



Local order in liquid phases of Al–Ga–Zn alloys

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Abstract

In this paper, neutron scattering experiments at different temperatures allow us to study local order in the different liquid phases which can exist in Al–Ga–Zn alloys. The ternary phase diagram of these phases has been established from calorimetry and X-ray diffraction results. This study showed that the liquid structure factors in these samples agreed with the presence of a local icosahedral order in the liquid state, when the sample is totally molten. For lower temperatures, the local order owns an analogous liquid cluster structure to that of the solid phase(s) in equilibrium with the liquid. The knowledge of structural data of liquid and the liquid local order variations with temperature has confirmed previous results obtained by calorimetry and X-ray diffraction.

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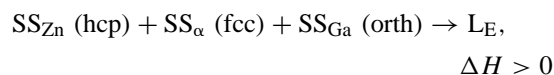
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1. Introduction

We have studied the Al–Ga–Zn ternary phase diagram by the isoplethic cut method [1–4]. This experimental study has been mainly carried out by differential scanning calorimetry [1–3], X-ray diffraction at various temperatures [1,2,4], SEM observations and micro-probe analysis [1,2,4]. These results have been completed by neutron scattering at various temperatures both on heating and cooling [2,5].

Five main isoplethic sections have been chosen for the experimental study: ZA7–Ga ($m_{\text{Al}}/(m_{\text{Al}}+m_{\text{Zn}}) = 0.07$ and Ga varying from 0 to 1)¹ [1,3,4], ZA15–Ga [1,3,4], ZA20–Ga [1,3,4], ZA40–Ga [2–5] and ZA55–Ga [2]. Two isobaric invariant reactions were observed:

- a ternary eutectic at 296 ± 1 K on heating:²



- a ternary metatectic at 396 ± 1 K on heating:

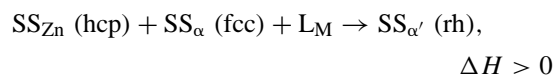


Fig. 1 presents, as an example, the ZA40–Ga isoplethic section. This cut shows these two isobaric ternary invariant reactions and also the existence of an important retrograde miscibility of gallium in the $\text{SS}_{\alpha'}$ ternary solid solution which protrudes into the ternary system starting from the Al–Zn binary one up to gallium concentration of about 30 wt.%.

Neutron scattering has been performed on selected samples, for which we expected to obtain the most

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¹ Compositions will always be given in mass percent.

² SS_{X} means solid solution of X.

