The origin of diffuse scattering in crystalline carbon tetraiodide

L Temleitner and L Pusztai

Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, PO Box 49, H-1525 Budapest, Hungary

E-mail: temleitner.laszlo@wigner.mta.hu

Received 26 February 2013, in final form 3 April 2013
Published 18 October 2013
Online at stacks.iop.org/JPhysCM/25/454209

Abstract
Total scattering neutron powder diffraction measurements were performed on the tetragonal phase ($a = 6.4202(5)$ Å, $c = 9.5762(12)$ Å) of Cl$_4$. The experiments were followed by reverse Monte Carlo (for powder diffraction) modelling. Detailed analyses of the resulting particle configurations revealed that the observed diffuse scattering originates from the libration of the molecules. By examining the partial radial distribution functions a distinct carbon–iodine peak at 4.5 Å is found, which appears as a consequence of corner-to-face mutual alignment of two molecules. The occurrence of edge-to-edge alignments is also significant within the first carbon–carbon coordination shell. (Some figures may appear in colour only in the online journal)

1. Introduction

Among the crystalline CX$_4$ halides that do not contain iodine (CF$_4$, CCl$_4$, CBr$_4$), monoclinic (CF$_4$ [1–5], CCl$_4$ [6] and CBr$_4$ [7]), face-centred cubic (CCl$_4$ [8] and CBr$_4$ [9]) and rhombohedral phases (CF$_4$ [4], CCl$_4$ [6] and CBr$_4$ [10]) are common. The structure of carbon tetraiodide has been debated for a long time. Initially it was classified as cubic (see the references in [11]) or monoclinic [12], analogous to the above carbon-tetrahalides. The crystal structure was eventually solved in 1981, when it was classified as tetragonal ($I42m$), on the basis of single crystal x-ray diffraction data [11]. The sample in that work was synthesized by the reaction of ethyl iodide and carbon tetrachloride, using the synthesis of McArthur et al [13].

Considering existing knowledge on XI$_4$ type crystals [14–19] that possess a cubic symmetry, this unusual structure has been explained by the close packing of I atoms and by an intermolecular I–I bond [11]. The observed large value of the ionization potential, found by ultraviolet spectroscopy, was explained also by the presence of this bond [20]. Recently, this system was exploited as a model for packing tetrahedra [19].

Another interesting feature of this class of material is the possible presence of plastic crystalline phases, appearing as the rhombohedral phase of carbon tetrafluoride [4] and the face-centred cubic phases of carbon tetrachloride [6, 21] and carbon tetrabromide [9]. The common feature of these phases is that while the centres of the molecules maintain translational (i.e., crystalline) symmetry, the molecules can rotate (for CF$_4$, see [22]). This rotation is not free, but hindered by neighbouring atoms. As a result, short-range order exists between ligands belonging to neighbouring molecules. This is manifested as diffuse scattering that becomes structured in reciprocal space, due to its relation to the average structure (e.g., for CBr$_4$, see [23–25]).

Detailed analyses were presented some years ago for some of the crystalline CX$_4$ compounds, applying reverse Monte Carlo modelling [26, 25] and molecular dynamics simulation [27]. These articles showed that the correlations between the ‘ligands’ (Cl atoms in CCl$_4$ and Br atoms in CBr$_4$) have a close relationship with those found for the corresponding liquid phase.

During our systematic studies of crystalline phases of carbon-tetrahalides, diffuse scattering in carbon tetraiodide has been found; this initiated the present study. Since an analysis of the Bragg pattern has already been carried out by Pohl [11], the present investigation focuses on pair correlations between atoms and on orientational correlations; concerning these issues, standard crystallographic analysis does not provide complete information on the structural details of the system.

© 2013 IOP Publishing Ltd  Printed in the UK & the USA
2. Experiment

The sample was provided by Aldrich (97% purity) and was further powdered before the experiment so that random orientation of the crystallites could be guaranteed.

Room temperature carbon tetraiodide was measured by neutron powder diffraction on the former SLAD diffractometer [28] (Studsvik NFL, Sweden). Using the standard wavelength of the instrument (1.119 Å), the diffraction pattern of the sample could be recorded in the 0.29–10.55 Å\(^{-1}\) range. Scattered intensities from the 8 mm diameter vanadium sample container, background and a solid vanadium rod were also determined. Standard data normalization and correction procedures [29] were performed by the CORRECT [30] computer program; absorption, normalization and correction procedures [29] were performed by the CORRECT [30] computer program; absorption, multiple and inelastic scattering contributions were taken into account during the process.

