ICOSAHEDRAL CLUSTERS AND NON UNIFORM MAGNETISM IN LIQUID PRECURSORS OF AlPdMn QUASICRYSTALS

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In a recent study of liquid AlPdMn alloys[1] leading to quasicrystalline or approximant phases by primary crystallisation[2], we put onto light a very strong local order. The close similarity between the intense Bragg peaks of the solid phase and the main peaks of the liquid structure factor suggests an icosahedral local order. On the other hand the liquid shows up a paramagnetic behaviour whereas the solid phases are non magnetic. The magnetic susceptibility of the liquid is proportional to the Mn content of the AlPdMn alloys ; it increases with increasing temperature, which could be associated to a decrease of the amount of icosahedral clusters[3].

Most structural models for quasicrystals involve packings of various icosahedral clusters with a large number of atoms, such as Mackay clusters (54 atoms) in AlPdMn quasicrystals or Bergman clusters (104 atoms) in AlLiCu quasicrystals. The same clusters are also found in the approximants of quasicrystals, which are periodic phases with large unit cells whose structures are closely related to that of quasicrystals. Clusters are not only a convenient geometrical description of these complex phases, but can also play a role in their properties. In the case of a liquid - icosahedral solid phase equilibrium, it might be expected that the local order in liquids forming quasicrystals reflects the local organization of atoms in the solid. Therefore we have undertaken simultaneously a simulation of the liquid local order based on icosahedral clusters and an extension of our experimental work up to higher temperatures and with several Mn compositions. Polarised neutrons have been used to investigate the Mn magnetic form factor in the liquid.

Neutron diffraction

Neutron scattering spectra measured on 7C2 spectrometer on the $Al_{72.1}Pd_{20.7}Mn_{7.2}$ alloy at 1143 K where the eutectic was molten (and hence the solid icosahedral phase coexisted with a small fraction of liquid) and at 1223 K just above the melting point (T_L=1160 K) are shown in figure 1. The broad maxima of the differential scattering cross-section in the liquid state correspond to the main Bragg peak groups of the icosahedral phase. At small Q values in the liquid state, a paramagnetic contribution is superimposed to the measured structure factor as explained later.

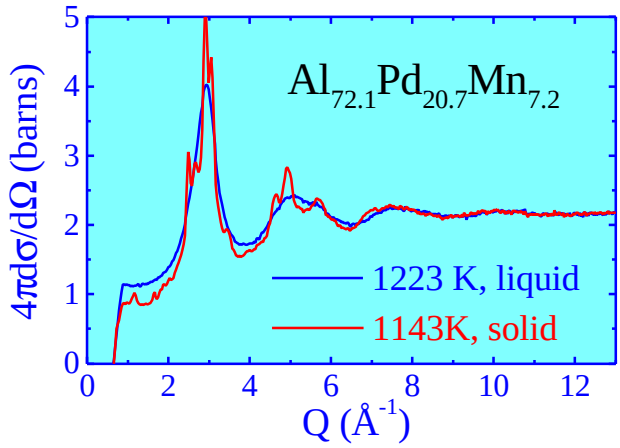

Figure 1. Structure factor of AlPdMn alloys in the solid state (just below the melting point) and in the liquid state (just above the melting point), measured on 7C2, LLB.

The similarity between the liquid and solid spectra extends up to the largest Q values. The same kind of observation holds for other studied alloys : $Al_{77}Pd_{18}Mn_5$ and $Al_{76.5}Pd_{20}Mn_{3.5}$. Such an observation suggests the presence of strong local order in the liquid state above T_L, reminiscent of that in the solid.

We have therefore searched for a possible evolution of the neutron scattered intensity with increasing temperature in the liquid state. This study was performed up to 1923 K, using the spectrometer D4B at ILL, on the $Al_{72.1}Pd_{20.7}Mn_{7.2}$ alloy whose primary crystallization gives rise to the largest proportion of icosahedral phase. Results are shown in figure 2.

As expected in liquid metallic alloys, the oscillations of the structure factor are broadened and their amplitudes decrease with increasing temperature.