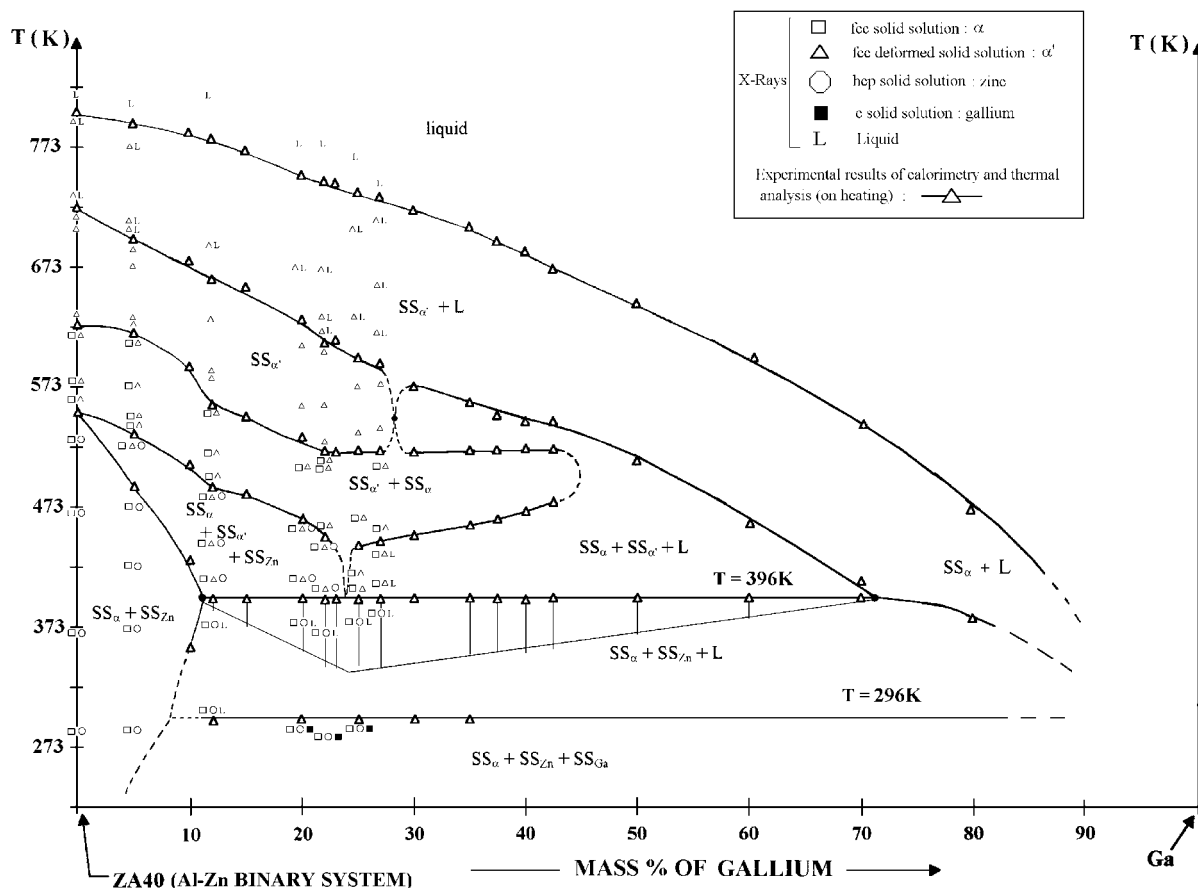


Fig. 1. ZA40–Ga isopleth section.

complete information concerning liquid local order, at different temperatures both on whole liquid and partially melted domains, in order to follow the local order variations of liquid phases. Like sample compositions have to be included between 24 and 29 wt.% of Ga, we chose two samples: ZA40–Ga25 and ZA40–Ga27. For practical reasons only the results of the second sample are presented in this paper but they are representative of the considered domains.

The starting hypothesis is that liquid clusters and solid phases in equilibrium with them have analogous symmetries.

2. Preparation of samples

High purity components (Al, Ga and Zn 99.999 wt.%) were mixed by melting under argon atmosphere

to prepare samples. The compositions were chosen according to the thermal analysis and X-ray diffraction results (Fig. 1).

The studied sample composition was 27 wt.% of gallium on the ZA40 isopleth cut. It presents a phenomenon of liquid phase crystallization on heating (transition from $SS_{\alpha} + SS_{\alpha'} + L$ to $SS_{\alpha} + SS_{\alpha'}$ at 448 ± 3 K) and moreover it runs through the α' solid single-phase domain at 519 ± 3 K and then melts partially at 592 ± 3 K. The studied sample is completely molten above 731 ± 3 K.

3. Experiments

Neutron scattering experiments were performed on the 7C2 spectrometer of the Orphee reactor at Leon Brillouin Laboratory (Nuclear Study Center of

Saclay), mainly on ZA40–Ga27 sample in different (solid or/and liquid) states up to 763 K. Table 1 sums up the nature of the different phases in equilibrium at the different temperatures chosen for neutron scattering on heating experiments. The scattered intensities were measured using a fixed 640-cell detector in a momentum transfer (q) range of 0.5 (or 0.7)–16 \AA^{-1} and with an incident neutron wave length λ of 0.7046 \AA .

