Structure of molten ScCl$_3$ and ScCl$_3$ studied by using neutron diffraction

Structure of molten $ScCl_3$ and ScI_3 studied by using neutron diffraction

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Abstract. The structure of the salts ScX_3, where X^- denotes Cl^- or I^-, was investigated by using neutron diffraction. On heating $ScCl_3$, a phase transition from the $FeCl_3$-type crystal structure to possibly the YCl_3-type crystal structure was observed whereas ScI_3 remained in its room temperature $FeCl_3$-type crystal structure up to the melting point. On melting, there is a reduction in the Sc–X coordination number from six to 4.8(2) for $ScCl_3$ and from six to 4.7(2) for ScI_3 and the Sc–Cl and Sc–I nearest-neighbour distances in the liquid are 2.48(2) Å and 2.76(2) Å respectively. The measured total structure factors of molten $ScCl_3$ and ScI_3 each have a prominent first sharp diffraction peak at a scattering vector value of 0.75(5) Å^{-1}. The results are discussed in the context of those available for several other trivalent metal halide systems which also melt from the closely related YCl_3-type and $FeCl_3$-type crystal structures.

1. Introduction

The object of this paper is to present neutron diffraction results on the structure of molten $ScCl_3$ and ScI_3 as part of a systematic study on the effect of ion size on the structure of liquid trivalent metal halides MX_3 and related compounds, where M^{3+} denotes the cation and X^- the anion (Wasse and Salmon 1998a, b, 1999, Wasse 1998). The first aim of the work is to discover how the structure of liquid $ScCl_3$ compares with that of liquid $AlCl_3$, $InCl_3$, $FeCl_3$ and YCl_3. All of these systems crystallize at room temperature in either the YCl_3-type or $FeCl_3$-type crystal structure which are closely related ionic structures wherein the cation is octahedrally coordinated. On melting, however, these systems show a rich diversity in their thermodynamic and transport properties (see table 1) which is indicative of different melting mechanisms and liquid structures (Ubbelohde 1978, Tosi *et al* 1991). The second aim is to investigate the effect of increasing the anion size on the structure of liquid ScX_3. As the anion radius is increased from 1.81 Å for Cl^- to 2.20 Å for I^- (Shannon 1976) the anion polarizability increases and there may be a concomitant change in the liquid structure. The third aim is to provide experimental results for enabling a test to be made of recent computer simulation studies on metal halide systems (Madden and Wilson 1996, Hutchinson *et al* 1999). These studies use an ionic interaction model that includes an account of ionic polarization phenomena and indicate that the basic microscopic properties of MX_3 materials might be understood in terms of the interplay between polarization effects and ion size.

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Table 1. The radius r_M for sixfold-coordinated cations (Shannon 1976), room temperature crystal structure, room temperature molar volume V_{RT}, cation Pettifor (1986) chemical parameter χ_M, melting point temperature T_m, entropy change on melting ΔS_m, volume change $\Delta V/V_m$ and electrical conductivity near the melting point κ_m for several MX_3 systems. The superscripts LS and HS stand for low spin and high spin respectively.

Salt	r_M (Å)	Crystal structure	V_{RT} (cm^3 mol^{-1})	χ_M	T_m (°C)	ΔS_m (cal K^{-1} mol^{-1})	$\Delta V/V_m$ (%)	κ_m (Ω^{-1} cm^{-1})
AlCl$_3$	0.54	YCl$_3$[a]	54.09[b]	1.66	193[c]	18.1[c]	46–48[d]	5.6×10^{-7}[e]
FeCl$_3$	0.55^{LS} 0.65^{HS}	FeCl$_3$[a]	55.47[a]	0.99	304[c]	17.9[c]	39[f]	0.04[f]
ScCl$_3$	0.75	FeCl$_3$[g]	62.89[g]	0.67	939[e]	13.0[h]	32[i]	0.48[e]
InCl$_3$	0.80	YCl$_3$[a]	63.60[a]	1.60	586[e]	—	39[e]	0.42[e]
YCl$_3$	0.90	YCl$_3$[a]	74.79[a]	0.66	714[j]	7.6[h]	0.6–3[e,j]	0.40[e]
ScI$_3$	0.75	FeCl$_3$[k]	90.63[k]	0.67	945[l]	15.5[m]	35[i]	—

[a] Wyckoff (1964).
[b] *Landolt–Börnstein* (1973).
[c] Pankratz (1984).
[d] Biltz and Voigt (1923), King and Seegmiller (1971).
[e] Klemm (1964).
[f] Price *et al* (1998).
[g] Fjellvåg and Karen (1994).
[h] Dworkin and Bredig (1971).
[i] See the text.
[j] Mochinaga and Irisawa (1974).
[k] Men'kov and Komissarova (1964).
[l] Metallinou *et al* (1991).
[m] O'Hare *et al* (1987).

