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Changes in the short-range order of gallium on melting and supercooling

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Abstract. Neutron diffraction has been used to study the diffuse scattering of gallium as it was heated from solid to liquid through the melting point, and then cooled from liquid to supercooled liquid. Little evidence was found of a pre-melting effect. A difference was observed in the rate of change of the diffuse scattering between the liquid and supercooled states from a slightly impure sample, but a high-purity sample showed little change in structure between +33 and –13.1 °C. Reverse Monte Carlo analysis has been applied to the supercooled liquid, confirming that its structure is very like that of the β -phase.

1. Introduction

Liquid gallium is stable over a very large temperature range, from $0.5T_m$ to $8.3T_m$ for small droplets, where the melting point, T_m , is 29.78 °C. The summary and work presented below refer to bulk samples. For these the maximum temperature of supercooling and the resultant crystal structure depend on the temperature from which the sample is cooled [1, 2]. This ‘memory effect’ is independent of the rate of cooling, but oxidation of the sample, large temperature gradients or shocks in the region of the apparatus do alter the results. There are two phases into which bulk liquid gallium can solidify. Orthorhombic α -Ga [3] is the stable form at ambient pressure, but monoclinic β -Ga [4] also occurs readily, with a melting point of –16.3 °C. While α -Ga is unusual in being less dense than the liquid, β -Ga is more dense. The nearest-neighbour distances in the two solids are different, with atoms in α -Ga having one neighbour at 2.44 Å and six neighbours at about 2.75 Å, and β -Ga having two neighbours at 2.68, four at 2.87, two at 2.90 and two at 3.17 Å.

There have been many structural studies of bulk liquid gallium [5–8]. A shoulder on the high- Q side of the first structure factor peak suggests that liquid gallium does not have a simple structure. In some way this indicates the presence of two different near-neighbour distances. It has been suggested that one of these is due to a ‘molecular’ unit, such as is found in α -Ga. The overall structure of the liquid is actually more like that of β -Ga [7, 8].

Most properties of the liquid have been found to change continuously into the supercooled region, for example the density. However, the temperature dependence of the Knight shift suggests that there is some change in the electronic structure [9]. The atomic structure shows a very slight sharpening [10] and on supercooling greatly the shoulder in the structure factor becomes a peak in its own right [11]. Several studies have looked for pre-melting phenomena in Ga. Measurements of Bragg peak height [12], lattice parameter [13] and heat capacity [14] found no anomalous changes. However, the density was found to decrease

less rapidly in the last 2 °C before melting [15], corresponding, perhaps, to the formation of interstitial- or Frenkel-type defects.

We have undertaken an investigation into changes in short-range atomic order on passing from the solid to the liquid and from the liquid to the supercooled liquid, using the technique of neutron diffraction. This follows similar work by this group on rubidium [16], where the diffuse scattering was found to show no discontinuity at the freezing point and no differences were observed between the liquid and supercooled liquid.

2. Experimental procedure

Two neutron diffraction experiments have been performed.

2.1. TAS6 experiment

The TAS6 spectrometer at the Risø National Laboratory (Denmark) was used with no energy analysis, and so sections of the total diffraction pattern were measured. To follow changes in the local atomic arrangement, measurements were made around the position of the first liquid structure factor peak, 2.54 \AA^{-1} , each minute as the temperature was varied very slowly. In the later discussion \hat{S} refers to the uncorrected, unnormalized intensity at this point. In the solid phase an increase in \hat{S} corresponds to an increase in the diffuse scattering and hence an increase in the amount of local disorder (since it is not at a Bragg peak position of the α -phase), while in the liquid the converse is true, with an increase in \hat{S} corresponding to an increase in the amount of local order.

A specially designed furnace was used [16], which gave a temperature stability of better than 0.02 °C and a temperature gradient of an estimated 0.02 °C. The sample was held in a stainless steel can. Stainless steel gives no Bragg peak at 2.54 \AA^{-1} , and its scattering at this point does not change observably over the temperature range of the measurement. Prior to the experiment itself the sample was heated in air during transfer into the container, which may have resulted in some sample oxidation.