The samples were melted directly in vanadium containers which do not react with molten Ga based alloys. They were then heated in a vanadium resistor furnace. The sample masses (cylindrical ingots) were

Table 1

Nature of phases of the studied sample (ZA40–Ga27) versus the temperature

Temperature of neutron scattering experiments (K)	Nature of phases in equilibrium
373	$SS_{\alpha} + SS_{Zn} + L$
413	$SS_{\alpha} + SS_{\alpha'} + L$
473	$SS_{\alpha} + SS_{\alpha'}$
503	$SS_{\alpha} + SS_{\alpha'}$
533	$SS_{\alpha'}$
563	$SS_{\alpha'}$
623	$SS_{\alpha'} + L$
763	L

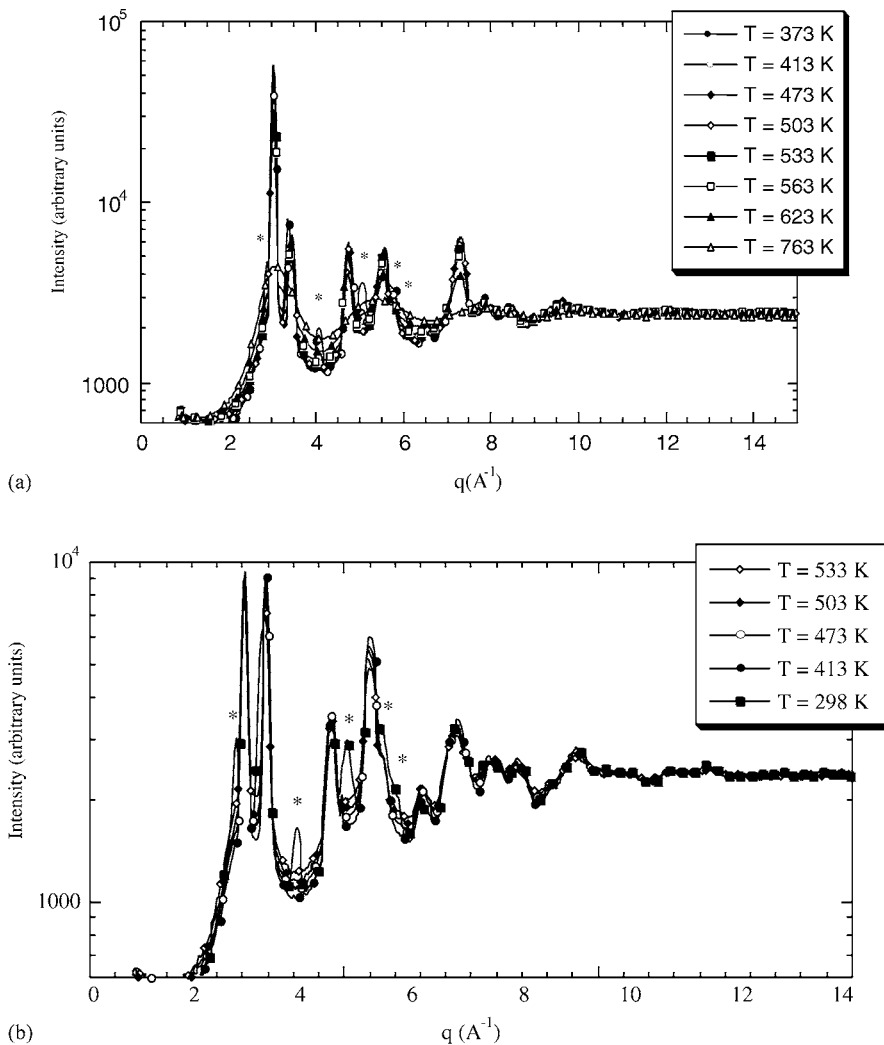


Fig. 2. Neutron scattering spectra on (a) heating and (b) cooling for the ZA40–Ga27 alloy. In (a) and (b) the intensities are plotted in logarithmic scale to display their variations between heating and cooling.

about 30 g. However, because of the low resolution of the spectrometer in the q space, Bragg contaminations could not be completely eliminated. The scattering of the empty container was measured at temperatures corresponding to those of the experiment before introducing the sample.