As it turned out later, the sealing of the sample holder had leaked during the measurement, and a small amount of sample had been evaporated from the can. In the pattern several additional Bragg-peaks appeared, which were thought to originate from the orthorhombic phase of I\(_2\) [31, 32] (spontaneous break-up of Cl\(_4\) molecules, due to the tight packing of large iodine atoms, is common). The most intense such ‘alien’ Bragg peak could be observed at 1.7 Å\(^{-1}\).

The lattice parameters were re-determined by the ‘Fox’ software [33]; they were found to be \(a = 6.4202(5)\,\text{Å}, \, c = 9.5762(12)\,\text{Å}\). The amount of I\(_2\) impurity was estimated by a joint fit of both compounds using the established structures [31, 32]; the amount was found to be about 2.8%. This corresponds well with the guaranteed purity of the commercially available compound. This indicates that the scattering from impurities originates from the sample, and not from the accidentally deposited, previously evaporated vapour from the container wall.

3. Structural modelling

Computer modelling was performed using the reverse Monte Carlo for powder diffraction (RMCPOW) software [34]. RMCPOW is capable of simulating both Bragg- and diffuse scattering in \(Q\)-space. The molecule has the shape of an ideal tetrahedron, with 2.157 Å bond length between carbon and iodine atoms [35, 36]. The molecular structure was maintained during the simulation by ‘fixed neighbour constraints’ (fnc) [37]. The carbon–iodine and iodine–iodine distances within the molecules were constrained to the regions between 2.1 and 2.2 Å and between 3.42 and 3.62 Å, respectively. These constraints, apart from keeping molecules together, allowed them to rotate by a series of single atomic moves. The intermolecular closest approach distances were set at 5.7, 4.0 and 3.3 Å for carbon–carbon, carbon–iodine and iodine–iodine pairs, respectively.

Initially, a supercell of \(10^3\) times the Bravais-cell was constructed, which corresponded to 2000 molecules. The atomic positions in the unit cell were set as published in [11], using the previously determined lattice parameters. At the end of the simulation, a goodness-of-fit \(R_{wp} = 9.54\%\) was reached and 20 independent configurations had been collected for further analyses. (Between two ‘independent particle configurations’, each atom in the simulation box has moved successfully at least once.)

4. Results and discussion

Diffuse scattering from a powdered crystalline sample may result from effects other than positional disorder in the bulk crystalline single phase. Here, it is assumed that positional disorder is the only reason for the observed diffuse scattering; before discussing the results from our calculations it is therefore necessary to consider some of the other possibilities.

First, one might argue that the origin is the molecular iodine (I\(_2\)) that is present in the sample as impurity; this is not really probable, due to its small contribution and due to the lack of intense diffuse scattering in the pure phase measurements [31, 32]. Another hypothesis is that the diffuse scattering might be related to the (small) size of the grains. However, no broadening of the Bragg-peaks was observed here that could be related to small grains. As yet another possible reason, the presence of an amorphous phase may be assumed. Amorphization has been reported for CCl\(_4\) (see, for example, [38]); this took place during vapour deposition on a cooled substrate. For SnI\(_3\) the presence of amorphous phase is reported at pressures over 25 GPa [39]. In contrast to these (somewhat extreme) cases, the present study was performed at ambient conditions (and on commercial samples) and no trace of any additional amorphous phase could be observed. We therefore can conclude that the observed diffuse scattering is related to the bulk phase structural properties of crystalline Cl\(_4\).

At the start of the simulation, we tried to remove the Bragg scattering part of the crystalline I\(_2\) traces from the full pattern, by extrapolating the components of the Debye–Waller factor from the low-temperature measured data [32]. This resulted in slightly better agreement with experimental data; still, some of the discrepancies remained, most probably due to the not-well-known magnitude of the Debye–Waller factors. This is why we decided not to bias the results with this complication and started the simulations without subtracting this kind of background. At the final stage of the RMCPOW calculation, the agreement shown in figure 1 was reached, which (with the \(R\)-factor value less than 10%) may justifiably be called satisfactory. A possible reason for the remaining differences between measured and calculated data is the presence of the Bragg-peaks of the small amount of I\(_2\); they are most apparent between 1.5 and 2.5 Å\(^{-1}\) where they caused small modulations of the diffuse scattering part of the simulated pattern.

