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## LETTER TO THE EDITOR

## Structure of molten $\text{TbCl}_3$ measured by neutron diffraction

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### Abstract

The total structure factor of molten  $\text{TbCl}_3$  at 617 °C was measured by using neutron diffraction. The data are in agreement with results from previous experimental work but the use of a diffractometer having an extended reciprocal-space measurement window leads to improved resolution in real space. Significant discrepancies with the results obtained from recent molecular dynamics simulations carried out using a polarizable ion model, in which the interaction potentials were optimized to enhance agreement with previous diffraction data, are thereby highlighted. It is hence shown that there is considerable scope for the development of this model for  $\text{TbCl}_3$  and for other trivalent metal halide systems spanning a wide range of ion size ratios.

Trivalent metal chloride systems,  $\text{MCl}_3$ , present a challenge to the development of a realistic model for their structure and behaviour within a single conceptual framework such as that based on polarizable ions (Hutchinson *et al* 1999, 2000, 2001). This follows from the marked changes observed in their physical behaviour with decreasing cation radius when effects that are sometimes attributed to ‘covalency’ become increasingly notable. In this context  $\text{TbCl}_3$  is an interesting case since the  $\text{Tb}^{3+}$  cation has a radius that is intermediate between those of large cations such as  $\text{La}^{3+}$  and small ones such as  $\text{Y}^{3+}$ . For example,  $\text{LaCl}_3$  crystallizes in the  $\text{UCl}_3$ -type structure (Morosin 1968), in which  $\text{La}^{3+}$  is ninefold coordinated by anions, and melts with a volume change of 16%, whereas  $\text{YCl}_3$  crystallizes in the  $\text{AlCl}_3$ -type structure (Templeton and Carter 1954), in which  $\text{Y}^{3+}$  is octahedrally coordinated by anions, and has a negligible volume change on melting (Wasse and Salmon 1999b). By comparison,  $\text{TbCl}_3$  adopts the  $\text{PuBr}_3$ -type structure at room temperature in which  $\text{Tb}^{3+}$  is eightfold coordinated by anions (Forrester *et al* 1964). At 510–517 °C it undergoes a solid–solid phase transition into a structure consisting of  $\text{TbCl}_6^{3-}$  double octahedra (Gunsilius *et al* 1988, Pankratz 1984) before melting at 582–587 °C with a negligible volume change (Pankratz 1984, Gunsilius *et al* 1988, Wasse and Salmon 1999b).

Neutron diffraction from molten salts provides information that acts as a useful benchmark for testing interaction models (Hutchinson *et al* 1999, 2000, 2001, Takagi *et al* 1999). In these experiments the neutron total structure factor

$$F(k) = c_M^2 b_M^2 [S_{MM}(k) - 1] + 2c_M c_X b_M b_X [S_{MX}(k) - 1] + c_X^2 b_X^2 [S_{XX}(k) - 1] \quad (1)$$

is first measured where  $c_\alpha$  and  $b_\alpha$  are the atomic fraction and coherent scattering length of chemical species  $\alpha$  respectively,  $k$  is the magnitude of the scattering vector and  $S_{\alpha\beta}(k)$  denotes a so-called Faber–Ziman partial structure factor. The corresponding real-space information is obtained from the Fourier transform relation

$$\begin{aligned} rG'(r) &= \frac{1}{2\pi^2 n_0} \int_0^\infty dk F(k) k M(k) \sin(kr) = \int_{-\infty}^\infty r_1 G(r_1) M(r - r_1) dr_1 \\ &= \int_0^\infty r_1 G(r_1) [M(r - r_1) - M(r + r_1)] dr_1 \end{aligned} \quad (2)$$

where  $n_0$  is the ionic number density. The modification function  $M(k \leq k_{\max}) = 1$ ,  $M(k > k_{\max}) = 0$  describes the finite measurement window of the diffractometer which is represented in real space by

$$M(r) = \frac{k_{\max}}{\pi} \text{sinc}(k_{\max} r) \quad (3)$$

where  $\text{sinc}(x) \equiv \sin(x)/x$ . The deconvoluted total pair distribution function is given by

$$G(r) = c_M^2 b_M^2 [g_{MM}(r) - 1] + 2c_M c_X b_M b_X [g_{MX}(r) - 1] + c_X^2 b_X^2 [g_{XX}(r) - 1] \quad (4)$$