At a given temperature the differential scattering cross-section of the sample $(d\sigma/d\Omega)(q)$ was obtained by subtracting from the spectrum of the full container, the spectrum of the empty vanadium container within the furnace and the spectrum of the empty furnace. Plazcek [6] corrections for inelastic scattering and a standard multiple scattering correction [7] were carried out. A vanadium sample with an identical geometry to that of the Al–Ga–Zn samples was measured in order to get an absolute normalization of the cross-sections. In all cases, the asymptotic value of $4\pi(d\sigma/d\Omega)(q)$ at large q coincides, within a few percent, with the calculated total scattering cross-section $\sigma_T = \sigma_i + 4\pi\langle b^2 \rangle$, with $\sigma_i = \sum c_j \sigma_{\text{inc}}^i$ and $\langle b^2 \rangle = \sum c_j \bar{b}_j^2$, where σ_{inc}^i is the intrinsic incoherent scattering cross-section (isotopic and nuclear spin mixture contributions), \bar{b}_j the average scattering length and c_j the concentration of the j th element (Al, Ga or Zn). Such agreements validated the corrections applied to the measured neutron intensities. In the following, we

have normalized the data so that the asymptotic value of the differential scattering cross-section at large q is equal to σ_T . The experimental structure factor $S_{\text{exp}}(q)$ is related to the differential scattering cross-section by the equation:

$$S_{\text{exp}}(q) = \frac{4\pi(d\sigma/d\Omega)(q) - \sigma_i}{4\pi\langle b^2 \rangle}$$

i.e. normalized to unity.

4. Results

Neutron scattering spectra established on the ZA40–Ga27 alloy at different temperatures on heating and cooling are shown in Fig. 2a and b, respectively. Firstly, we have to notice that the slight instrumental resolution of the 7C2 spectrometer does not permit us to separate SS_α and SS_α' Bragg peaks, contrary to the previous measurement by X-ray diffractometer [1–4]. Hence, we can note that the first diffuse band of the spectrum in the liquid state (at 763 K) correspond to the main Bragg peak groups of the spectra measured at lower temperatures (on heating and on cooling), where almost one solid phase (in equilibrium with the liquid) exists. But this similarity between the liquid

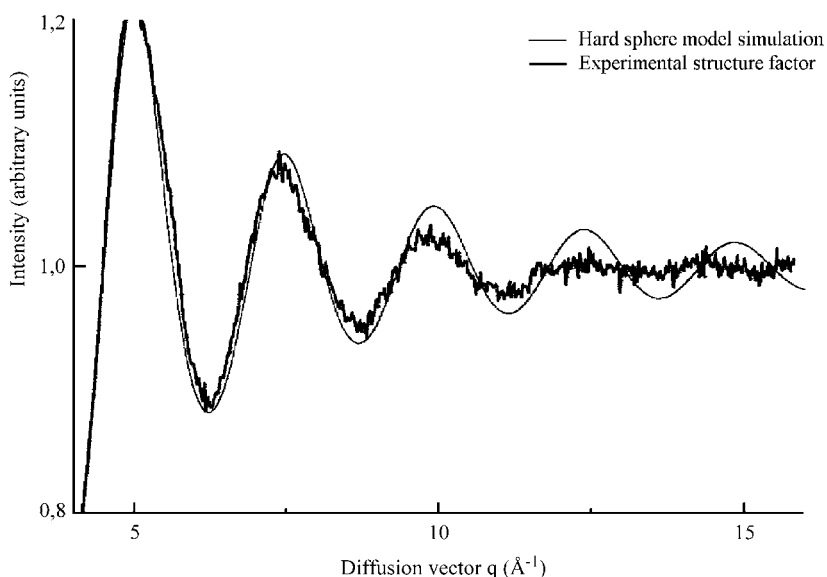


Fig. 3. Comparison of the measured structure factor at 763 K (thick solid line) with the results of a hard sphere model simulation (thin solid line).

and solid spectra does not extend up to the largest q values. On heating, the SS_{Zn} Bragg peaks disappear at temperatures higher than 413 K (as the metatectic invariant temperature is 396 K). This phenomenon can be explained by a hysteresis related to a kinetic reaction which was displayed by calorimetry and X-ray diffraction [1]. Moreover, the important variations of the intensity of the two first diffraction lines are due to a very strong preferential orientation which will be studied in a further paper presenting the crystallographic aspect of solid phases.