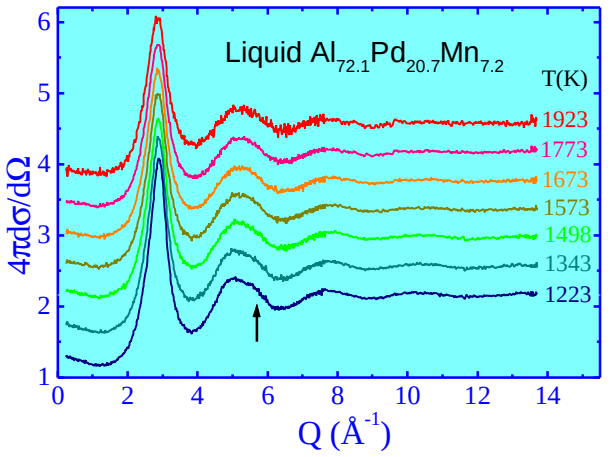

Figure 2. Differential neutron scattering cross-section versus temperature for the $Al_{72.1}Pd_{20.7}Mn_{7.2}$ in the liquid state (measured on D4, ILL). The vertical scale corresponds to the data measured at 1223 K. The curves at successive temperatures have been shifted by steps of 0.5 barns.

An evolution of the liquid structure is suggested by the fact that the second peak shoulder (shown by an arrow around 5.5 Å^{-1}), well defined just above the melting point, is progressively damped with increasing temperature. Simultaneously the low Q limit of the intensity increases which indicates an increase of the magnetic moment. Finally it must be emphasized that the oscillations at larger Q remain well defined up to 1923 K and **their position is unchanged**, while the position of the first peak shifts towards small Q as expected from thermal expansion.

Polarized neutron scattering

Polarized neutron scattering experiments were performed on the D7 spectrometer at ILL (Grenoble) at room temperature and at 1170 K, just above the liquidus temperature[4]. Incident neutrons were sequentially polarized along the three perpendicular directions. For each direction of polarization, the spin-flip and non-spin-flip scatterings were alternately measured. Paramagnetic and nuclear spin incoherent scatterings give rise to both spin-flip and non-spin-flip processes, while the nuclear coherent and incoherent (isotopic and chemical) scatterings are non-spin-flip. By suitable combinations of the measured spin-flip and non-spin-flip signals, the contributions of the nuclear spin incoherent scattering, the nuclear scattering and the paramagnetic scattering can be determined. The differential magnetic scattering cross-sections at 300 K and 1170 K (obtained by averaging spin-flip and non-spin-flip measurements) are shown in Figure 3. Very large error bars are due to small counting rates resulting from the significant attenuation of the incident and scattered beams within the neutron polarizer and analyzer devices. Nevertheless, in agreement with previous results, a paramagnetic scattering is detected in the liquid state, while it is not measurable in the solid state. The differential nuclear scattering cross-section has been extracted as well it ascertains that the chemical incoherent scattering increases on melting and reaches its maximal value in the liquid state above T_L. Thus the increase of the differential scattering cross-section measured with unpolarized neutrons on melting is not only due to the onset of paramagnetic scattering in the liquid, but also to an increase of the chemical incoherent scattering.

Knowing the chemical incoherent scattering contribution, the differential paramagnetic scattering cross-section in the liquid can be calculated from the differential scattering cross-section measured using unpolarized neutrons. In the $Al_{72.1}Pd_{20.7}Mn_{7.2}$ alloy, at 1223 K, from $\sigma_0 = 1.2 \pm 0.06$ barns at Q = 0.2 Å^{-1} one obtains $4\pi(d\sigma/d\Omega) = 0.49$ barns which is much larger than the signal measured using polarized neutrons ($\cong$ 0.075 ± 0.015 barns). This discrepancy is probably due to the quasi-elastic nature of the paramagnetic scattering. On D7 the integration on energy is limited, on the neutron energy loss side, by the low incident neutron energy (E_i =3.5 meV) and, on the neutron energy gain side, by an effective cut-off (around 10 meV) due to the progressive decrease of the efficiency of the neutron spin analyzers with increasing energy.

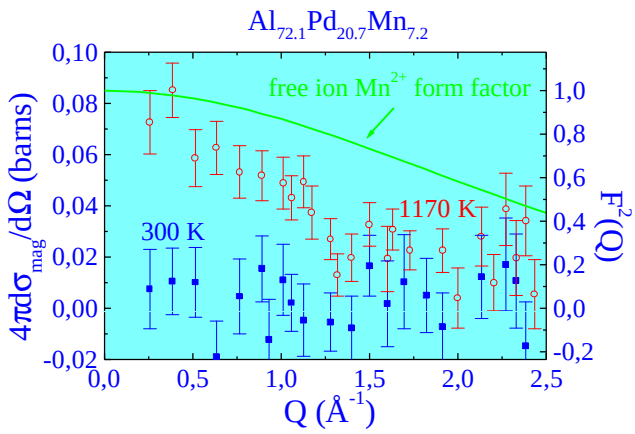

Figure 3 . Polarized neutron scattering measurements performed on D7, ILL : Q dependence of the differential paramagnetic scattering cross-section in $Al_{72.1}Pd_{20.7}Mn_{7.2}$ at 300 K (full blue squares) and at 1170 K in the liquid state (open red circles). There is a paramagnetic scattering in the liquid state and no such signal in the solid state. The data in the liquid state, normalized to 1 at Q=0 (right vertical scale), are compared to the form factor of a free Mn^{2+} ion (solid line).