2. Theory

In a neutron diffraction study on molten ScX_3 the total structure factor $F(k)$ derived from the coherent scattered intensity can be expressed as

$$F(k) = A[S_{ScSc}(k) - 1] + B[S_{ScX}(k) - 1] + C[S_{XX}(k) - 1] \tag{1}$$

where $A = c_{Sc}^2 b_{Sc}^2$, $B = 2c_{Sc}c_X b_{Sc} b_X$ and $C = c_X^2 b_X^2$. Here $S_{\alpha\beta}(k)$ denotes a Faber–Ziman partial structure factor, k is the magnitude of the scattering vector and c_α, b_α denote the atomic fraction and coherent neutron scattering length of chemical species α respectively. The values of the coefficients, calculated using $b_{Sc} = 12.29(11)$ fm and $b_{Cl} = 9.5770(8)$ fm or $b_I = 5.28(2)$ fm (Sears 1992), are $A = 94(2)$ mb, $B = 441(4)$ mb, $C = 515.9(1)$ mb for ScCl$_3$ and $A = 94(2)$ mb, $B = 243(2)$ mb, $C = 157(1)$ mb for ScI$_3$. The scattering lengths give the cation correlations an increasing relative weighting with anion size.

The total pair distribution function corresponding to the total structure factor is obtained from the Fourier transform relation

$$G(r) = \frac{1}{2\pi^2 n_0 r} \int_0^\infty dk\, F(k)k \sin(kr)$$
$$= A[g_{ScSc}(r) - 1] + B[g_{ScX}(r) - 1] + C[g_{XX}(r) - 1] \tag{2}$$

where $g_{\alpha\beta}(r)$ denotes a partial pair distribution function and n_0 is the atomic number density of the melt. The mean number of particles of type β contained in a volume defined by two concentric spheres of radii r_i and r_j, centred on a particle of type α, is given by

$$\bar{n}_\alpha^\beta = 4\pi n_0 c_\beta \int_{r_i}^{r_j} r^2 g_{\alpha\beta}(r)\, dr. \tag{3}$$

3. Experimental details

The $ScCl_3$ (99.99%) and ScI_3 (99.999%) salts, supplied by Aldrich, had a water content of less than 100 ppm and were handled either in high vacuum or under a high-purity argon gas atmosphere having an oxygen and water content both less than 10 ppm. The powders were pre-melted to increase their packing fraction and were subsequently sealed under vacuum in cylindrical silica cells of 5 mm internal diameter and 1 mm wall thickness which had been cleaned using chromic acid and then etched with a 25%-by-mass solution of hydrofluoric acid. The neutron diffraction experiments were performed using the LAD instrument at the ISIS pulsed neutron source, Rutherford Appleton Laboratory. The complete experiment comprised the measurement of the diffraction patterns for the samples in their container in a cylindrical vanadium furnace, the empty container in the furnace, the empty furnace and a vanadium rod of 8.31(4) mm diameter for normalization purposes. The data analysis was made using the ATLAS suite of programs (Soper *et al* 1989) and the nuclear cross-sections were calculated using the values of Sears (1992).

LAD comprises 14 groups of detectors at scattering angles of $\pm 5°$, $\pm 10°$, $\pm 20°$, $\pm 35°$, $\pm 60°$, $\pm 90°$ and $\pm 150°$ corresponding to instrumental resolution functions ($\Delta k/k$) of 11%, 6%, 2.8%, 1.7%, 1.2%, 0.8% and 0.5% respectively. The final $F(k)$ were constructed by merging all those diffraction patterns from the different groups that showed good agreement and it was checked that the resultant $F(k)$ tend to the correct high-k limit and obey the usual sum rule relation, and that there is good overall agreement between $F(k)$ and the back-Fourier transform of the corresponding $G(r)$ after the unphysical low-r oscillations have been set to their calculated $G(0)$ limit (Salmon and Benmore 1992). The temperatures of the $ScCl_3$ and ScI_3 melts were 980(3) °C and 955(3) °C respectively and the full experimental details are given by Wasse (1998).

