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Short-range order in undercooled and stable melts forming quasicrystals and approximants and its influence on nucleation

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Abstract
An icosahedral short-range order (ISRO) has been predicted to prevail in undercooled metallic melts. For melts of pure metals this hypothesis was recently experimentally confirmed by diffraction experiments.

This work presents results of neutron scattering experiments on the short-range order of stable and undercooled liquids of alloys forming quasicrystals and polytetrahedral crystals. The studies indicate that an icosahedral topological short-range order prevails in all of the investigated melts. The influence of this icosahedral short-range order on the nucleation behaviour of solid phases from the undercooled liquid is discussed.

Keywords: undercooling, short-range order, quasicrystals, nucleation, solid-liquid interfacial energy

1. Introduction
Following a consideration of Frank [1], an icosahedral short-range order (ISRO) should be energetically favourable in undercooled melts of systems consisting of atoms of roughly spherelike geometrical symmetry such as metals. An icosahedron is a polytetrahedron built up from 13 atoms. It is characterized by six fivefold symmetry axes. If atomic interactions according to a Lennard-Jones potential are assumed, the energy of an icosahedral cluster is about 8.4% smaller than that of 13 atoms clusters with fcc- or hcp-structure. While this argument is concerned with small clusters, later the idea of a polytetrahedral short-range order (SRO) in undercooled melts was confirmed also for larger systems by molecular dynamics computer simulations on Lennard-Jones liquids [2,3], which revealed an increasing degree of ISRO with increasing undercooling, $\Delta T$, of the melt.
While Frank’s hypothesis of an icosahedral short-range order dates from 1952, from the experimental side the question of the short-range order in undercooled metallic melts remained unsolved for about fifty years. In 2000 the structure of liquid Pb on a Si (001) substrate was studied at the solid (Si) -liquid (Pb) interface by X-ray diffraction at temperatures, $T$, above the liquidus temperature, $T_L$ [4]. The experiments provide evidence of a fivefold local symmetry of the liquid lead at the Si(001) interface and thus ISRO. In these experiments, however, the SRO was not studied in the bulk liquid.

Recently, we have investigated the SRO of bulk liquids of the pure metals Fe, Zr, Ni and Co in the stable and deeply undercooled regime by diffraction of neutron- and synchrotron radiation [5,6]. The melts were undercooled using the containerless processing technique of electromagnetic levitation. These studies provide a direct experimental proof of an ISRO prevailing all examined bulk metallic melts, independent on the structure of the corresponding solid phase. The ISRO becomes more pronounced at lower temperatures.

By Lee et al. [7] the SRO of stable and undercooled liquid Ni and Ti was investigated by combination of the undercooling technique of electrostatic levitation with diffraction of synchrotron radiation. This work confirms our results on liquid Ni. For melts of Ti indications for distortions of the ISRO are reported.

The above mentioned studies are concerned with monoatomic systems. For alloys, despite aspects of the topological SRO also those of a possible chemical order must be considered. Moreover, if an alloy consists of atoms with a large difference in the atomic radii, even a topological SRO different from ISRO may be favoured for geometric reasons. Nevertheless, as long as the atomic radii of the alloy components are close, an ISRO will still be advantageous. A small concentration of slightly smaller or larger atoms may even stabilize icosahedral clusters because the interatomic distance between the atoms on the surface of an icosahedron is approximately 5% larger than the distance between the surface atoms and the central atom [8]. Hence, placing a smaller atom into the center of an icosahedron or larger atoms on its surface is energetically favourable.

Jónsson and Andersen [9] investigated a binary Lennard-Jones liquid model consisting of 1500 atoms. 20% of these atoms were 25% larger than the other species. In the deeply undercooled liquid, 138 interpenetrating and interconnected icosahedra were found, such that 61% of all atoms were within an icosahedral environment.

