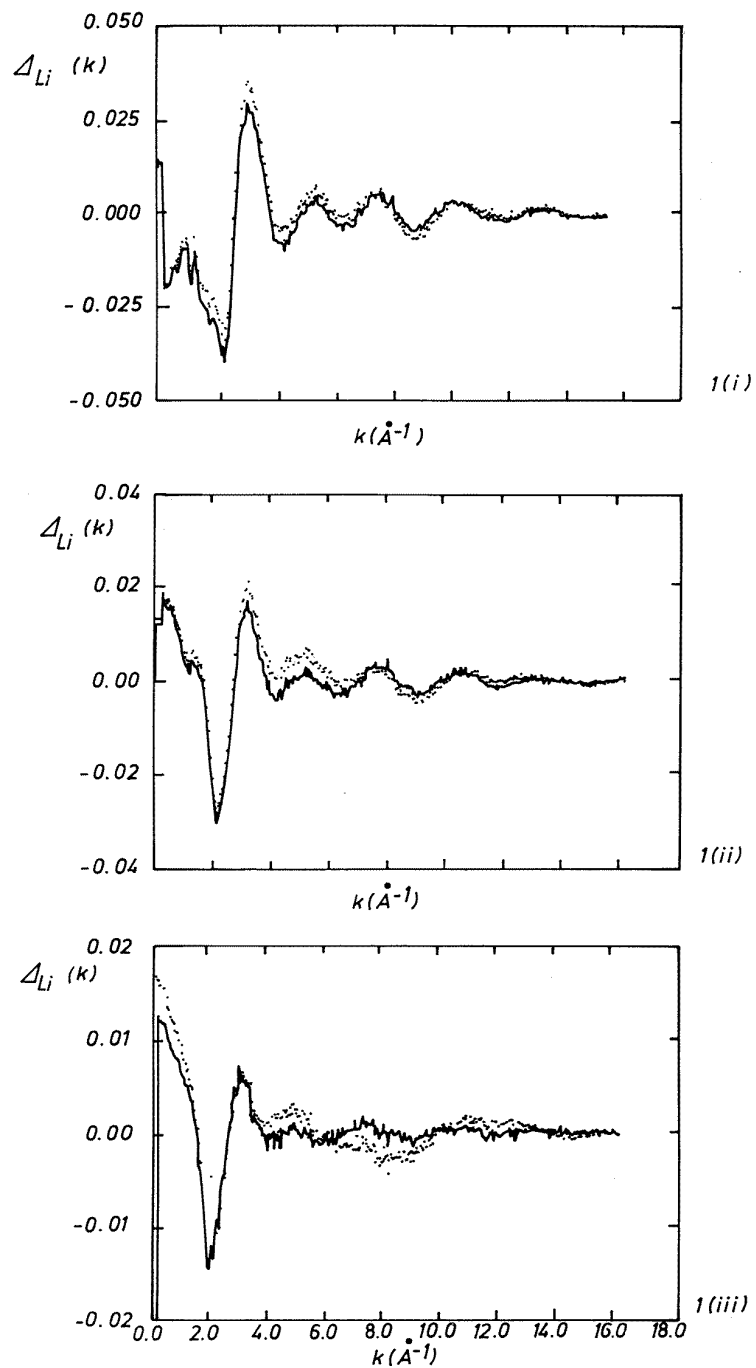


Figure 1. Total Li⁺ first-order difference functions, $\Delta_{Li}(k)$, for solutions of lithium chloride in heavy water: (i) 14 molal; (ii) 3.6 molal; (iii) 1 molal. The dots represent the data derived directly from the scattered intensities of the samples, and the full curves through these points are the 'back' Fourier transformations of the full curves shown in figure 2. The units of $\Delta_{Li}(k)$ are barns sr^{-1} .