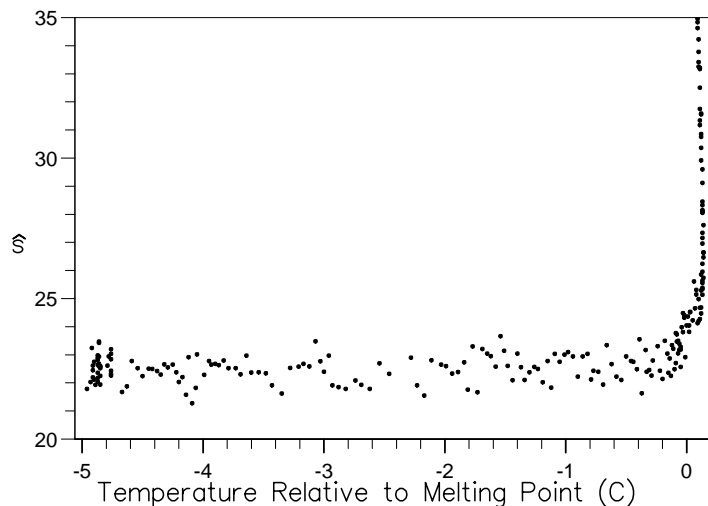
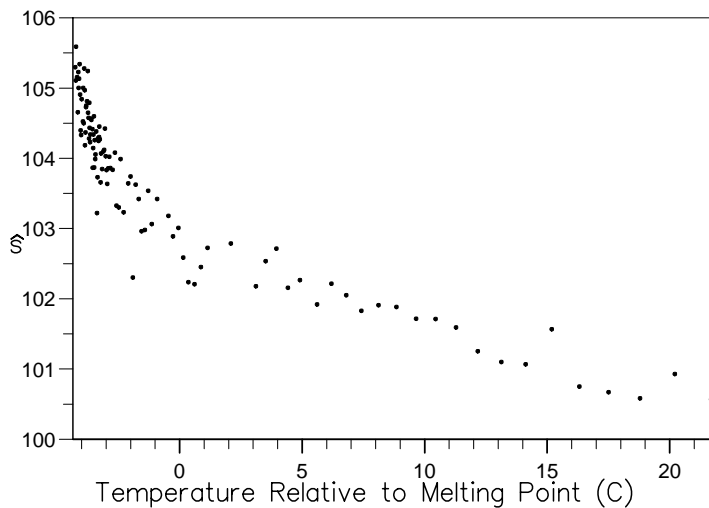
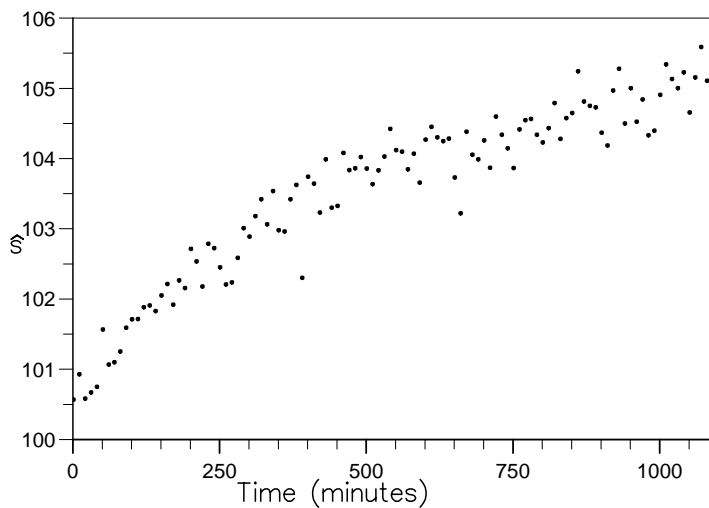


Figure 1. Values of \hat{S} (see the text for the definition) on heating and during the initial stages of melting. Each point represents a one-minute measurement.