Of special scientific interest is the investigation of the SRO of alloy melts that form quasicrystalline or the structurally closely related crystalline approximant phases. These phases are characterized by ISRO in the solid state. At temperatures above $T_L$ the SRO of the quasicrystal-forming alloy Al$_{60}$Mn$_{20}$ [10] was studied by neutron scattering. Atomic pair potentials have been inferred from these experiments, which were subsequently used for molecular dynamics calculations [11]. These calculations revealed an icosahedral ordering even in stable melts ($T > T_L$), while in the undercooled regime ($T=0.8T_L$) this SRO is even more pronounced.

Neutron diffraction studies on stable quasicrystal-forming Al-Pd-Mn melts delivered structure factors, $S(Q)$, which could be simulated under the assumption that icosahedral clusters with Mn- or Pd-atoms located in the centre of the icosahedron [12] prevail in the liquid. For other SROs, for instance those of hcp or fcc symmetry, the calculated $S(Q)$ do not deliver such a good fit of the experimental results.

This paper presents the results of our recent neutron diffraction investigations on the SRO of undercooled melts of Al-based alloys forming quasicrystals and approximants (Al$_{60}$Cu$_{33}$Fe$_6$, Al$_{65}$Cu$_{25}$Co$_{10}$ and Al$_{135}$(Co,Fe)$_4$). The impact of the SRO in the melt on the nucleation behaviour of solid phases of different structure is discussed. All of the quasicrystal-forming alloy systems studied here possess only a moderate difference of the
atomic radii. Hence, an ISRO should be favourable in the liquid state from the theoretical point of view.

2. Short-range order in melts forming quasicrystals and approximants

In order to deeply undercool melts, heterogeneous nucleation at foreign phases such as container walls or impurity sites must be suppressed [13]. Therefore, the melts are containerlessly processed under high purity conditions by use of the electromagnetic levitation technique [13]. Elastic neutron scattering experiments were performed on the electromagnetically levitated samples approximately 1 g in mass at the high-intensity two-axis diffractometer D20 of the Institut-Laue-Langevin (ILL) in Grenoble, France. Experimental setup and data treatment are described in ref. [14].

Figure 1 shows the structure factor, $S(Q)$, of Al$_{60}$Cu$_{34}$Fe$_4$ melts forming an icosahedral quasicrystalline I-phase that was determined by neutron diffraction at different temperatures ($T = 1090$ K, $T = 1225$ K and $T = 1325$ K) above and below the liquidus temperature of $T_L = 1164$ K. The $S(Q)$ of the Al$_{60}$Cu$_{34}$Fe$_4$ melts exhibit a shoulder on the right side of the second oscillation. Moreover, at small $Q$ vectors a prepeak occurs that suggests the existence of a medium-range order. Both features of $S(Q)$ become better defined, if $T$ is decreased.

A similar shape of $S(Q)$ was observed in our neutron scattering investigations on Al$_{55}$Cu$_{25}$Co$_{10}$ melts forming a decagonal quasicrystalline D-phase [15]. Also diffraction investigations with synchrotron radiation performed by Kelton et al. [16] on Ti$_{39.5}$Zr$_{39.5}$Ni$_{21}$ melts forming an I-phase, which have been undercooled by electrostatic levitation, revealed the characteristic shoulder on the second oscillation of $S(Q)$.

A similar shoulder was observed in the $S(Q)$ of monoatomic metallic melts [5,6]. It is considered as a first indication of an icosahedral topological SRO [8]. For alloys, however, this interpretation is not as unambiguous as for monotatonic systems due to the fact that the total $S(Q)$ measured for alloys is affected by both the topological and the chemical structure.