Nevertheless, it is necessary to specify that neutron scattering results agree well with those obtained by X-ray diffraction at various temperatures. Particularly, the liquid crystallization on heating has been shown by both diffraction techniques.

On the basis of these results, we will try to analyse the different liquid structure factor more precisely and quantitatively.

5. Data exploitation

The first approach was based on the hard sphere model simulation. This simulation result shown in Fig. 3 (for the liquid at 763 K) follows the Ashcroft and Langreth [8] derivation of the Percus Yevick equation for a binary mixture and the ternary liquid is assumed to be a pseudo-binary system constituted of mean “Al–Ga” atoms and Zn atoms. The hard cores (2.56 Å for “Al–Ga” and 2.48 Å for Zn) and the packing fraction (0.40) were chosen in order to fit the first peak of the structure factor. It is clear that a hard sphere model is unable to account for the positions and intensities of the oscillations of the structure factor at larger q .

Although simulations of the measured structure factors in the whole q -range are a very complex task, an analysis of the structure factor at large q is possible in several conditions and it indeed brings very interesting information on the local order. The principle of the method, initially introduced to describe molecular solids [9–11] is the following.

The considered system is constituted of N particles of N_m identical molecules, each molecule containing N_{at} atoms. This model permits us to split the atomic position fluctuations around their mean values into translational motion of the molecular center of

mass around its mean value and intramolecular motions. Then one can introduce the Debye–Waller factor relative to the motion of the center of mass of the molecule and the Debye–Waller factor corresponding to the thermal changes of the distance between two atoms belonging to the same molecule. For large enough q , the first Debye–Waller factor is vanishing, while the second remains finite because atoms within the molecule are rigidly bounded together while the molecules are only weakly coupled.

This formalism has been used to describe the structure factor at larger q , which corresponds to the local order and consequently to the different liquid phases contained in the studied sample at different temperatures. Two requirements are needed for the application

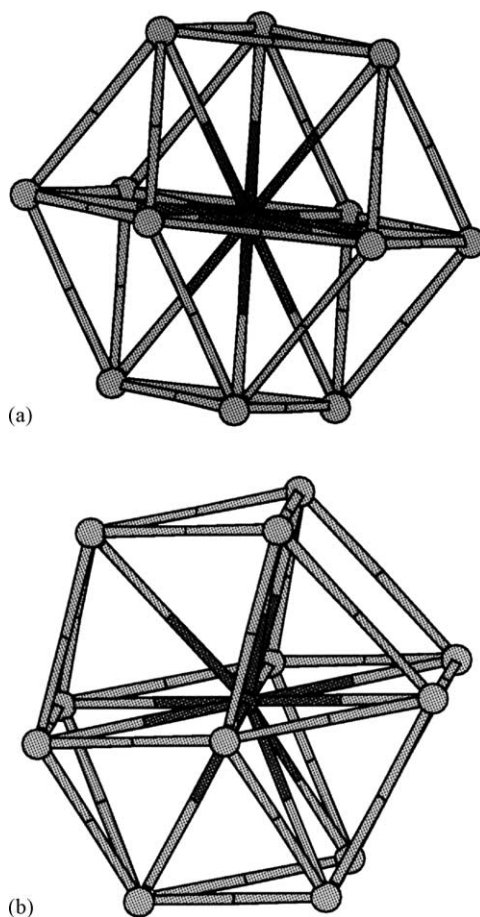


Fig. 4. (a) fcc and (b) hcp structure factor of liquid clusters.