where  $g_{\alpha\beta}(r)$  is a partial pair distribution function. Provided  $k_{\max}$  is sufficiently large that the high- $k$  oscillations in  $F(k)$  are negligible,  $M(r)$  has no discernible effect on  $rG(r)$ . Otherwise the modification function causes a broadening and distortion of the peaks in  $rG(r)$ , effects that become increasingly more significant as the value of  $k_{\max}$  becomes smaller. The mean number of particles of type  $\beta$  contained in a volume defined by two concentric spheres of radii  $r_i$  and  $r_j$ , centred on a particle of type  $\alpha$ , is given by

$$\bar{n}_\alpha^\beta = 4\pi n_0 c_\beta \int_{r_i}^{r_j} r^2 g_{\alpha\beta}(r) dr. \quad (5)$$

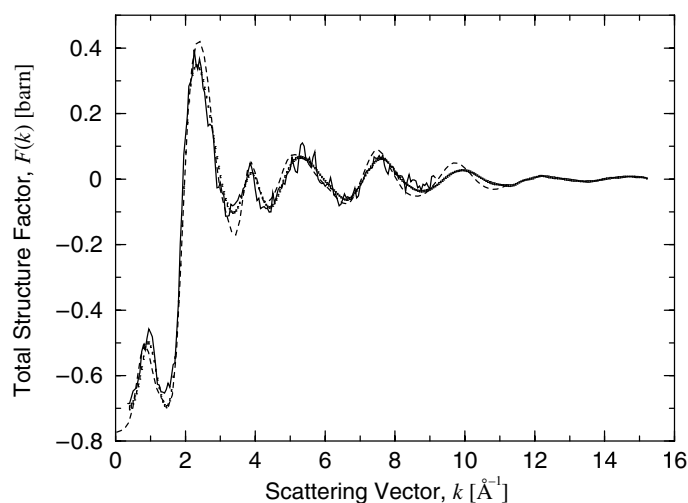
In the cases of molten  $\text{LaCl}_3$  and  $\text{YCl}_3$  previously studied (Wasse and Salmon 1999a, 1999b) the total structure factor  $F(k)$  was measured with the LAD diffractometer, at the ISIS pulsed neutron source, using a large measurement window ( $0.3 \leq k \text{ (\AA}^{-1}) \leq 20$ ). For these systems it is found that although molecular dynamics simulations made using the polarizable ion model reproduce the main structural features, a fully quantitative description is not forthcoming even when the interaction potentials are refined to optimize agreement with diffraction experiments; e.g. the simulated first peak in  $G(r)$  is too sharp (Hutchinson *et al* 2001). By comparison, the previous  $F(k)$  for  $\text{TbCl}_3$  was measured (Wasse and Salmon 1999b) with the SLAD diffractometer, at the Studsvik neutron reactor source, with a measurement window restricted to  $0.35 \leq k \text{ (\AA}^{-1}) \leq 9.15$ . In this case  $M(r)$  has a large effect and the experimental  $G'(r)$  can be reproduced by the molecular dynamics results of Hutchinson *et al* (2001) provided that a window function with  $k_{\max}$  set at the experimental value is applied to the simulated  $F(k)$  on application of equation (2). We have therefore been motivated to re-measure  $F(k)$  for molten  $\text{TbCl}_3$ , but over an *extended*  $k$ -range, in order to determine whether the agreement between experiment and molecular dynamics simulation arises from a regime of ion sizes for which the polarizable ion model works particularly well or from an artefact of a limited measurement window.

The neutron diffraction experiment was made using the instrument D4C at the Institut Laue-Langevin, Grenoble, operating at an incident wavelength of 0.7095 Å to give a net