In order to separate effects resulting from the chemical SRO from those due to the topological SRO, partial structure factors must be determined. For such investigations we have chosen Al$_{13}$(Co,Fe)$_4$ alloys forming approximant phases. The melting temperatures of the alloys are nearly independent of the Co/Fe ratio (ranging between approximately $T_L = 1420$ K for Al$_{13}$Fe$_4$ and $T_L = 1440$ K for Al$_{13}$Co$_4$). When assuming an isomorphous substitution of Co by Fe the transition metal atoms (TM) can be considered as one component of a quasi-binary Al-TM alloy and changing the Fe/Co ratio allows to vary the coherent neutron scattering cross section of the TM-component. From at least three neutron scattering examinations with different scattering contrast of the components (Al, TM) the complete set of partial structure factors within the Faber-Ziman formalism [17] and the Bhattach-Thorton formalism [18] can be determined. The Faber-Ziman structure factors $S_{AIA}(Q)$, $S_{AITM}(Q)$ and $S_{TM TM}(Q)$ are the contributions to $S(Q)$, which result from the three different kinds of atomic pairs (Al-Al, Al-TM and TM-TM). Within the Bhattach-Thorton formalism the partial structure factor $S_{NN}(Q)$ describes exclusively the topological SRO of the system, $S_{CC}(Q)$ the chemical SRO and $S_{NC}(Q)$ the correlation of density and concentration. We measured the total $S(Q)$ of stable and undercooled melts of five different Al$_{13}$(Co,Fe)$_4$ alloys, such that the equation system to determine the partial structure factors is overdetermined. The partial structure factors inferred from one subset of three measurements agree with those inferred from other subsets of data within the statistical error limits that correspond to the spread of the data points. This allowed us to verify the hypothesis of an
isomorphous substitution of the TM-atoms with hindsight [19].

Figure 2 shows the Faber-Ziman (a) and the Bhatia-Thornton (b) partial structure factors determined from the five neutron scattering measurements for moderately undercooled melts at \( T = T_L - 60 \) K. The results obtained at \( T = T_L - 150 \) K are shown in Fig. 2 of ref. [19] and those determined at \( T = T_L + 150 \) K are depicted in Fig. 2 of ref. [20].

It is noteworthy that at all temperatures \( S_{NN}(Q) \) exhibits the characteristic shoulder on the right hand side of the second oscillation indicating that this feature also visible in the \( S(Q) \) of the Al\(_{60}\)Cu\(_{34}\)Fe\(_{6}\) (see figure 1) and Al\(_{65}\)Cu\(_{25}\)Co\(_{10}\) [15] melts results from the topological SRO. Consequently, similar as for melts of pure metals [5,6], this shoulder is an indication of an ISRO prevailing in the liquid [8]. This interpretation is confirmed by simulations of \( S_{NN}(Q) \) at large \( Q \) vectors by assuming that the melt contains separate tightly bound clusters. The best fit of the experimental results is obtained if an ISRO is assumed to prevail in the liquid [19]. There are indications that this ISRO consists of larger polytetrahedral aggregates such as dodecahedral clusters with 33 atoms.

Apart from this icosahedral topological SRO the analysis of the partial pair correlation functions, which are shown in ref. [19] for all investigated temperatures, indicates the existence of a chemical SRO in Al\(_{13}\)(Co,Fe)\(_4\) melts, such that the formation of Al-TM nearest neighbours is favoured, while TM-TM nearest neighbours are avoided [19]. This chemical short-range order explains the occurrence of the prepeaks in the total structure factors of Al\(_{13}\)(Co,Fe)\(_4\), Al\(_{60}\)Cu\(_{34}\)Fe\(_6\) and Al\(_{65}\)Cu\(_{25}\)Co\(_{10}\).

3. Impact of the short-range order on the nucleation behaviour of undercooled liquids

According to classical nucleation theory [21] for the intrinsic case of homogeneous nucleation the steady-state nucleation rate of a solid phase in an undercooled melt is given by:

\[
I_{SS} \approx 10^{39} \cdot \exp\left(\frac{-\Delta G^*}{k_B T}\right) \text{[m}^{-3} \text{s}^{-1}] \quad \text{with} \quad \Delta G^* = \frac{16\pi r^3}{3\Delta G_v^2} . \tag{1}
\]

Here \( k_B \) denotes Boltzmann’s constant, \( \Delta G^* \) the activation threshold for nucleation, \( \Delta G_v \) the difference of the Gibbs free energies of liquid and solid and \( \gamma \) the solid-liquid interfacial energy, which will depend on the structure of both the liquid and of the solid.