For molten $ScCl_3$ a number density of 0.0259(3) Å^{-3} was estimated by using the mass density of 1.63(1) g cm^{-3} at ≈ 1000 °C measured by Klemm (1926). This corresponds to a large volume change $\Delta V/V_m$ of 32% where $\Delta V = V_m - V_{RT}$; V_m is the molar volume of the liquid at the melting point temperature T_m and V_{RT} is the molar volume of the salt at room temperature. A smaller volume change $\Delta V/V_m$ of 25%, corresponding to $n_0 = 0.0288$ Å^{-3}, was calculated by using the Tallon–Robinson (1982) relation between the entropy change on melting ΔS_m (table 1) and $\Delta V/V_m$ with the parameters for trivalent metal halides given by Akdeniz and Tosi (1992), i.e.

$$\Delta S_m/R = 5.0 \ln 2 + 12.4 \, \Delta V/V_m \qquad (4)$$

where R is the molar gas constant. To assess the effect of an uncertainty in n_0, the data analysis for $ScCl_3$ was repeated using this higher number density. Experimental information on the density of liquid ScI_3 does not appear to be available in the literature. A volume change $\Delta V/V_m$ of 35% was, however, calculated by using equation (4) and ΔS_m reported in table 1 which corresponds to a number density of 0.0173(3) Å^{-3} (cf. O'Hare *et al* (1987) where a volume change of 30% for ScI_3 was estimated).

4. Results

On heating the $ScCl_3$ sample, a solid–solid phase change was observed below 680 °C from the $FeCl_3$-type structure, which is the stable phase at room temperature (Klemm and Krose 1947, Fjellvåg and Karen 1994), to a structure having a diffraction pattern which resembles that of crystalline YCl_3 (Templeton and Carter 1954). It was checked that the $FeCl_3$-type phase was recovered on cooling the liquid to room temperature at the end of the diffraction experiment.

This solid–solid phase change for $ScCl_3$ has not previously been reported and will be the subject of a forthcoming paper. However, it is noteworthy that a change from the $FeCl_3$-type to the YCl_3-type structure has been observed for $CrCl_3$ on heating above ≈ -33 °C (Morosin and Narath 1964). No corresponding solid-state phase change was observed for ScI_3 which melted from its room temperature $FeCl_3$-type structure (Men'kov and Komissarova 1964, McCollum *et al* 1990).
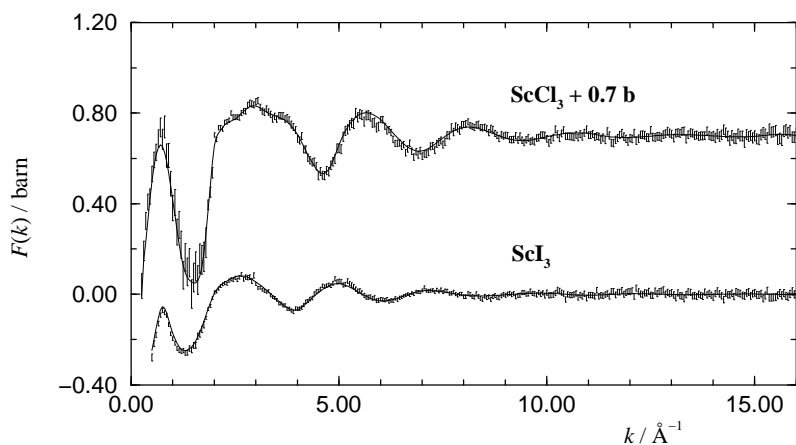

Figure 1. The measured total structure factors $F(k)$ for molten $ScCl_3$ at 980(3) °C and molten ScI_3 at 955(3) °C. The bars represent the statistical errors on the data points and the solid curves are the Fourier back-transforms of the corresponding $G(r)$ given by the solid curves in figure 2.