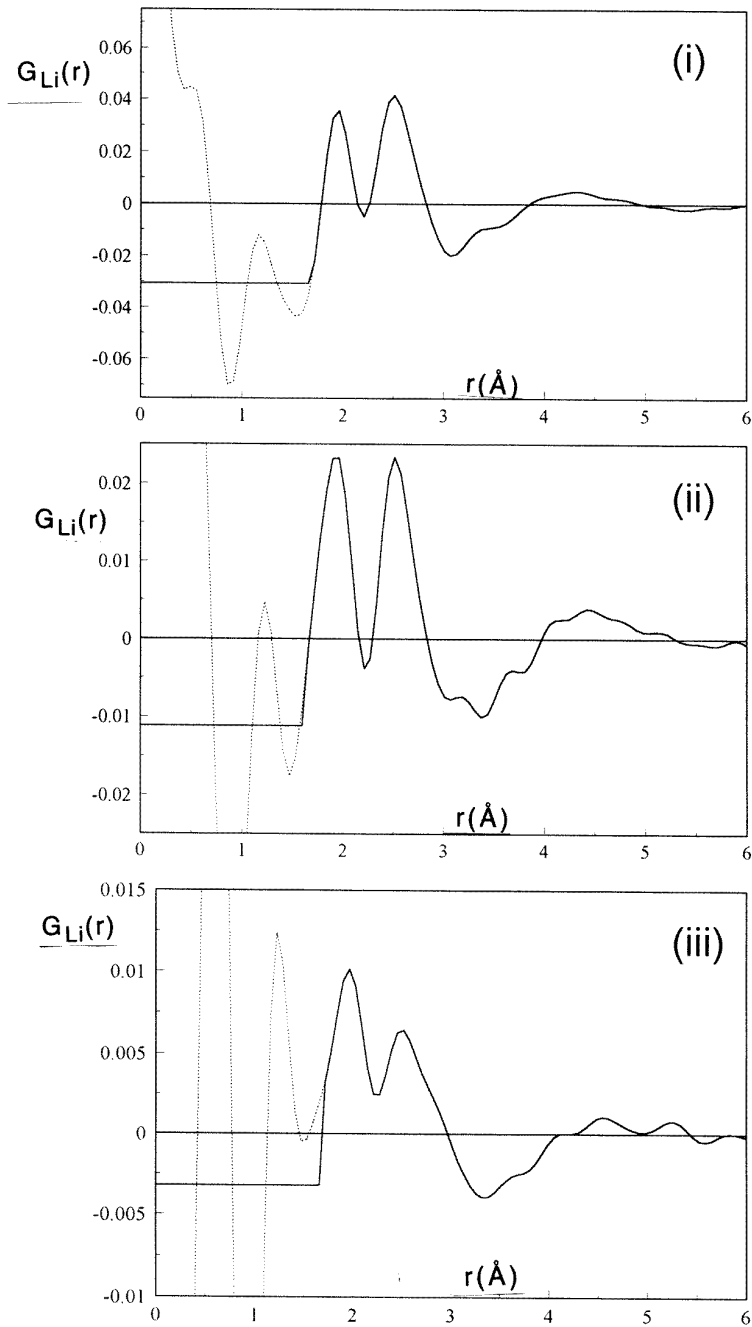


Figure 2. The total Li^+ radial distribution function, $G_{\text{Li}}(r)$, derived from Fourier transformation of data in figure 1, for solutions of lithium chloride in heavy water: (i) 14 molal; (ii) 3.6 molal; (iii) 1 molal. The dots at 'low' r are a result of termination errors in the Fourier transform of the data points in figure 1. A straight line has been drawn through them to correspond to the calculated $G_{\text{Li}}(0)$.

The Li–O and Li–D nearest-neighbour distances are $r_{LiO} = 1.95(2)$ Å and $r_{LiD} = 2.52(2)$ Å respectively and are independent of concentration. There is also evidence for a second hydration shell of water molecules over the range $3 \leq r$ (Å) ≤ 5 at all three concentrations, although it is less pronounced in the result at 1 molal. The fact that $G_{Li}(r) \geq 0$ in the region beyond the first hydration shell indicates that Li⁺–water molecule interaction is not strong enough to form a well defined pseudo-molecular complex as observed in the hydration of divalent and trivalent cations [9]. This result also has implications for the solute structure, which shows that at equivalent ion concentrations the probability of direct contact between anions and cations is significantly greater for systems which do not possess a strongly defined hydration shell [10].

These results compare favourably with others derived from the same technique (table 3). The early work of Newsome *et al* [4] is less accurate than the present study, a consequence of improvements in sample preparation methods, sample characterization, and diffractometer performance; the Newsome data were gathered on the original D4, which had a count rate of around 1/100 of the present D4B. Nevertheless, the general conclusions drawn in that paper are confirmed by the results of this study, which has extended the concentration range in both directions. In particular, the value of n_{Li}^O is greater than six for concentrations below 3.6 molal, and is significantly less than four at concentrations above 10 molal, reflecting the presence of water bridging at high concentrations. This latter observation is consistent with results obtained from pulsed source experiments in which the NDIS method [11] was used (table 3). Interestingly, however, there appears to be an appreciable difference between the distances within the Li⁺ hydration shell as determined from the various neutron diffraction experiments. Narten and coworkers [12] did not employ the NDIS method but used a combination of x-ray and total neutron diffraction data. Their results were therefore of inherently lower resolution as they relied strongly on a modelling procedure to fit the data. Of more concern is the difference between our data and those obtained with pulsed source neutrons [13]; the discrepancy could be a consequence of either data analysis of highly absorbing materials which require sophisticated procedures to deal with wavelength dependent corrections to the pulsed source data, or poorer resolution at low to intermediate values of k .

Comparison with results of NDIS experiments of Li⁺ hydration in other systems is of additional interest [14, 15]. Results obtained from diffraction experiments on the 7C2 diffractometer sited on the Orphee Reactor (CE Saclay) give results which agree in terms of distances within the Li⁺ hydration shell, but disagree in terms of the value of n_{Li}^O , which has a value closer to four in solutions of lithium polyacrylic acid, lithium bromide and lithium hydroxide, all at concentrations close to those of the present study. This result suggests that the Li⁺ hydration is sensitive to counterion. However, it is unclear at present whether this observation is a consequence of the size of the counterions or of the relatively strong influence of Cl[−] in aqueous solution.