One model for \( \gamma \) that considers structural aspects and depends only on experimentally measureable parameters is the negentropic model [22,23,24,8]. Here, \( \gamma \) is expressed by:

\[
\gamma(T) = \alpha \Delta S_f T (N_L V_m)^{1/3} . \tag{2}
\]

\( V_m \) denotes the molar volume, \( N_L \) Avogadro’s number and \( \Delta S_f \) the entropy of fusion per mol. The dimensionless solid-liquid interfacial energy \( \alpha \) depends on the structure of the solid. For non complex crystalline phases with fcc, hcp or bcc structure \( \alpha \) has been analytically determined [22,23,24,8]. These estimations base upon the assumption of tetrahedral SRO in the solid-liquid interface. This is motivated by Frank’s prediction of a polytetrahedral SRO in the melt, which - as shown above - has meanwhile been experimentally verified for metallic systems. Because for structurally complex phases an analytical calculation of \( \gamma \) is
impossible, the negentropic model was recently extended in order to numerically estimate \( \alpha \) also for such phases [26,27]. The calculations were performed for different solid structures: the icosahedral quasicrystalline I-phase in Al-Pd-Mn, the polytetrahedral phases \( \lambda\)-Al\(_{13}\)Fe\(_5\) and \( \mu\)-Al\(_{33}\)Fe\(_5\), the \( \sigma' \)-phase in Ni-V, which is a Frank-Kasper phase with a Z14 coordination polyhedron and the hard magnetic phase \( \Phi\)-Nd\(_{14}\)Fe\(_{6}\)B\(_5\). The \( \Phi \)-phase is a structurally complex solid, but different from the other investigated structures, it is not a polytetradedral phase. The results of the numerical calculations [26,27] and of the analytical estimations by Spaepen and Thompson [22,23,24,8] are summarized in the following relation:

\[
\alpha_{\text{calc}} = 0.34 < \alpha'_{\text{calc}} = 0.36 < \alpha^\Phi_{\text{calc}} = 0.37 < \alpha^\lambda_{\text{calc}} = 0.39 < \alpha^\mu_{\text{calc}} = 0.43 < \alpha^{bcc}_{\text{calc}} = 0.70 < \alpha^{fcc/hcp}_{\text{calc}} = 0.85. \tag{3}
\]

The quasicrystalline I-phase exhibits the lowest value of \( \alpha \), while for the structurally non-complex phases with bcc, fcc and hcp structures the largest \( \alpha \)-factors are estimated. For the structurally complex phases \( \lambda \), \( \mu \), \( \sigma' \) and \( \Phi \) remarkably low values of \( \alpha \) are predicted. The fact that the \( \Phi \)-phase is not a polytetrahedral structure highlights that a small \( \alpha \) is not only anticipated for solid phases with a polytetrahedral SRO which resembles that of the liquid phase. The modelling suggests that the geometrical constraints during construction of the solid-liquid interface, which result from structural complexity, give rise to a low \( \alpha \).

Because \( \gamma \) determines \( \Delta G^* \) in the third power (eq. (1)), the relation (3) of \( \alpha \) implies a strong dependence of the maximum undercoolability of metallic melts on the topological structure of the solid phases formed from the undercooled liquids. This structure dependence was systematically studied for Al-based quasicrystal forming liquids undercooled by electromagnetic levitation [25,26,27]. Maximum relative undercoolings of only \( \Delta T^*/T_L^* = 0.1 \) were measured for the I-phases in Al-Cu-Fe and Al-Pd-Mn, while for the decagonal quasicrystalline D-phases in Al-Cu-Co, Al-Ni-Co and Al-Co \( \Delta T^*/T_L^* = 0.15 \) is obtained. \( \Delta T^*/T_L^* = 0.13 \) was observed for the \( \lambda \)-phase in Al(-Cu)-Fe and \( \Delta T^*/T_L^* = 0.14 \) for the \( \mu \)-phase in Al-Fe. The crystalline \( \beta \)-phase in Al-Cu-Co of CsCl structure (topological structure equivalent to a bcc phase) exhibits the largest undercoolability (\( \Delta T^*/T_L^* = 0.25 \)).