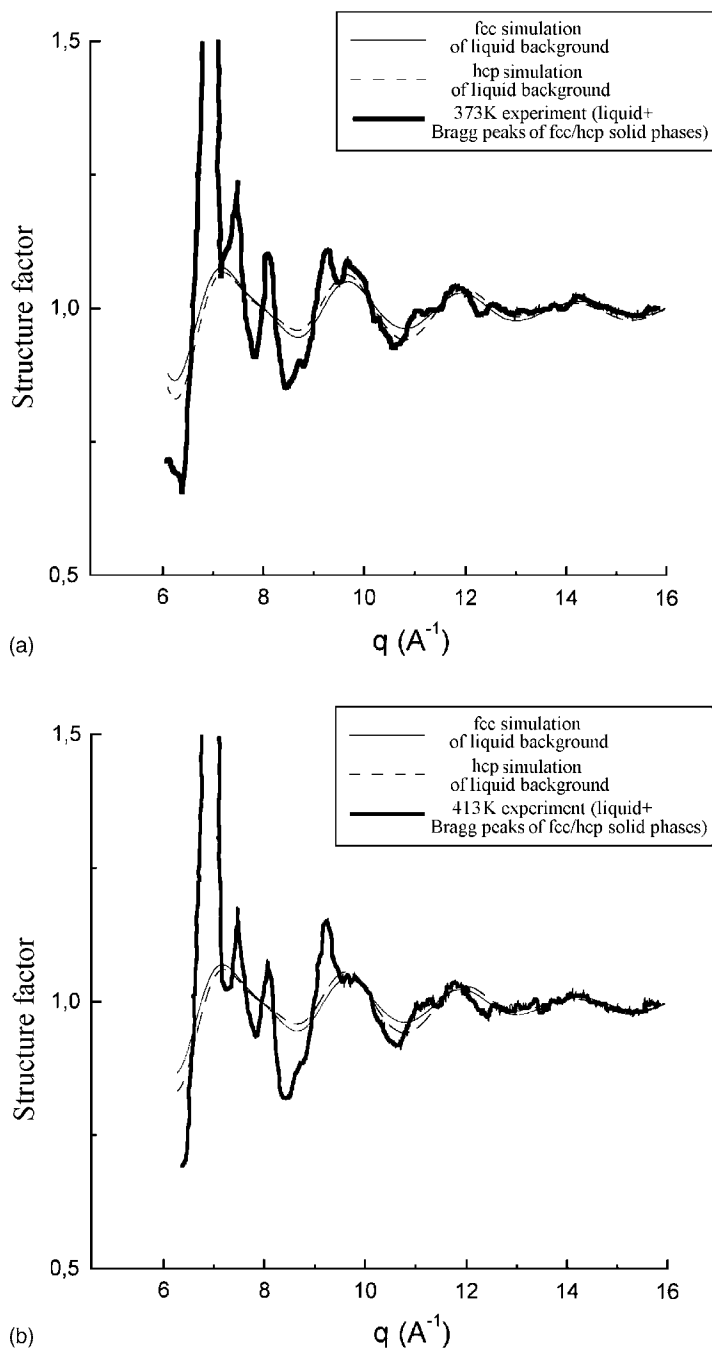


Fig. 5. Comparison of the fcc and hcp calculated structure factor of liquid clusters with the experimental one established at: (a) 373 K (at this temperature, the phase ratio is 77 wt.% of $(\text{Zn} + \alpha)$ solid solution and 23 wt.% of liquid phase); (b) 413 K (at this temperature, the phase ratio is 95 wt.% of $(\alpha + \alpha')$ solid solution and 5 wt.% of liquid phase); (c) 623 K (at this temperature, the phase ratio is 59 wt.% of α' solid solution and 41 wt.% of liquid phase); (d) 763 K (at this temperature, the phase ratio is 100 wt.% of liquid phase).