The coherent neutron scattering lengths of carbon and iodine are 6.646 and 5.28 fm [40] respectively. Thus, the contributions of partial structure factors to the measured total scattering structure factor are 5.7%, 36.4% and 57.9% for carbon–carbon, carbon–iodine and iodine–iodine pairs, respectively. C–I and I–I correlations may therefore be determined well, whereas the positions of C atoms (and, hence, C–C correlations) are influenced mostly by the applied
fixed neighbour constraints. Since none of the 2a and 8i Wyckoff sites restrict the reflection conditions (in comparison with the general 16j Wyckoff site), the above contributions of the partials are valid for all Bragg-reflections too.

Figure 2 shows a condensed view of the supercell as reduced to one Bravais-cell. This picture represents not just the average structure but also the effect of thermal displacements. The latter are manifested as the difference between instantaneous and average positions. Intuition based on inspecting the spread of the instantaneous atomic positions around their equilibrium values suggests that the major contribution to the measured diffuse scattering must come from the sizeable displacements of I atoms or, in other words, the libration of the molecules.

4.1. Partial radial distribution functions

Partial radial distribution functions (prdf), as calculated from the final configuration, are shown in figure 3. Among the carbon-tetrahalides, the closest analogue of the ordered phase of carbon tetraiodide is the ordered phase of carbon tetrabromide; for the sake of comparison, rescaled prdfs [25] of CBr$_4$ in phase II (monoclinic) are also shown. Since the two structures do not belong to the same space group, exact rescaling (connected to the different sizes of Br and I atoms) is not possible. The scaling factor along the 'x' axis was chosen to be 1.06 for carbon–carbon and carbon–iodine pairs, taking into account the approximate positions of maxima of the carbon–carbon prdf. For iodine–iodine correlations a factor of 1.1 was chosen, taking into account the minimum positions between the first and second maxima.

On comparing the two phases, the carbon–carbon prdf of carbon tetraiodide looks much more ordered; the main origin of this difference is the different crystalline structure (and perhaps the fact that the CBr$_4$ data were measured only about 20 K below the phase transition temperature is also an issue in this respect). The C–C maxima in CI$_4$ can be found at approximately 6.5, 9.1, 11.2 and 13.1 Å (and larger distances too); these values nearly correspond to the shortest lattice side (6.42 Å), half of the body diagonal (6.59 Å), the 'xy' diagonal (9.08 Å), the second neighbour half body diagonal (11.22 Å) and the full body diagonal (13.15 Å) values, respectively.

It may be appropriate to briefly discuss here the sharp (unphysical) ‘cut-offs’ of the C–C and I–I partials at the shortest distances. Usually, this feature may have two sources: (1) the higher than real intermolecular cut-off and (2) non-physical short period oscillations in Q-space. Taking into account that the iodine–iodine cut-off distance is lower than the intramolecular low limit, the observed phenomena must be the result of the program trying to fit the Bragg-peaks of I$_2$.

On comparing the centre–ligand and ligand–ligand prdfs with the corresponding prdfs of CBr$_4$ phase II, CI$_4$ again appears to be a more ordered system. Concerning the
short-range behaviour, the I–I maxima are at 4.05, 4.4 and 6.6 Å; the first and the last ones are distinct. Although the peak at 4.05 Å appears, which should possess a crucial role in explaining the formation of the tetragonal lattice [11, 20], it is not so well defined in terms of pair correlations. In contrast, the carbon–iodine peak at 4.5 Å looks much more characteristic. For the assignment of the observed peaks to local orientations, see section 4.2.