In order to estimate \( \alpha \) from the measured undercoolings, \( \Delta T \), we assume homogeneous nucleation and that at least one nucleation event occurs during the experiment time \( t_N \) within the sample volume, \( V \), for the onset of solidification at the nucleation temperature \( T_N \). \( I_{ss}(T_N)\cdot V \cdot t_N \geq 1 \). With eq. (1) and (2) the dimensionless solid-liquid interfacial energy, \( \alpha \), can be estimated from experimental results on the maximum undercoolability under assumption of homogeneous nucleation, because all other parameters are measurable or can be estimated by models. As described in detail in ref. [26], this gives a similar sequence of \( \alpha \) as relation (3):

\[
\alpha^I = 0.3 < \alpha^\lambda = 0.33 < \alpha^\mu = 0.37 < \alpha^\sigma = 0.45 < \alpha^\beta = 0.63 \tag{4}
\]

The structure dependence of \( \gamma \) has a decisive impact on the phase selection during solidification of undercooled melts. Although \( \Delta G_s(T) \) is always lower for stable solid phases than for metastable ones, at a given \( T < T_L \), \( \Delta G^*(T) \) may be smaller for a metastable phase, if this phase has a sufficiently lower \( \gamma(T) \), resulting in the nucleation of metastable phases.

For example, under equilibrium conditions Al\(_{13}\)Cu\(_{33}\)Fe\(_5\) melts form the \( \lambda \)-phase at the liquidus temperature of \( T_L^\lambda = 1164 \) K and, in a second solidification step, the I-phase is peritectically formed from \( \lambda \) and the liquid at \( T_L^I = 1115 \) K [28]. If, however, the melt is undercooled deeply enough, the I-phase crystallizes primarily [26,28]. This phase selection behaviour is consistent with relation (3) which suggests that \( \gamma \) and therefore also \( \Delta G^* \) is lower for the I-phase than for the \( \lambda \)-phase. It must be stressed that our neutron scattering
experiments on $\text{Al}_{60}\text{Cu}_{34}\text{Fe}_6$ melts (figure 1) are indicative of an ISRO, such that a direct link between the SRO in the liquid phase and the undercooling and phase selection behaviour has been established for this alloy. Also the phase selection properties of other undercooled melts of Al-Cu-Fe alloys such as $\text{Al}_{65}\text{Cu}_{25.5}\text{Fe}_{12.5}$ can be explained by the structure dependence of $\gamma$ as predicted by relation (3) [28].

4. Conclusions

The SRO of undercooled and stable melts forming quasicrystals and their approximants ($\text{Al}_{60}\text{Cu}_{34}\text{Fe}_6$, $\text{Al}_{65}\text{Cu}_{25}\text{Co}_{10}$ and $\text{Al}_{13}(\text{Co,Fe})_4$) was studied by neutron scattering. For the $\text{Al}_{13}(\text{Co,Fe})_4$ melts partial Faber-Ziman- and Bhatia-Thornton structure factors were determined. The experiments provide evidence of an icosahedral topological short-range order prevailing in the melts even at temperatures above the melting temperature. There are indications that this SRO consists not only of simple icosahedral clusters with 13 atoms but of larger polytetrahedral aggregates such as dodecahedra. Similar results were obtained from diffraction studies on melts of several pure metals [5,6]. This suggests that ISRO is a universal property of most metallic melts independent of the structure of the corresponding solid phases, provided that the atomic radii of the components are not too different.

The energy of the interface between a solid nucleus and an undercooled melt was modeled in the framework of the negentropic model. This model bases on the assumption of a polytetrahedral SRO in the solid-liquid interface as proven to exist in metallic melts by our diffraction studies. A pronounced dependence of the solid-liquid interfacial energy on the structure of the solid phase is predicted by the model. This structure dependence is able to explain the undercooling behaviour of melts of Al-based alloys forming solid phases of different structure as well as the phase selection behaviour during solidification.

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References

$\text{Al}_{60}\text{Cu}_{34}\text{Fe}_6; \ T_L = 1164 \text{ K}$

$T = 1090 \text{ K}$

$T = 1225 \text{ K}$

$T = 1325 \text{ K}$