(a)



(b)

Figure 2. Values of \hat{S} (see the text for the definition) averaged over ten-minute intervals on cooling from 52 °C; (a) shows the variation of this parameter as a function of temperature and (b) shows the variation as a function of time. The melting point was reached after 340 minutes.

The sample was heated very slowly from room temperature to 29.80 °C (i.e. $T_m + 0.02$ °C) and left at this temperature for approximately 11 hours. After an initial overshoot of 0.12 °C the sample temperature remained constant at 29.80 ± 0.02 °C. It took approximately ten hours to melt totally, partly because we were so close to the melting point, and partly because the heat of fusion of α -Ga is large. \hat{S} during this heating run is shown in figure 1. To enable the pre-melting region to be more clearly seen, only the values of \hat{S} during the early stages of melting are shown. The sample was subsequently heated to about 52 °C and left at that temperature for some hours. It was then cooled slowly to 25.5 °C. The cooling rate decreased as the temperature reached that of the surroundings, as there was no means of artificial cooling. Figure 2(a) shows \hat{S} as a function of temperature in this first cooling

run, whilst figure 2(b) shows the same data, but plotted as a function of the time of the measurement. In both cases the statistics has been improved by averaging over ten points.

A second cooling run was performed after the sample was re-heated to 29.82 °C. In this case the sample temperature was decreased to 29.3 °C and then held constant for three hours, before cooling to 28.3 °C for three hours, to investigate whether we were cooling at a rate at which the sample was kept close to equilibrium, or whether there was any sample evolution with time when cooling was ceased.

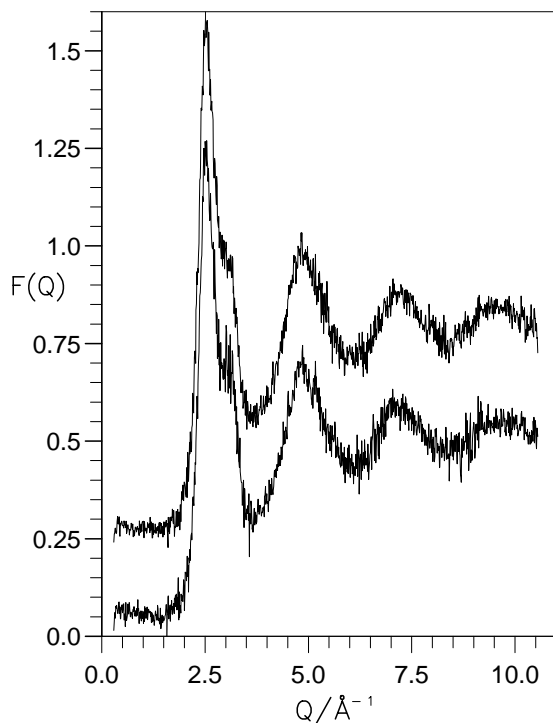


Figure 3. Corrected structure factors for liquid gallium at 33 °C (upper line) and -13.1 °C (lower line).

2.2. SLAD experiment

The second series of measurements were performed using the SLAD liquids and amorphous diffractometer at NFL, Studsvik (Sweden). This instrument allows a larger Q -range, up to approximately 10.5 \AA^{-1} , to be measured by moving the detector just once. However, the flux is such that measurements take longer. The sample was purchased from Aldrich with a stated purity of 99.9999%. It was handled in an inert atmosphere, and sealed under vacuum in a silica container. During the neutron measurement this silica can was in good thermal contact with a large stainless steel block, to provide improved temperature stability, and temperature variation was achieved by placing this complete assembly within a closed-cycle refrigerator. The sample was initially heated to above 70 °C. Diffraction measurements, directly comparable with those on TAS6, were made between 45 and -13.1 °C, with higher-statistics measurements at 33, 32, 31, 30.2, 29.0, 27.1, 26.1, 22.1, 20.0, 14.5, 10.2, 5.3, -1.7 and -13.1 °C. The temperature stability was $\pm 0.2 \text{ °C}$ in all cases. The data were

corrected and normalized using standard routines. Figure 3 shows a comparison between the structure factors at 33 °C and at -13.1 °C.