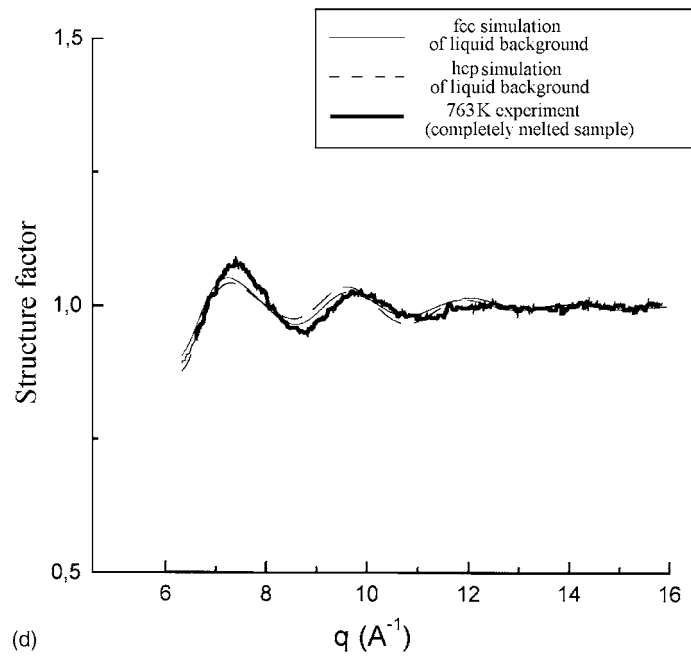
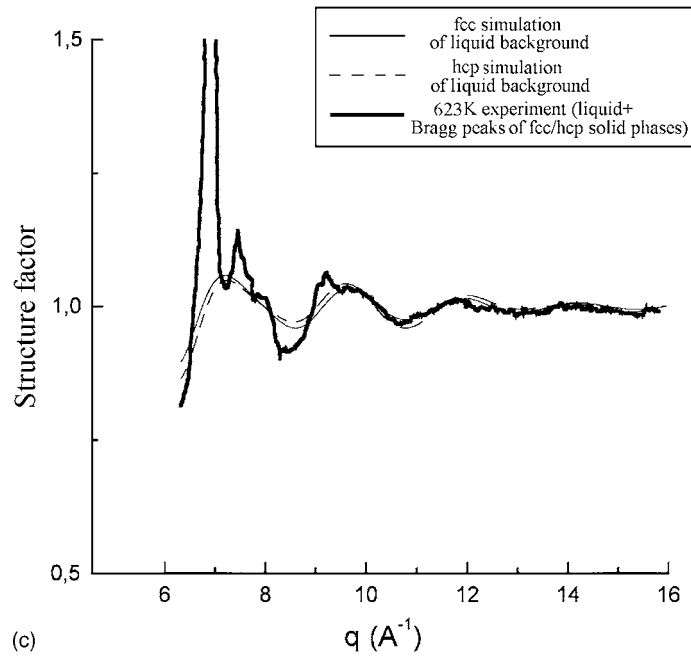


Fig. 5. (Continued).

of this model: the first is the existence of well-defined clusters in the liquid, the second is that the clusters have a lifetime compatible with thermal neutron scattering.

The application of this method to liquid Al–Ga–Zn alloys implies that a cluster can be defined in the liquid and that the atoms within the clusters are much more rigidly bounded together than to atoms belonging to other clusters. Note that this method does not allow one to determine the structure and the chemistry of the cluster but indicates whether a given cluster model is compatible with the experimental data or not, by comparing the calculated structure factor at large q to the measured one. The comparison is done in a q -range of $6 \leq q \leq 16 \text{ \AA}^{-1}$.

The choice of cluster model in liquid was guided by the structural description of SS_{α} (fcc), $SS_{\alpha'}$ (rhombohedral) and SS_{Zn} (hcp) solid phases. But, as the SS_{α} and $SS_{\alpha'}$ phases cannot be separated on the 7C2 spectrometer experiments, the both cluster structure factor (fcc and hcp—see Fig. 4a and b, respectively) have been simulated and compared to experimental one.