4.2. Angular and orientational correlations

The angular distributions (figure 4) C–C–C and C–I–C were investigated in the following way. Atomic triples contributed to the statistics if the distance between carbon atoms was less than 7.5 Å and the distance between carbons and iodines was less than 4.85 Å. These values are upper limits of the first coordination shells of the corresponding prdfs (see section 4.1). For C–C–C triplets maxima at 60°, 90°, 120° and 180° appear, which correspond well to the local symmetry of the crystal. However, the spread around the regular angles is not the same: the narrowest maximum is the 180° one, which shows chain-like ordering of the ‘a’ sides of the unit cell and through the body diagonal. Less ordered is the body diagonal–‘a’ side combination (at 60° and 120°) and the broadest one is between the ‘a’ sides.

For C–I–C correlations, a maximum is found around 165° (−0.965 in cosines) and two less intense ones at 120° and 90°. The first one is at a larger angle than the crystallographic result [11] (153.6° (cosine: −0.896)), showing that iodine atoms prefer to be close to, but not exactly on, the carbon–carbon connecting line. Since the intensities of the remaining two maxima are much smaller (note the logarithmic scale in the figure), supposedly they are spurious intensities arising from C–I correlations that can be found at the high end of the distance range. This kind of correlation is then responsible for the observed peak of the C–I prdf at 4.5 Å. It is instructive to note that if we calculate the average angle from the known maxima of the partial rdfs (C–C: 6.5 Å, C–I: 4.5 Å and bond length of 2.157 Å), then we obtain almost the same result as the one derived from crystallography. That is, the average value is actually somewhat misleading here; clearly, the distribution represents the proper characteristics of the structure.

For the description of orientational correlations between pairs of tetrahedral molecules as a geometrical unit, the classification scheme of Rey [41] has been used. This is based on the number of atoms of each of the two molecules found between two parallel planes, where the planes contain the centres of the corresponding molecules and are perpendicular to the line connecting the two centres. Based on this consideration, six classes exist: 1:1 (corner–corner), 1:2 (corner–edge), 2:2 (edge–edge), 1:3 (corner–face), 2:3 (edge–face), 3:3 (face–face). The asymptotic limits of the probabilities of 1:1 and 3:3 are the same; this is also true for the 1:2 and 2:3 arrangements. These equivalences come from the fact that there should be four atoms on average between the two planes. In the case of tetrahedral liquids this resulted in an alternating behaviour between the 1:1 and 3:3, and between the 1:2 and 2:3 orientation probabilities (cf [41–45]). Similar behaviour was observed in the plastic crystalline phases of the corresponding materials [25, 44].

Figure 5 shows the probabilities of each class as a function of the distance between the centres of two molecules. A general observation is that only the 2:2 and 1:3 arrangements play major roles in the system, the others are marginal. It should be noted that there are distance ranges where the carbon–carbon prdf contains only a very few atoms in a given distance bin (which is quite normal for a crystal)—i.e., the definition of any ‘distribution’ would be meaningless. This is the reason why between 7.5 and 8.2 Å no intensities are shown in figure 5.

Edge–edge arrangements are the most probable ones; we can find them in great numbers around the maxima of the carbon–carbon prdf. However, the first maximum of the 2:2 distribution appears at a shorter distance than the position of the first maximum of the C–C prdf. Comparing with the monoclinic phase of CBr₄, the 2:2 arrangement there is much less preferred at shorter distances; instead, the phase change from the ordered to the plastic crystalline phase of CBr₄ is explained by the transformation of several classes into 2:2 in the plastic crystalline phase [25]. The large number of 2:2 pairs at the ‘contact’ (very short) distance seems to be a distinct feature of tetragonal ClI₄. At medium range (above 8 Å), the two crystalline materials have similar characteristics.

Similarly, Apollo-like 1:3 arrangements appear in the first shell with quite a large probability; in contrast to the 2:2 class, 1:3 pairs are most frequent around the exact position of the first maximum of the C–C prdf. According to the angular analysis above, the iodine close to the line connecting neighbouring carbon atoms would suggest a longer centre–centre distance (6.6 Å) than is observed (6.5 Å); this kind of distortion is shown in figure 5. As a consequence of the crystalline symmetry, the 1:3 arrangement becomes very probable also at 13.3 Å, which corresponds to the length of the body diagonal of the Bravais-cell. (The slight difference between observed expected distances seems to propagate along the body diagonal.) We found similar characteristics in...
the monoclinic phase of CBr_4 at medium range. A general observation concerning the two most important orientations is that along the body diagonal, 1:3 arrangements dominate, whereas along the ‘a’ vector, 2:2 pairs are more abundant.