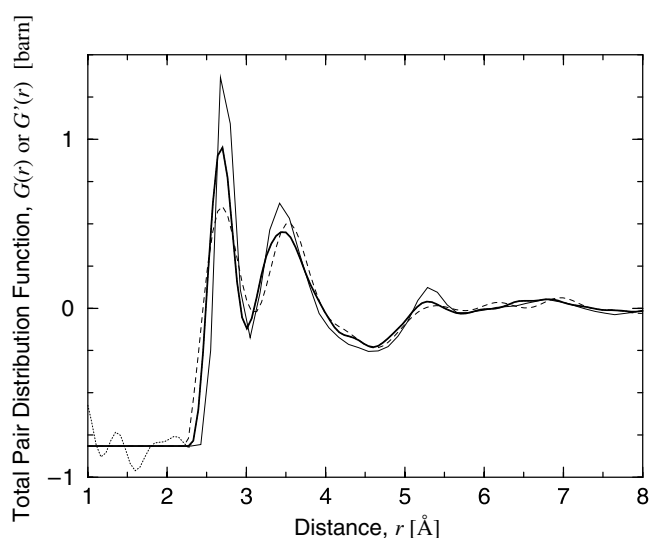
measurement range of  $0.40 \leq k \text{ (\AA}^{-1}\text{)} \leq 15.2$ . The  $\text{TbCl}_3$  (Aldrich 99.99%) was sealed in a cylindrical silica ampoule of internal diameter 5 mm and 1 mm wall thickness. Diffraction patterns were taken for the sample in its container in a cylindrical vanadium furnace, the empty container in the furnace, the empty furnace and a vanadium rod of dimensions comparable to the sample for normalization purposes. The intensity for a cadmium neutron-absorbing rod of similar diameter to the sample was also measured to account for the effect of the sample self-shielding on the background count rate at small scattering angles. The total paramagnetic scattering cross-section of  $\text{Tb}^{3+}$  at the incident wavelength (3.55 barn (b)) and its paramagnetic differential scattering cross-section were calculated using the methods described by Wasse and Salmon (1999a). The scattering length and nuclear cross-sections were taken from Sears (1992) and the data analysis procedure followed the scheme described elsewhere (Salmon 1988). It was necessary to make a small correction for hydrogen which was estimated to be present at the level of  $\approx 1$  mol% (Salmon and Lond 1992). The coefficients of the Tb–Tb, Tb–Cl and Cl–Cl terms in equations (1) and (4) are 34.0(3), 265(1) and 515.9(1) mb respectively, while the molten salt was held at 617(3) °C, where  $n_0 = 0.0327(3) \text{ \AA}^{-3}$  (Wasse and Salmon 1999b). Like in the previous neutron diffraction experiments on molten  $\text{LaCl}_3$  and  $\text{YCl}_3$  (Wasse and Salmon 1999a, 1999b), the cation–anion and anion–anion correlations for  $\text{TbCl}_3$  receive the largest weighting in the measured diffraction patterns.

As illustrated in figure 1, the new  $F(k)$  for molten  $\text{TbCl}_3$  measured using neutron diffraction is in agreement with the old  $F(k)$  of Wasse and Salmon (1999b) within the experimental errors and features a first sharp diffraction peak at  $0.93(2) \text{ \AA}^{-1}$  which is a signature of ionic ordering on an intermediate-range length scale (Salmon 1992, 1994). The corresponding  $G'(r)$  are shown in figure 2 and reveal that the function obtained from the extended  $k$ -space data set has sharper features and a second peak that is shifted to smaller  $r$ . By comparison with the crystalline phase, the first peak at  $2.68(2) \text{ \AA}$  is attributed to Tb–Cl correlations and the second peak at  $3.46(2) \text{ \AA}$  will have a strong contribution from Cl–Cl correlations. To investigate the effect of the measurement window, the first two peaks in  $rG'(r)$  were fitted by representing the individual  $rg_{\alpha\beta}(r)$  by Gaussians convoluted with  $M(r)$  (cf Petri *et al* 2000). By contrast with the SLAD data, no significant distortion of the Gaussians by  $M(r)$  could be found for the D4C data; i.e. the oscillations in the new  $F(k)$  at  $k_{\text{max}}$  appear to be sufficiently well damped that the finite measurement window of the diffractometer causes no significant modification of the desired total pair distribution function. The first peak, for both data sets, could be fitted using a Gaussian corresponding to a coordination number  $\bar{n}_{\text{Tb}}^{\text{Cl}} = 5.7(2)$ . The ratio of the first to second peak positions in  $G'(r)$  for the D4C data is 1.29(1) which suggests a deformation of  $\text{MCl}_6^{3-}$  conformations from regular octahedral geometry for which a ratio of  $\sqrt{2}$  is expected. The  $G'(r)$  measured using SLAD could be reproduced by using the  $F(k)$  measured using D4C provided that  $k_{\text{max}}$  in equation (2) is set at the correspondingly smaller value of  $9.15 \text{ \AA}^{-1}$ .