3. Results and discussion

Figure 1 shows \hat{S} as a function of temperature on heating and during the initial stages of melting in the TAS6 experiment. \hat{S} changes little on heating until melting occurs, indicating that there is almost no change in the local order. However, in the last degree before T_m , \hat{S} does begin to increase slightly more rapidly, and this increase in the diffuse scattering indicates either that the solid disorders more quickly in this region, or that there is some surface melting. This is, however, a very small effect and differs from the behaviour of rubidium, where the diffuse scattering increases rapidly up to the melting point, with no discontinuity in \hat{S} from solid to liquid [16]. In gallium, continuity of this scattering would not be expected if, as proposed by many authors [7, 8] and confirmed below, the liquid is similar to the β -phase, rather than the α -phase from which it melts. However, the small change in \hat{S} also means that the reorganization of the atoms required to go from the α -phase to the β -like liquid phase all occurs on or after melting.

\hat{S} during the first cooling run on TAS6 is shown in figure 2. From figure 2(a) it can be seen that \hat{S} increases as the temperature is lowered towards the melting point. This is the expected trend in liquids, and results from an increase in local order as the temperature is lowered. However, in our experiments it was found that the rate of increase of \hat{S} with decreasing temperature was more rapid in the supercooled than in the normal liquid region, and became larger in the supercooled region as the temperature was decreased further. Because there was slower cooling at the lower temperatures it was possible that the change in \hat{S} was a function of time. However, plotting the same data as a function of time, as is shown in figure 2(b), suggested that this was not the case. The second cooling run confirmed this, since \hat{S} was found to remain unchanged during periods of several hours when the temperature was kept constant. Hence the observed change in the slope of \hat{S} against temperature is not related to the need for a finite time for structural rearrangement in the supercooled liquid. These TAS6 observations cannot be explained by formation of the solid, since the α -phase, which is the only one stable for bulk samples at these temperatures, does not have significant diffuse or Bragg scattering at the Q -value of the measurement.

To further investigate these results, measurements were performed on SLAD. Figure 3 shows the measured structure factors at 33 and -13.1 °C, and it can be seen that there is negligible difference except in the region of the high- Q shoulder on the first structure factor peak. In particular, the first-structure-factor peak height change is less than 2% between these temperatures and is much smaller than that expected from the observations in the supercooled region on TAS6. The main difference between these two experiments was in the purity of the samples (see section 2), which is therefore suggested to be responsible for the observed differences in the peak height change.

One plausible explanation for the observations is that the increased rate of change of the first peak height is a precursor to the freezing transition, and that the purer sample would show a similar effect sufficiently close to its freezing point. The freezing point can be as low as -30 °C for very pure samples [1], but is higher in impure samples of gallium, as the impurities act as nucleation centres. This explanation is consistent with the observations of Vahvaselka [5], where for the lower-purity sample the height of the structure factor peak, equivalent to \hat{S} in the present work, increased considerably between 35 and 20 °C, whilst for the higher-purity sample such a rise only occurred below 20 °C, with the differences appearing to be outside the internal errors of the experiment. However,

while this can explain the observed change in the rate of increase of \hat{S} for the impure sample, it does not explain why that rise occurred specifically below T_m , unless this was just coincidental.