The results are also useful as a test of computer simulation (table 4). Although there is good general agreement between our results and simulation, there are significant differences in detail. This is most noticeable in the distances within the Li⁺ hydration shell. As mentioned in the previous study of Newsome *et al* the simulation results appear to favour a ‘lone-pair’ conformation for the Li⁺–D₂O moiety, with distances much longer than found experimentally. By contrast, recent *ab initio* calculations [3] on an Li⁺–[H₂O]₄ unit give a distance of $r_{LiO} = 1.9713$ Å which is in excellent agreement with NDIS results in table 3. However, the value of $r_{LiH} = 2.6$ Å which can be calculated from values of $r_{OH} = 0.95$ Å and an Li–OH bond angle of 128.3° is not in agreement with the NDIS result of 2.52(2) Å.

Table 4. The Li⁺ hydration structure calculated from computer simulation.

Concentration (numbers of H ₂ O molecules to Li ⁺ ions)	r_{LiO} (Å)	r_{LiD} (Å)	$\bar{n}_{Li}^{D_2O}$	Reference
200:8	2.06	2.60	5.7(2)	[16]
200:1	1.95	2.60	5	[17]
215:1	2.10	2.70	5.97(2)	[18]
64:1	2.04	2.60	6	[19]
144:36	2.00	2.70	5.2	[20]
129:43	2.00	2.68	3.6	[21]
216:1	1.93	2.65	4	[22]

4. Conclusion

To summarize, the NDIS method has enabled us to determine the Li⁺ hydration at three ionic concentrations. Improvements in diffractometer performance, sample characterization and data analysis means that experiments are now feasible on aqueous solutions which contain highly absorbing materials of light nuclei at relatively low concentrations. It is anticipated that the Li⁺ cation will continue to be used to probe the microscopic properties of a wider variety of materials and under changing physical conditions. For example, the above results will provide a useful reference for studies of Li⁺ counterion condensation in polyelectrolyte solutions [15].

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References

- [1] See e.g. Franks F (ed) 1973 *Water, A Comprehensive Treatise* vols 1 & 3 (New York: Plenum)
- [2] Szasz G I, Heinzinger K and Palinkas G 1981 *Chem. Phys. Lett.* **78** 194
- [3] Rudolph W, Brooker M H and Pye C C 1995 *J. Phys. Chem.* **99** 3793
- [4] Newsome J R, Neilson G W and Enderby J E 1980 *J. Phys.: Solid State Phys.* **13** L923
- [5] Powell D H, Neilson G W and Enderby J E 1989 *J. Phys.: Condens. Matter* **1** 8721
- [6] Sears V F 1984 *Thermal Neutron Scattering Lengths and Cross Sections* AECL-8490 (Chalk River: Chalk River National Laboratories)
- [7] Enderby J E and Gullidge P M N 1987 *Methods Exp. Phys.* **B 23** 473
- [8] Howell I and Neilson G W 1993 *PhD Thesis* University of Bristol manuscript in preparation
- [9] Neilson G W, Broadbent R D, Howell I and Tromp R H J *J. Chem. Soc. Faraday Trans.* **89** 2927
- [10] Ansell S, Neilson G W and Tromp R H 1995 *J. Phys.: Condens. Matter* **7** 1513
- [11] Ichikawa K, Kaneda Y, Matsumoto T and Misawa M 1984 *J. Phys. C: Solid State Phys.* **17** L725
- [12] Narten A H, Vaslow F and Levy A H H L 1973 *J. Chem. Phys.* **58** 5017
- [13] Yamagami M, Yamaguchi T, Wakita H and Misawa M 1994 *J. Chem. Phys.* **100** 3122
- [14] Cartailleur T, Kunz W, Turq P and Bellissent-Funel M-C 1992 *J. Phys.: Condens. Matter* **3** 9511
- [15] v d Maarel J R C, Powell D H, Jawahier A K, Leyte-Zuiderweg Neilson G W and Bellissent-Funel M C 1989 *J. Chem. Phys.* **90** 6709
- [16] Heinzinger K and Vogel P C 1976 *Z. Naturf.* a **31** 463

- [17] Clementi E and Barsotti R 1978 *Chem. Phys. Lett.* **59** 21
- [18] Mezei M and Beveridge D L 1980 *J. Chem. Phys.* **74** 6902
- [19] Bounds D G 1985 *Mol. Phys.* **54** 1335
- [20] Bopp P, Okada I, Ohtaki H and Heinzinger K 1985 *Z. Naturf.* a **40** 116
- [21] Tanaka K, Ogita N, Tamura Y, Okada I, Ohtaki H, Palinkas G, Spohr E and Heinzinger K 1987 *Z. Naturf.* a **42** 29
- [22] Romero C 1991 *J. Chim. Phys.* **88** 765
- [23] Hughes D J and Harvey J A 1955 *Brookhaven National Laboratory Report* BNL 325