In the high-temperature crystalline phase of  $\text{TbCl}_3$  each chloride ion is surrounded by 13 other chloride ions in the range from 3.53 to 4.58  $\text{\AA}$  and each terbium ion has one nearest-neighbour terbium ion at 4.02  $\text{\AA}$  and four next-neighbour terbium ions at 4.85  $\text{\AA}$  (Gunsilius *et al* 1988). There is a negligible volume change on melting (Wasse and Salmon 1999b) which indicates comparable short-range ordering in the liquid phase. Integrating the area of the first two peaks in  $G'(r)$  for the melt to the first minimum at 4.60  $\text{\AA}$  and assuming  $\bar{n}_{\text{Tb}}^{\text{Cl}} = 6$  gives an area consistent with  $\bar{n}_{\text{Cl}}^{\text{Cl}} = 12.2(3)$  if  $\bar{n}_{\text{Tb}}^{\text{Tb}} = 0$  or  $\bar{n}_{\text{Cl}}^{\text{Cl}} = 12.0(3)$  if  $\bar{n}_{\text{Tb}}^{\text{Tb}} = 1$ . Thus, as for systems such as  $\text{YCl}_3$  that also melt with a negligible volume change, the cation–anion coordination number does not change substantially on melting but there is some evidence for a reduction in the packing fraction of chloride ions (Saboungi *et al* 1991, Wasse and Salmon 1999b).



**Figure 1.** The total structure factors,  $F(k)$ , for molten  $\text{TbCl}_3$  measured by using the D4C (present work—points with error bars) and SLAD (Wasse and Salmon 1999b—solid curve) diffractometers at 615(3) and 617(3) °C respectively. The total structure factor obtained from the polarizable ion model molecular dynamics simulation of Hutchinson *et al* (2001) is shown by the dashed curve.



**Figure 2.** The real-space function,  $G'(r)$ , for molten  $\text{TbCl}_3$  obtained by using equation (2) to Fourier transform the  $F(k)$  of figure 1 as measured using either D4C with  $k_{\text{max}} = 15.2 \text{ \AA}^{-1}$  (thick solid curve) or SLAD with  $k_{\text{max}} = 9.15 \text{ \AA}^{-1}$  (dashed curve). The latter shows considerable distortion owing to the finite measurement window of SLAD, whereas the former is an excellent approximation to the required total pair distribution function  $G(r)$ —see the text. The unphysical low- $r$  oscillations for the D4C data are shown by the dotted curve and the  $G(r)$  obtained from the polarizable ion model molecular dynamics simulation of Hutchinson *et al* (2001) is shown by the thin solid curve.

The new data show that significant discrepancies occur between experiment and the polarizable ion model molecular dynamics simulation of Hutchinson *et al* (2001) for  $\text{TbCl}_3$  in which the interaction potentials were refined to optimize agreement with the previous neutron

diffraction results of Wasse and Salmon (1999b). The oscillations in  $F(k)$  at high  $k$  appear to be out of phase and in  $r$ -space the simulated first peak is too sharp. The agreement between the real-space experimental and simulation results reported by Hutchinson *et al* (2001) for liquid  $\text{TbCl}_3$  is, therefore, largely an artefact of the limited measurement window of the diffractometer used in the previous neutron diffraction work. Thus for  $\text{TbCl}_3$ , as for most other  $\text{MCl}_3$  (Hutchinson *et al* 1999, 2001) and  $\text{MBr}_3$  (Wasse *et al* 2000, Hutchinson *et al* 2000) systems, notable discrepancies are observed between the simulated and measured structures. Features such as the excessive sharpness of the simulated first peak in  $g_{\text{MX}}(r)$  will have serious ramifications for predicting the correct dynamics; e.g. the ionic mobilities obtained from the simulations are too small (Hutchinson *et al* 1999). The present work therefore demonstrates a need to consider afresh issues such as the repulsive part of the cation–anion potential and the anion compressibility in different environments if a truly transferable model for the interactions in trivalent metal halides is to be developed within the framework of the polarizable ion model across the entire range of ion size ratios.

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