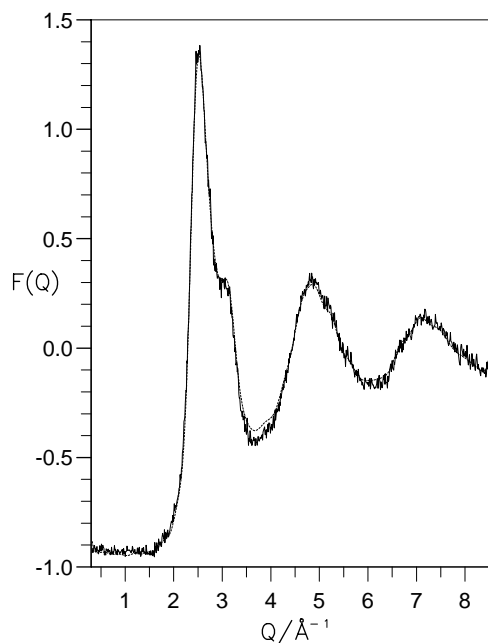


Figure 4. A reverse Monte Carlo fit to the 30.2 °C structure factor of liquid gallium. The data are given by the solid line, the fit by the dashed one.

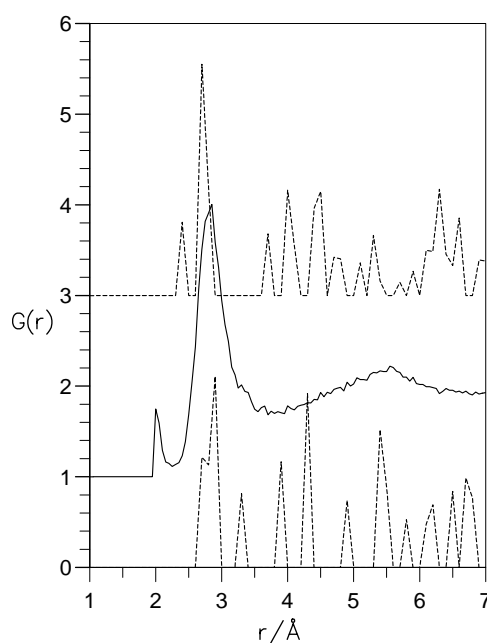


Figure 5. The pair distribution function, $G(r)$, from a reverse Monte Carlo fit to the 30.2 °C structure factor of liquid gallium (solid line). The dashed lines show the neighbour distances in α -Ga (upper line) and β -Ga (lower line).

Reverse Monte Carlo (RMC) analysis [17] was applied to the 30.2 and -13.1 °C data sets. In this modelling technique the positions of atoms in a large configuration are varied to produce a structure factor in agreement with experiment. In both cases the initial configuration was a random arrangement of 4000 gallium atoms, moved such that no two atomic centres were within 2.0 Å of each other. This minimum distance was maintained during fitting as it is unphysical for two gallium atoms to approach each other more closely than this. However, it was found difficult to obtain a fit which gave a pair distribution function with no spike at this 2.0 Å cut-off. (The pair distribution function of figure 5—see later—gives an example of this 2.0 Å spike.) This indicates that there are some errors in the data. Re-correction did not enable these errors to be completely removed, and they did not appear to be due to incorrect subtraction of the silica container scattering. Hence a series of RMC fits were performed to the 30.2 °C data, to test the sensitivity of the results to these errors. In one RMC fit no constraint on the closest approach of the gallium atoms was applied. The low- r region (below 2.0 Å) of the pair distribution function obtained from this fit was set to zero and the structure factor obtained from it by Fourier transformation was also used to perform RMC fitting on. In a third case only structure factor data between 2 and 8.8 Å $^{-1}$ were used in the modelling, removing the regions believed (by the back-transformation just described) to be least accurate. The resulting atomic configurations were analysed and in all cases the results were, within statistics, identical to those obtained in

the initial fitting. Figure 4 shows the quality of fit obtained, with the corresponding pair distribution function in figure 5.

Figure 5 shows the pair distribution function from the RMC fit to the 30.2 °C data, compared to the neighbour distances for the α - and β -phase solids. The peaks for the solid phases have been slightly broadened for ease of viewing, but are calculations rather than models obtained from real data. In cases where the liquid structure is similar to the solid structure the neighbour distances in the two are similar, and so the peaks in the solid and liquid pair distribution functions agree. In the present case the positions of the liquid pair distribution function maxima do not correspond to the neighbour distances in the α -phase, but are similar to those in the β -phase. The triplet correlation function obtained from our RMC model is shown in figure 6. Its shape is again similar to that from the β -phase (and also amorphous gallium) [19], re-emphasizing the similarity between liquid and β -phase.