Although their role is marginal, it is still worth briefly discussing the remaining four classes of orientations. The 1:1 and 3:3, and 1:2 and 2:3 arrangements are in phase (not like in the corresponding liquid phases [43]), which can only be explained by a well defined crystalline structure. These pairs appear with relatively larger probabilities where the intensity of the carbon–carbon prdf is low. The only exception is the 2:3 arrangement which shows up with a considerable probability in the region of the closest molecule–molecule distance. Its presence may be taken as deviation from the (nearly uniform) 2:2 alignment and, thus, it may contribute to the observed diffuse scattering intensity.

5. Conclusions

We performed total neutron scattering diffraction measurements on the tetragonal crystalline phase of carbon tetraiodide. The experimental total scattering structure factor was modelled successfully by the RMCPOW [34] algorithm. As seen unambiguously by displaying the atomic positions (see figure 2), the observed diffuse scattering comes from an enhanced positional disorder of iodine atoms, i.e. from molecular librations. The previously suggested [11] intermolecular iodine–iodine correlation at 4.05 Å was found, although its manifestation in terms of the prdf was not very distinct. The carbon–iodine correlation centred around 4.5 Å was found to be significant; this feature of the corresponding prdf results from ‘Apollo-like’ (1:3) mutual arrangements. The cosine distribution of the C–I–C intermolecular angles suggests that iodine atom positions close to, but not on, the intermolecular carbon–carbon connecting line are preferred. Analysis of mutual orientations of two molecules showed that edge–edge and corner–face (Apollo-like) near neighbours are the most important and also that these types of arrangements remain distinct at larger intermolecular distances too. This behaviour is completely different from that found for the monoclinic phase of CBr_4 [25].

Acknowledgments

LT is grateful to Anders Mellergård and Per Zetterström for sharing their knowledge on RMCPOW. Financial support was provided by the Hungarian National Research Fund (OTKA), via grant No. 083529.

References

[1] Greer S C and Meyer L 1969 CF_4: crystal structure and solid phase diagram with At J. Chem. Phys. 51 4583
[2] Bol’shutkin D N, Gasan V M, Prokhvatilov A I and Erenburg A I 1972 The crystal structure of α-CF_4 Acta Crystallogr. B 28 3542
[3] Pepe G and Gay J-M 1989 Structure of α-CF_4 at low temperature J. Chem. Phys. 90 5733
[4] Fitch A N and Cockcroft J K 1993 The structure of solid carbon tetrafluoride Z. Krist. 203 29
[5] Klimenko N A, Gal’tsov N N and Prokhvatilov A I 2008 Structure of the high-temperature phase of tetrafluoromethane CF_4 Low Temp. Phys. 34 960
[6] Rubman R and Post B 1966 Carbon tetrachloride: a new crystalline modification Science 154 1009
[7] More M, Baert F and Lefebvre J 1977 Solid-state phase transition in carbon tetrabromide CBr_4. I. The crystal structure of phase II at room temperature Acta Crystallogr. B 33 3681
[8] Nishikawa K and Tohji K 1981 The intermolecular arrangement in the plastic crystal (phase Ia) of carbon tetrachloride studied by x-ray diffraction J. Chem. Phys. 74 5817
[9] More M, Lefebvre J and Fouret R 1977 Solid-state phase transition in carbon tetrabromide. II. The crystal structure of phase I Acta Crystallogr. B 33 3862
[10] Levi R, Barrio M, Veglio N, Tamarit Ll J, Negrier P, Pardo L C, Sanchez-Marcos J and Mondieig D 2008 From the two-component system CBrCl_3 + CBr_4 to the
high-pressure properties of CBr₄. J. Phys. Chem. B 112 13916

[11] Pohl S 1982 Die Kristallstruktur von Cl₂. Z. Krist. 159 211

[12] Finbak C and Hassel O 1937 Kristallstruktur und Molekülbau von Cl₂ und CBr₄. Z. Phys. Chem. B 36 301

[13] McArthur R E, Simons J H and Beck K M 1950 Carbon tetraiodide Inorganic Syntheses vol 3, ed L F Audrieth (New York: McGraw-Hill) p 37 chapter 4