The measured $F(k)$ for molten $ScCl_3$ and ScI_3 are shown in figure 1 and have similar overall features. Each function has a prominent first sharp diffraction peak (FSDP) which is a signature of intermediate-range order (see e.g. Salmon 1994). Its position, height and full width at half-maximum are 0.75(5) Å^{-1}, 0.71(3) b and 0.63(3) Å^{-1} for $ScCl_3$, and 0.75(5) Å^{-1}, 0.20(2) b and 0.34(2) Å^{-1} for ScI_3, respectively.
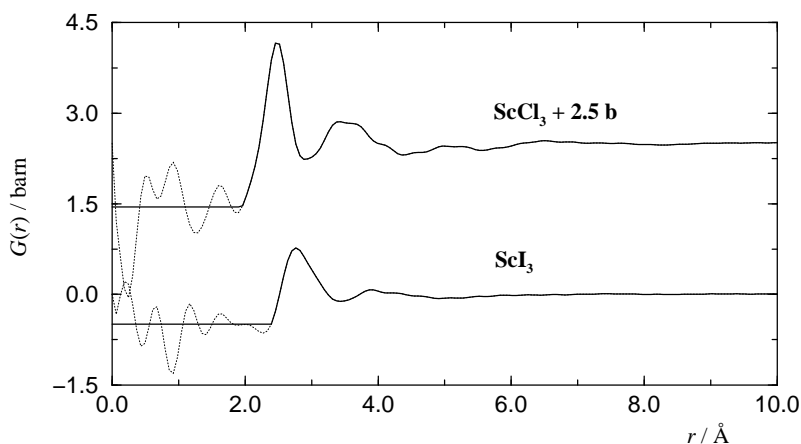

Figure 2. The total pair distribution functions $G(r)$ for molten $ScCl_3$ at 980(3) °C and molten ScI_3 at 955(3) °C obtained by Fourier transforming the $F(k)$ given by the error bars in figure 1. The unphysical low-r oscillations about the $G(0)$ limits are shown by the broken curves.

The first peak in $G(r)$ for molten $ScCl_3$ (figure 2) at 2.48(2) Å is followed by a broader feature having a maximum at 3.42(3) Å and shoulder at 4.14(3) Å. The first peak may be identified with nearest-neighbour Sc–Cl correlations by comparison with the room temperature crystal structure of $ScCl_3$, where Sc^{3+} is octahedrally coordinated to six Cl^- at 2.52(1) Å (Fjellvåg and Karen 1994), and also with the structure of YCl_3 (Templeton and Carter 1954) which is tentatively identified with the high-temperature phase of $ScCl_3$. Its integration over the range $1.96(2) \leqslant r$ (Å) $\leqslant 3.01(2)$ to the first minimum gives a coordination number $\bar{n}_{Sc}^{Cl} = 4.8(2)$. On repeating the data analysis for molten $ScCl_3$ with the higher number density obtained from equation (4), functions very similar to those given in figures 1 and 2 are obtained and the first peak in $G(r)$ gives a comparable coordination number of $\bar{n}_{Sc}^{Cl} = 5.2(2)$. The second-peak region will, by comparison with the structures of both YCl_3 and room temperature $ScCl_3$, have a strong contribution from the Cl–Cl correlations.

The first peak in $G(r)$ for molten ScI_3 (figure 2) at 2.76(2) Å is, by analogy with $ScCl_3$, assigned to Sc–I correlations and its integration over the range $2.39(2) \leqslant r$ (Å) $\leqslant 3.44(2)$ to the first minimum gives a coordination number $\bar{n}_{Sc}^{I} = 4.7(2)$. Likewise, the second peak at 3.89(3) Å will have a strong contribution from I–I correlations. When compared with $G(r)$ for $ScCl_3$, the second peak is less intense relative to the first, in keeping with the reduced relative weighting of the anion–anion correlations: the C:B ratio in equation (2) is 1.170 for $ScCl_3$ and 0.646 for ScI_3.

5. Discussion

The FSDP for $ScCl_3$ is intriguing since it occurs at a k-value that is smaller than for the other MCl_3 melts listed in table 2 and it would therefore be useful to have information on its origin. The relative contributions of the partial structure factors cannot, however, be uniquely determined on the basis of the present total-structure-factor measurement.

Table 2. The position of the FSDP, k_{FSDP}, and the local coordination environment of several molten MX_3 systems which have the same or closely related ionic crystal structures at room temperature. The liquid temperature is denoted by T.