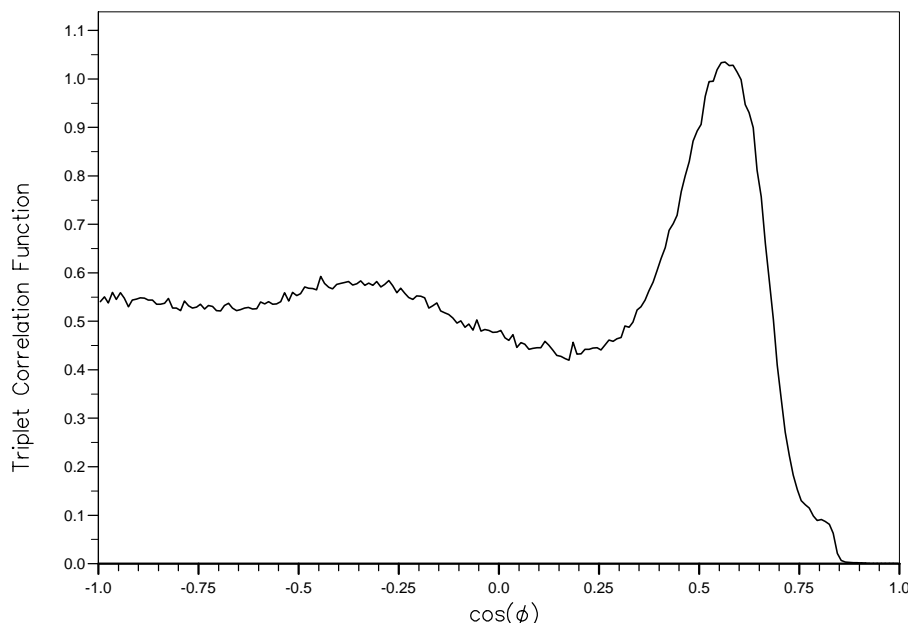


Figure 6. The nearest-neighbour triplet correlation function for liquid gallium at 30.2 °C, obtained by RMC fitting.

The coordination number, obtained by fitting the radial distribution function up to the position of the first minimum in the pair distribution function (3.7 Å), was 11.3(1) at 30.2 °C, consistent with the literature values [5, 18], given the differing definitions used. More detailed study of the atomic separations in the models shows no evidence for any type of ‘molecular’ species at a distance like that in α -Ga, nor for any specific type of clustering. Indeed the first peak of the pair distribution function agrees with that expected for a simple liquid, except that it is slightly narrower and higher than is usual. The second peak, however, is more asymmetric than is usual, but this is due to it resulting from a number of the neighbour distances present in the solid β -phase, as shown in figure 5. Little difference was found between the -13.1 and 30.2 °C structures, with both pair and triplet correlation functions indistinguishable within statistics. Hence no information has been obtained on the reason for the increase in the high- Q shoulder of the first structure factor peak on cooling.

4. Conclusion

In conclusion we have found no evidence for a significant pre-melting change in the short-range order of gallium. This is perhaps surprising, given that our reverse Monte Carlo study has confirmed that the liquid structure is very like the structure of the solid β -phase, rather than the α -phase from which it melts. No evidence was found for 'molecular' pairs, or any clustering in the liquid. Results from a high-purity sample show that the liquid structure changes very little between +33 and -13.1 °C. However, for a lower-purity sample the rate at which the local atomic environment becomes more ordered is different for the liquid and supercooled liquid, with the evolution becoming faster as one moves away from the melting point into the supercooled state. It is suggested that this may be a precursor change to freezing, but further work is required to confirm this.

Acknowledgments

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