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Bond-orientational order in liquid aluminium$_{80}$-transition metal$_{20}$ alloys

M. Maret (1), F. Lançon (2) and L. Billard (2)

(1) Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques (*), ENSEEI, BP 75, 38402 St-Martin d'Hères Cedex, France
(2) Département de Recherche Fondamentale sur la Matière Condensée. SP2M/MP, CENG, BP 85X, 38041 Grenoble Cedex, France

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Abstract. — The structures of liquid Al$_{80}$Mn$_{20}$ and Al$_{80}$Ni$_{20}$ are simulated by molecular dynamics using interatomic potentials derived from neutron diffraction data. For these two alloys, the generated three dimensional particle configurations are consistent with the experimental partial pair correlation functions. The characterization of the local symmetries by both the construction of the Voronoï polyhedra and the calculation of the second-order invariants of spherical harmonics allows us to confirm the existence of a local icosahedral order in the quasicrystal-forming liquid Al$_{80}$Mn$_{20}$ and its absence in liquid Al$_{80}$Ni$_{20}$ about 70 K above the liquidus line. Molecular dynamics simulations of the corresponding supercooled liquids show that this order increases strongly for Al$_{80}$Mn$_{20}$ and starts to develop for Al$_{80}$Ni$_{20}$. An improvement of the agreement between the experimental and calculated pair correlation functions by the reverse Monte Carlo method yields liquid configurations characterized by the same most frequently observed Voronoï polyhedra as those obtained in the molecular dynamics configurations, but with lower percentages.

1. Introduction.

The discovery of quasicrystalline phases in Al-Mn alloys [1] has stimulated the research of local icosahedral order in the corresponding liquid alloys. Such bond-orientational order has already been observed in a supercooled monoatomic liquid by the molecular dynamics method [2] but never above the liquidus line. The neutron scattering experiments performed recently in the aluminium-based liquid alloys — Al$_{80}$M$_{20}$ [3], Al$_{60}$M$_{40}$ [4] (M = Mn or the equiatomic mixture Fe-Cr) and Al$_{80}$Ni$_{20}$ [5] — have yielded a description of the local structure of the liquid in terms of partial pair correlations (i.e. a set of coordination numbers and nearest-neighbour distances). Since the symmetries of the environment around the different species were not accessible from these neutron experiments, no firm conclusion in favour of an icosahedral order could be drawn.

(*) CNRS URA 29.
Nevertheless, from a Landau description of short-range icosahedral order [6] some features in the topological ordering function of the Al-Mn quasicrystal forming liquid alloys (the number-number structure factor \( S_{NN}(q) \) in the Bhatia-Thornton formalism [7]) are suggestive of local icosahedral order. These features are the existence of a first peak exceptionally intense for a liquid, the shape of the second peak which tends to form a double-component peak at positions close to 1.7 \( q_1 \) and 2 \( q_1 \) (\( q_1 \) is the first peak position). In contrast, these features are absent in the \( S_{NN}(q) \) function of the liquid Al\(_{80}\)Ni\(_{20}\) which forms no quasicrystal.

The object of this paper is to determine the local symmetries in the two different liquid alloys, Al\(_{80}\)Mn\(_{20}\) and Al\(_{80}\)Ni\(_{20}\), from their structure simulated by molecular dynamics using interatomic potentials derived from our previous neutron diffraction data. Information on symmetry is deduced from the 864 atomic positions of the simulated structure: either by dividing into Voronoi polyhedra which can be constructed around each atom or by calculating the bond order parameters introduced in reference [2] which are the second order invariants \( Q_2 \) formed from the spherical harmonics associated with every bond joining near neighbour atoms. Part of the calculations for Al\(_{80}\)Mn\(_{20}\) has been briefly presented in reference [8].

In section 2, we present the derivation of the three interatomic pair potentials from neutron data for both liquid alloys, Al\(_{80}\)Mn\(_{20}\) and Al\(_{80}\)Ni\(_{20}\). The results of molecular dynamics (MD) performed at 1320 K (i.e., about 70 K above the melting temperature, \( T_m \)) in these two alloys are reported in section 3. The polyhedron topology statistics and the bond orientational order parameters corresponding to the simulated liquid structures are compared with those calculated in the cubic \( \alpha \)-AlMnSi phase [9] and the model of AlMnSi relaxed quasicrystal [10], built from the model of Duneau and Oguey [11]. In these two descriptions, we examine more particularly the parameters characterizing the icosahedral order. Changes in the local symmetries when decreasing the temperature are then discussed from the undercooled liquid configurations obtained at 0.8 \( T_m \) by molecular dynamics. In section 4, we present refined simulated liquid configurations using the reverse Monte Carlo (RMC) method, which yield partial correlation functions in excellent agreement with the experimental curves. The local symmetries characterizing the RMC configurations are finally compared with those found in the MD configurations.