Salt	T (°C)	k_{FSDP} (Å^{-1})	r_{MX} (Å)	$\bar{n}_M^X$	Reference
$AlCl_3$	200	0.92(2)	2.11(2)	4.0(2)	Badyal *et al* (1994)
$FeCl_3$	325	0.95	2.23(2)	3.8(2)	Badyal *et al* (1997)
$ScCl_3$	980	0.75(5)	2.48(2)	4.8(2)	Present work
$InCl_3$	605	—	2.35(2)	≈ 5–6	Price *et al* (1993)[a]
YCl_3	747	0.95	2.71(2)	5.9	Saboungi *et al* (1991)
	760	0.95(5)	2.67(3)	5.7(4)	Wasse and Salmon (1998a)
ScI_3	955	0.75(5)	2.76(3)	4.7(2)	Present work

[a] The low-k region was not accessible in the neutron diffraction experiment owing to the large neutron absorption cross section of indium.

The salts $AlCl_3$, $FeCl_3$, $ScCl_3$, $InCl_3$ and YCl_3 all crystallize at room temperature into either the YCl_3-type or $FeCl_3$-type structure (table 1). These structures can be viewed as comprising layers of edge-sharing octahedra which are stacked to give either a cubic close packing or hexagonal close packing of the chloride ions respectively (Müller 1993). Although $AlCl_3$ and YCl_3 crystallize in the same structure, rather different effects are observed on melting. For example, the salt with the smallest cation, $AlCl_3$, melts at a low temperature with a large entropy and volume change into a liquid with a small electrical conductivity. By contrast, the salt with the largest cation, YCl_3, melts at a much higher temperature with a smaller entropy change and

a much smaller volume change into a liquid with an electrical conductivity which is orders of magnitude larger. These macroscopic properties suggest different liquid structures, as borne out by several microscopic probes which show that aluminium is tetrahedrally coordinated by chlorine (Harris *et al* 1951, Badyal *et al* 1994), probably in the form of rather stable Al_2Cl_6 charge-neutral dimers (Hutchinson *et al* 1999), and that yttrium is sixfold coordinated by chlorine in distorted octahedra which may edge share to form a 'loose' ionic network melt (Papatheodorou 1977, Saboungi *et al* 1991). It therefore appears as though $AlCl_3$ changes from an ionic to a 'molecular' system on melting whereas YCl_3 remains an ionic material in both its solid and liquid phases (March and Tosi 1980, Saboungi *et al* 1991, Tosi *et al* 1991, Akdeniz and Tosi 1992).

The salt $ScCl_3$ also has relatively large volume and entropy changes on melting and the present work shows that there is a reduction in the coordination number $\bar{n}_{Sc}^{Cl}$ from six to about five. Unlike the cases for $AlCl_3$ and $FeCl_3$, however, the interactions in molten $ScCl_3$ appear to retain a more ionic character (see tables 1 and 2). For example, the first peak in $G(r)$ does not return to the $G(0)$ limit on its high-r side as for typical molecular liquids, the Pettifor (1986) chemical parameters χ_M for scandium and yttrium are comparable and the solid has both a high melting point temperature and high electrical conductivity. The physico-chemical properties of $ScCl_3$, many of which are comparable to those of $InCl_3$, therefore characterize it as intermediate between $AlCl_3$ and $FeCl_3$ on the one hand and YCl_3 on the other. It will be interesting to find out the extent to which computer simulation studies, using an ionic interaction model that includes an account of ionic polarization phenomena, can reproduce its microscopic structure and dynamics (Hutchinson *et al* 1999).

The reduction in the Sc–X coordination number from six to about five on melting in both ScX_3 systems implies that species other than ScX_6^{3-} octahedra are present in the liquid state. It is therefore interesting that Raman spectroscopy studies on molten ScI_3–CsI mixtures containing up to 60% ScI_3 (Metallinou *et al* 1991) suggest that octahedral and tetrahedral ionic species predominate in the equilibrium

$$ScI_6^{3-} \leftrightharpoons ScI_4^- + 2I^- \tag{5}$$

and that a third binuclear Sc species, possibly $Sc_2I_9^{3-}$, is also present at high ScI_3 concentrations.

6. Conclusions

On heating $ScCl_3$, a solid–solid phase transition was observed from the $FeCl_3$-type structure to possibly the YCl_3-type structure whereas ScI_3 was found to remain in its room temperature $FeCl_3$-type structure up until the melting point. The total structure factor for both melts has a prominent first sharp diffraction peak which occurs in the chloride melt at a relatively small k-value. On melting, there is a reduction in the Sc–X coordination number for both systems from six to about five.