On the contrary, the high incident energies used on the 7C2 and D4B spectrometers ($E_i \cong$ 170 meV) permit an integration of a much larger fraction, or almost the whole, of the paramagnetic response.

Assuming the whole signal is integrated on 7C2 and D4B, then only 15% of the paramagnetic signal was detected on D7 at 1170 K. However, even with such a poor precision in the data, one can observe a narrowing of the form factor compared to that of the Mn^{++} ion, which suggests strong magnetic correlations in this liquid alloy.

Icosahedral local order of the liquid state

The great similarity found between the structure factor of the liquid AlPdMn alloys and the diffraction spectrum in the solid quasicrystalline phase led us to assume the presence of a strong local icosahedral order in the liquid. In order to ascertain this hypothesis, we analyze more quantitatively the liquid structure factor through numerical simulations based on icosahedral clusters.

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 under several conditions and indeed brings very interesting information on the local order. The principle of the method, initially introduced to describe molecular solids, implies that a cluster can be defined in the liquid and that the atoms within the cluster are much more rigidly bound together than to other atoms in the system. The structure factor can be written as :

$$S(Q) = \frac{1}{N_{at}^{c}\left\langle b^{2}\right\rangle}\sum_{i,j=1}^{N_{at}^{c}} b_i b_j \frac{\sin Qr_{ij}}{Qr_{ij}} e^{-W_{ij}}$$

It is compared to the experiment on figure 4a.

Because of the similarity between local order in the icosahedral solid and in the liquid, the choice of the cluster was guided by the structural description of several AlMn and AlPdMn approximant phases. We assumed therefore an icosahedral cluster of Al centered on a Mn Atom[6]. The first icosahedron edge Al-Al distance $<r_1>$ was taken equal to 2.6 Å and the mean square variation $<\delta r_1^2>$ of this distance was 0.015 $Å^2$ as expected from the results of structure refinement of solid phases. $<r_0>$ is the Mn-Al distance (see insert of the figure 1b). The other icosahedron distances are then fixed. Their mean square variation can be obtained assuming that : $<\delta r_i^2> = <\delta r_1^2> (<r_i>/<r_1>)^2$.

The Debye-Waller term is then defined with: $W_{ij} = <\delta r_i^2>/3$.

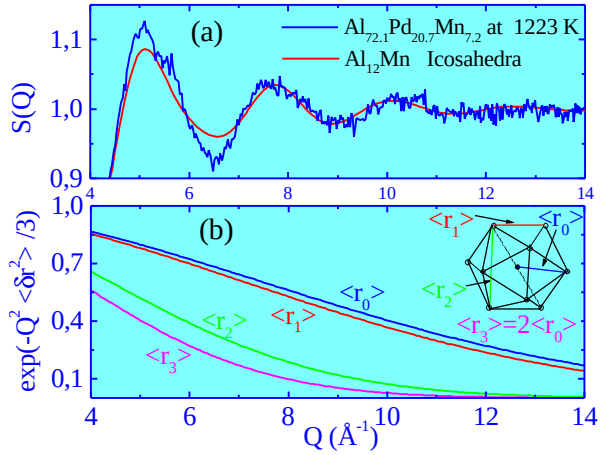

Figure 4.(a): Comparison for Q > 4.5Å^{-1} of the measured structure factor at 1223 K in $Al_{72.1}Pd_{20.7}Mn_{7.2}$ (blue) with the calculated structure factor assuming $Al_{12}Mn$ icosahedra (red solid line)
(b) Q dependence of the Debye-Waller factors for the four pair distances within the $Al_{12}Mn$ icosahedron

Conclusion

In this work, by using a cluster based numerical simulation, we have proven the existence of **icosahedral clusters** with lifetime greater than the typical neutron interaction time with the cluster (i.e. 10^{-10} seconds).

The existence of such clusters with the same geometry up to very high temperatures, is the signature of a **molecular type** local order in a liquid **metallic alloy**.

Moreover this liquid is **non homogeneous** as far as no change occurs in intracluster distances, while bulk density strongly decreases.

We have shown that the unexpected behaviour of the magnetic properties of these alloys can be understood under the assumption than **Mn becomes magnetic outside of the $Al_{12}Mn$ clusters**.

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