2. Interatomic potentials.

In order to obtain reliable descriptions of the structure of liquid Al\(_{80}\)Mn\(_{20}\) and Al\(_{80}\)Ni\(_{20}\) by the molecular dynamics method, we use interatomic pair potentials \( \phi_{ij}(r) \) derived from our previous neutron diffraction data. They are calculated in the Percus-Yevick approximation [12] extended to binary systems, which from a previous study on the accuracy of the liquid theory approximate methods [13] appears to be more accurate than the hypernetted-chain equation in the region of the main peak:

\[
\phi_{ij}(r) = k_B T \ln \left[ 1 - C_{ij}(r)/g_{ij}(r) \right].
\]

(1)

In equation (1), \( C_{ij}(r) \) are the direct correlation functions which are of shorter range than \( g_{ij}(r) \). They are obtained by Fourier transformation of the functions \( \tilde{C}_{ij}(q) \) which are related to the experimental Ashcroft-Langreth partial structure factors \( S_{ij}(q) \) [14] as follows:

\[
\tilde{C}_{ij}(q) = (1 - S_{ij}(q) D(q))/n_i
\]

\[
\tilde{C}_{ij}(q) = S_{ij}(q) D(q)/\sqrt{n_i n_j}
\]

(2)

with

\[ D(q) = 1/(S_{ij}(q) S_{ij}(q) - S_{ij}^2(q)) \quad \text{and} \quad n_i = c_i n. \]

\( c_i \) is the atomic concentration of species \( i \) and \( n \) the total number density.
The main difficulty for deriving reliable $\phi_{ij}(r)$ arises from the determination of $\tilde{C}_{ij}(q)$ at small scattering vectors. Small errors on $S_{ij}(q)$ yield large noise in the values of $\tilde{C}_{ij}(q)$ (as shown in Figs. 1 and 2). In order to improve the extraction of $\phi_{ij}(r)$ which are sensitive to the low-$q$ part of $\tilde{C}_{ij}(q)$, the experimental points of $\tilde{C}_{ij}(q)$ derived from equation (2) have been smoothed from 0 to about 1 Å$^{-1}$ by forcing $\tilde{C}_{ij}(q)$ to tend at $q = 0$ towards the thermodynamic limit $\tilde{C}_{ij}(0)$, deduced from the limits $S_{ij}(0)$. The calculations of $S_{ij}(0)$ from the following thermodynamic quantities: the molar volume $V_m$, the isothermal compressibility $K_T$, and the limit $S_{CC}(0)$ (related to the Gibbs free energy), were presented in references [3] and [5] for Al$_{80}$Mn$_{20}$ and Al$_{80}$Ni$_{20}$.

Thus, the accuracy in $\tilde{C}_{ij}(0)$ is limited by the experimental precision in the thermodynamic quantities. By way of illustration, we report in table I the errors in $\tilde{C}_{ij}(0)$ calculated starting with realistic errors of 1% in $V_m$ and $K_T$, and 5% in $S_{CC}(0)$. While for the two liquids the relative errors in the limit $\tilde{C}_{AlAl}(0)$ of the majority atoms remain small, some of them can be very large such as in $\tilde{C}_{NiAl}(0)$. Several calculations of $\phi_{ij}(r)$ by changing the values of $\tilde{C}_{ij}(0)$ in the range given in table I have shown that for any atomic pair a decrease of
Table I. — Thermodynamic limits of the functions $\tilde{C}_{ij}(q)$ for the liquid alloys Al$_{80}$Mn$_{20}$ and Al$_{80}$Ni$_{20}$, M = Mn, Ni (see also text).

<table>
<thead>
<tr>
<th>ATOMIC PAIR</th>
<th>Al$<em>{80}$Mn$</em>{20}$</th>
<th>Al$<em>{80}$Ni$</em>{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M - M</td>
<td>-277 (± 50)</td>
<td>-410 ± 75</td>
</tr>
<tr>
<td>M - Al</td>
<td>-450 (± 40)</td>
<td>-76 ± 50</td>
</tr>
<tr>
<td>Al - Al</td>
<td>-1032 (± 35)</td>
<td>-992 ± 35</td>
</tr>
</tbody>
</table>

$\tilde{C}_{ij}(0)$ yields a more repulsive potential but does not change the general shape of $\phi_{ij}(r)$ significantly, and in particular its oscillations are not phase-shifted. We have checked that at low $q$ the three pair partial structure factors are reconstructed in a satisfying way from the three adjusted parts of $\tilde{C}_{ij}(q)$. Our method appears to be more accurate than the method used by Li and Cowlam [15] to extract pair potentials for metallic glasses, which consists in extrapolating the three curves $S_{ij}(q)$ freehand down to $q = 0$ and then in calculating the $\tilde{C}_{ij}(q)$ functions.