Acknowledgments

References

Akdeniz Z and Tosi M P 1992 *Proc. R. Soc.* A **437** 85
Badyal Y S, Allen D A and Howe R A 1994 *J. Phys.: Condens. Matter* **6** 10 193
Badyal Y S, Saboungi M-L, Price D L, Haeffner D R and Shastri S D 1997 *Europhys. Lett.* **39** 19
Biltz W and Voigt A 1923 *Z. Anorg. Allg. Chem.* **126** 39
Dworkin A S and Bredig M A 1971 *High Temp. Sci.* **3** 81
Fjellvåg H and Karen P 1994 *Acta Chem. Scand.* **48** 294
Harris R L, Wood R E and Ritter H L 1951 *J. Am. Chem. Soc.* **73** 3151
Hutchinson F, Walters M K, Rowley A J and Madden P A 1999 *J. Chem. Phys.* at press
King L A and Seegmiller D W 1971 *J. Chem. Eng. Data* **16** 23
Klemm W 1926 *Z. Anorg. Allg. Chem.* **152** 235
Klemm W 1964 *Molten Salt Chemistry* ed M Blander (New York: Interscience) pp 535–606
Klemm W and Krose E 1947 *Z. Anorg. Allg. Chem.* **253** 218
Landolt–Börnstein New Series 1973 Group III, vol 7a, ed K-H Hellwege and A M Hellwege (Berlin: Springer) p 366
Madden P A and Wilson M 1996 *Chem. Soc. Rev.* **25** 339
March N H and Tosi M P 1980 *Phys. Chem. Liq.* **10** 39
McCollum B C, Dudis D S, Lachgar A and Corbett J D 1990 *Inorg. Chem.* **29** 2030
Men'kov A A and Komissarova L N 1964 *Zh. Neorg. Khim.* **9** 766
Metallinou M M, Nalbandian L, Papatheodorou G N, Voigt W and Emons H H 1991 *Inorg. Chem.* **30** 4260
Mochinaga J and Irisawa K 1974 *Bull. Chem. Soc. Japan* **47** 364
Morosin B and Narath A 1964 *J. Chem. Phys.* **40** 1958
Müller U 1993 *Inorganic Structural Chemistry* (Chichester: Wiley)
O'Hare P A G, Johnson G K, Tasker I R, Flotow H E and Struck C W 1987 *J. Chem. Thermodyn.* **19** 77
Pankratz L B 1984 *Thermodynamic Properties of Halides* Bulletin 674 (Washington, DC: US Bureau of Mines)
Papatheodorou G N 1977 *J. Chem. Phys.* **66** 2893
Pettifor D G 1986 *J. Phys. C: Solid State Phys.* **19** 285
Price D L, Saboungi M-L, Badyal Y S, Wang J, Moss S C and Leheny R L 1998 *Phys. Rev.* B **57** 10 496
Price D L, Saboungi M-L, Howells W S and Tosi M P 1993 *Proc. Int. Symp. on Molten Salt Chemistry and Technology*
    vol 93–9, ed M-L Saboungi and H Kojima (Pennington, NJ: Electrochemical Society) p 1
Saboungi M-L, Price D L, Scamehorn C and Tosi M P 1991 *Europhys. Lett.* **15** 283
Salmon P S 1994 *Proc. R. Soc.* A **445** 351
Salmon P S and Benmore C J 1992 *Recent Developments in the Physics of Fluids* ed W S Howells and A K Soper
    (Bristol: Hilger) p F225
Sears V F 1992 *Neutron News* **3** 26
Shannon R D 1976 *Acta Crystallogr.* A **32** 751
Soper A K, Howells W S and Hannon A C 1989 *Rutherford Appleton Laboratory Report* RAL-89-046
Tallon J L and Robinson W H 1982 *Phys. Lett.* A **87** 365
Templeton D H and Carter G F 1954 *J. Phys. Chem.* **58** 940
Tosi M P, Pastore G, Saboungi M-L and Price D L 1991 *Phys. Scr.* T **39** 367
Ubbelohde A R 1978 *The Molten State of Matter* (Chichester: Wiley)
Wasse J C 1998 *PhD Thesis* University of East Anglia, UK
Wasse J C and Salmon P S 1998a *Physica* B **241–243** 967
Wasse J C and Salmon P S 1998b *J. Phys.: Condens. Matter* **10** 8139
Wasse J C and Salmon P S 1999 *J. Phys.: Condens. Matter* **11** 1381
Wyckoff R W G 1964 *Crystal Structures* 2nd edn, vol 2 (New York: Interscience)