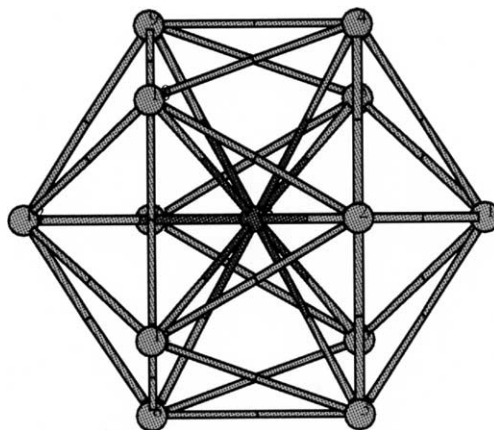


Fig. 6. Icosahedral structure factor of liquid clusters.

Fig. 5a–d show the comparison of the simulation of fcc and hcp liquid cluster structure factor with experimental results measured on the scattering background at 373, 413, 623 and 763 K, respectively. In a qualitative viewpoint (concerning Fig. 5a–c), local order is well described by this two cluster simulations. In

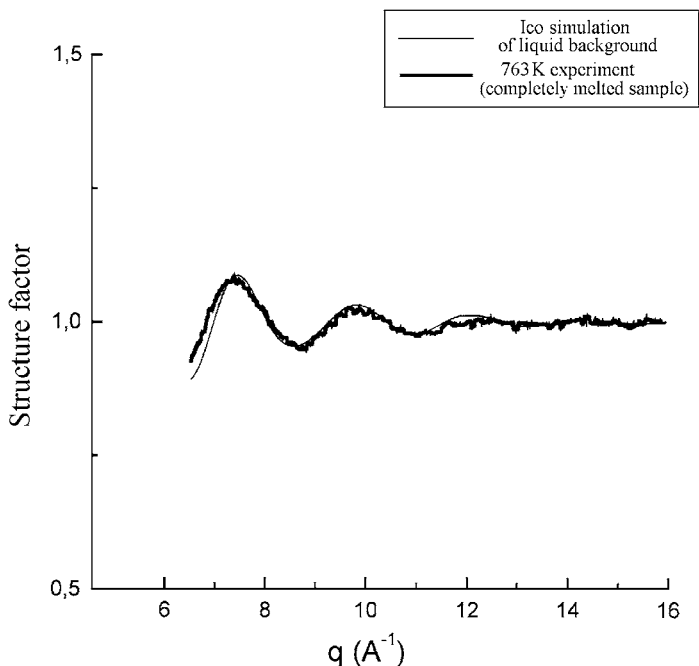


Fig. 7. Comparison of the icosahedral calculated structure factor of liquid clusters with the experimental one established at 763 K (at this temperature, the phase ratio is 100 wt.% of liquid phase).

these three cases, the sample contains both a liquid phase and a (or several) solid phase(s) since it is in the following domains: “ $SS_{\alpha} + SS_{Zn} + L$ ” at 373 K, “ $SS_{\alpha} + SS_{\alpha'} + L$ ” at 413 K and “ $SS_{\alpha} + SS_{\alpha'}$ ” at 623 K. This lets one think that the local order in these domains has a structure analogous to the solid phase one.

On the other hand, the results of these fcc and hcp cluster based simulations are not in good agreement with the experimental structure factor measured at 763 K, when the sample is entirely molten. That is why another cluster model (with icosahedral symmetry, see Fig. 6) has been used, it has the same coordination number (12) as fcc and hcp clusters. The icosahedral calculated structure factor well describes the experimental one at 763 K is shown in Fig. 7.

6. Conclusion

According to previous results [1–5] and those of the present study, we have confirmed the existence of an inversed crystallization-fusion phenomenon on heating. Moreover, we can conclude that the measured structure factors in an Al–Ga–Zn alloy agree with the presence of a local icosahedral order in the liquid state, when the sample is totally molten. For lower temperatures, in domains where solid and liquid phases are

in equilibrium, the local order has an analogous liquid cluster structure to that of the solid phase(s).

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