The direct correlation functions $C_{ij}(r)$ are obtained by Fourier transformation of the adjusted functions $\tilde{C}_{ij}(q)$ such as:

$$C_{ij}(r) = \frac{1}{2\pi r^2} \int_{0}^{q_{\text{max}}} q \tilde{C}_{ij}(q) \sin(qr) \left[ \exp\left(-\frac{q^2}{q_{\text{max}}^2} \ln A \right) \right] dq .$$

(3)

In integral (3) the exponential term is a damping factor of the oscillations of $\tilde{C}_{ij}(q)$ (for $A = 0.5$ the oscillations are decreased by a factor of 2 at $q_{\text{max}}$). The truncation values $q_{\text{max}}$ in integral (3) are identical to those chosen for the calculation of $g_{ij}(r)$ from $S_{ij}(q)$ (see Refs. [3] and [5]).

The potentials $\phi_{ij}(r)$ using equation (1) are calculated from minimal distances such that $g_{ij}(r)$ are strictly positive. For Al$_{80}$Mn$_{20}$ these distances of 2.2 Å are identical for the three atomic pairs: for Al$_{80}$Ni$_{20}$ they are slightly different and equal to 2.1, 1.5 and 2.1 Å for the NiNi, NiAl and AlAl pairs, respectively. Since $g_{ij}(r)$ are positive, $\phi_{ij}(r)$ are calculable provided $C_{ij}(r)$ are smaller than $g_{ij}(r)$. From the functions $\tilde{C}_{ij}(q)$ adjusted at low $q$ this condition is always satisfied, while it is not when the raw functions are used. This point also emphasizes the importance of the long-wavelength limits in the extraction of pair potentials which determine the slopes of $\tilde{C}_{ij}(q)$ at small $q$.

A damping factor was only applied for Al$_{80}$Ni$_{20}$. Indeed the function $g_{\text{NNN}}(r)$ in reference [5] exhibits negative values beyond the first neighbour peak. Since $C_{\text{NNN}}(r)$ is still lower in this region, $\phi_{\text{NNN}}(r)$ cannot be derived. A means of removing this spurious effect due to the unaccuracy of $S_{\text{NNN}}(q)$ is to use a damping factor similar to that used for $\tilde{C}_{\text{NNN}}(q)$ in the calculation of the Fourier transform of $S_{\text{NNN}}(q)$. In order to get comparable interatomic interactions for any atomic pair in the molecular dynamics simulations, the same damping factor (here $A = 0.3$) was used for the calculations of all the functions $g_{ij}(r)$ and $C_{ij}(r)$. The effect of such a factor is to reduce the amplitudes of the oscillations of $\phi_{ij}(r)$.

In figure 3, we present the interatomic potentials in Al$_{80}$Mn$_{20}$ and Al$_{80}$Ni$_{20}$ obtained from the adjusted functions $\tilde{C}_{ij}(q)$. They exhibit strong oscillations in the first neighbour region, then damp down rapidly beyond 6 Å. The first minima which are positive or negative correspond quite well to the first maximum positions of the experimental pair correlation functions shown in figures 4 and 5. For instance, in $\phi_{\text{NNN}}(r)$ the two minima at 2.35 and 2.8 Å
Fig. 3. — Interatomic pair potentials $\phi_{ij}(r)$ (in mRy) derived from diffraction data for liquid $\text{Al}_{80}\text{Mn}_{20}$ (----) and $\text{Al}_{80}\text{Ni}_{20}$ (-----) ($M = \text{Mn or Ni}$).

Fig. 4. — Partial pair correlation functions $g_{ij}(r)$ obtained from neutron diffraction (----) and molecular dynamics (-----) for liquid $\text{Al}_{80}\text{Mn}_{20}$.