[14] Jaeger F M, Terpstra P and Westenbrink H G K 1925 On the crystal structure of germanium-tetraiodide Proc. Royal Academy Amsterdam 28 747–66

[15] Walz L, Thiery D, Peters E-M, Wendel H, Schönherr E and Wojnowski M 1993 Crystal structure of GeI₂ at 100 K and 297 K. Z. Krist. 208 207

[16] Dickinson R G 1923 The crystal structure of tin tetra-iodide J. Am. Chem. Soc. 45 958

[17] Mellor F and Fankuchen I 1955 The crystal structure of tin tetraiodide Acta Crystallogr. 8 343–4

[18] Hamaya N, Sato K, Usui-Watanabe K, Fuchizaki K, Fujiy Y and Ohishi Y 1997 Amorphization and molecular dissociation of SnI₂ at high pressure Phys. Rev. Lett. 79 4597

[19] Wolf A K, Glinnemann J and Schmidt M U 2008 Packing of tetrahedral EX₄ molecules with E = C, Si, Ge, Sn, Pb and X = F, Cl, Br I. Cryst. Eng. Commun. 10 1364

[20] Sato N and Inokuchi H 1987 Ionization potentials of carbon tetraiodide and tetraiodoethylene in the solid state Chem. Phys. 113 445

[21] Post B 1959 The cubic form of carbon tetrachloride Acta Crystallogr. 12 349

[22] Aston J G, Stattlemyer Q R and Murray G R 1960 Molecular rotation in crystals. Line narrowing in carbon tetrafluoride J. Am. Chem. Soc. 82 1281

[23] More M, Lefebvre J, Hennion B, Powell B M and Aston J G, Stattlemyer Q R and Murray G R 1960 Molecular rotation in crystals. Line narrowing in carbon tetrafluoride J. Am. Chem. Soc. 82 1281

[24] More M, Lefebvre J, Hennion B, Powell B M and Zeyen C M E 1980 Neutron diffuse scattering in the disordered phase of CBr₂-I. Experimental. Elastic and quasi-elastic coherent scattering in single crystals J. Phys. C: Solid State Phys. 13 2833

[25] Folmer J C W, Withers R L, Welberry T R and Martin J D 2008 Coupled orientational and displacive degrees of freedom in the high-temperature plastic phase of the carbon tetrabromide—CBr₄. Phys. Rev. B 77 144205

[26] Temleitner L and Pusztai L 2010 Local order and orientational correlations in liquid and crystalline phases of carbon tetrabromide from neutron powder diffraction measurements Phys. Rev. B 81 134101

[27] Pardo L C, Tamarit Ll J, Veglio N, Bermejo F J and Cuello G J 2007 Comparison of short-range-order in liquid- and rotator-phases of simple molecular liquid: a reverse Monte Carlo and molecular dynamics of neutron diffraction data Phys. Rev. B 76 134203

[28] Rey R 2008 Orientational order and rotational relaxation in the plastic crystal phase of tetrahedral molecules J. Phys. Chem. B 112 344

[29] Rey R 2008 Orientational order and rotational relaxation in the plastic crystal phase of tetrahedral molecules J. Phys. Chem. B 112 344

[30] Rey R 2008 Orientational order and rotational relaxation in the plastic crystal phase of tetrahedral molecules J. Phys. Chem. B 112 344

[31] Pardo L C, Tamarit Ll J, Veglio N, Bermejo F J and Cuello G J 2007 Comparison of short-range-order in liquid- and rotator-phases of simple molecular liquid: a reverse Monte Carlo and molecular dynamics Simulations J. Chem. Phys. 130 064503

[32] Caballero N B, Zuriaga M, Carignano M and Serra P 2012 The plastic and liquid phases of CCl₄Br studied by molecular dynamics simulations J. Chem. Phys. 136 094515

[33] Pothoczki Sz, Temleitner L, Pardo L C, Cuello G J, Rovira-Esteva M and Tamarit Ll J, Comparison of the atomic level structure of the plastic crystalline and the liquid phases of CBr₂Cl₂: neutron diffraction and reverse Monte Carlo modelling J. Phys.: Condens. Matter 25 454216