Fig. 5. — Partial pair correlation functions $g_{ij}(r)$ obtained from neutron diffraction (----) and molecular dynamics (-----) for liquid $\text{Al}_{80}\text{Ni}_{20}$.
reflect the two components in the distribution of the first neighbours NiNi. The strongly repulsive part of \( \phi_{\text{NiNi}}(r) \) around 3.5 Å comes from the very small values of \( g_{\text{NiNi}}(r) \) in this region. The most interesting feature is certainly the repulsive character of the potentials \( \phi_{\text{AIAI}}(r) \) in the first neighbour region with the existence of a repulsive hump besides the repulsive core. For both liquids \( \phi_{\text{AIAI}}(r) \) becomes attractive only at the upper limit of the second neighbour shell. It is worth emphasizing that, on the one hand, this shape of potential in the first neighbour region was already calculated by Duesbery et al. [16] for pure aluminium and was attributed to the choice of electron gas screening, on the other hand, the pair potential derived from Al liquid X-ray data [17] was also found positive up to 4.2 Å. Consequently, the pair potential \( \phi_{\text{AIAI}}(r) \) for Al\(_{80}\)Ni\(_{20}\) derived from our experimental results [5] seems to be more reliable than that extracted from neutron data using also the Percus-Yevick approximation in the same liquid alloy twenty years earlier [18], which presents a negative potential well in the first neighbour region.


3.1 Procedure. — The molecular dynamics simulations were carried out for a system of 691 Al atoms and 173 M atoms (M = Mn or Ni) in a cubic box with periodic boundary conditions at constant volume and constant temperature (\( T = 1323 \text{ K} \) for Al\(_{80}\)Mn\(_{20}\) and Al\(_{80}\)Ni\(_{20}\)) with constrained equations of motions [19]. The size of the box is chosen in such a way that the density of the 864 particles’ systems is equal to that of the liquid (\( n = 0.058 \text{ at/Å}^3 \) for Al\(_{80}\)Mn\(_{20}\) and 0.06 at/Å\(^3\) for Al\(_{80}\)Ni\(_{20}\)). The initial atomic positions are randomly chosen with the constraint of a minimal interatomic distance of 2.2 Å, together with a Gaussian distribution of initial velocities, such that the mean kinetic energy corresponds to the chosen temperature. The instantaneous forces on each particle due to its neighbours are computed from the interatomic potentials described in section 2. The potentials \( \phi_{ij}(r) \) are represented by cubic splines. They are set to zero from the nodes beyond which the oscillations of \( \phi_{ij}(r) \) are largely damped down. The truncation values for the atomic pairs MM, MAI and AIAI are equal to 6, 5.4 and 5.1 Å for Al\(_{80}\)Mn\(_{20}\) and 6.1, 5.7 and 6.5 Å for Al\(_{80}\)Ni\(_{20}\), respectively.

For Al\(_{80}\)Mn\(_{20}\) a total of 80 000 molecular dynamics time steps (\( t_s = 1.5 \times 10^{-16} \text{ s} \)) have been performed; the instantaneous potential energy \( E_p \) of the system has attained its equilibrium value after roughly 20 000 steps, beyond \( E_p \) fluctuates around this mean value. For Al\(_{80}\)Ni\(_{20}\), 160 000 steps have been realized and the system tends towards its equilibrium configuration after 60 000 steps. For both liquids, the pressure of the 864 particles’ system in the equilibrium state remains considerably high (\( p = 10^5 \text{ atm} \)) and could be attributed to the fact that only the repulsive part of the potential \( \phi_{\text{AIAI}}(r) \) is taken into consideration in the calculation of the interatomic forces.

3.2 Partial pair correlation functions. — The calculated pair correlation functions, shown in figures 4 and 5, are the curves averaged over 60 configurations taken among the last 60 000 steps for Al\(_{80}\)Mn\(_{20}\) and 100 configurations among the last 100 000 steps for Al\(_{80}\)Ni\(_{20}\) at intervals of 1 000 steps. For both liquids, the overall agreement between experiment and molecular dynamics calculations is rather good. Small features such as the shoulder at the right side of the first peak of \( g_{\text{MAI}}(r) \), the asymmetry of the first peak in \( g_{\text{NiAl}}(r) \) and the double-component first peak in \( g_{\text{NiNi}}(r) \) are well reproduced. However, for Al\(_{80}\)Mn\(_{20}\) some differences in the intensities of the first peaks in \( g_{\text{AIAI}}(r) \) and \( g_{\text{MnMn}}(r) \) are observed, and for Al\(_{80}\)Ni\(_{20}\) a phase-shift between the experimental and calculated curves for \( g_{\text{NiNi}}(r) \) appears in the second-neighbour region nevertheless.
3.3 Number-number structure factor. — In figures 6 and 7, we present the calculated number-number structure factors $S_{NN}(q)$ obtained by inverse Fourier transformation of the corresponding $g_{NN}(r)$ functions together with the experimental curves. For both liquids, the overall agreement is satisfying. In the same manner as for the $g_{ij}(r)$'s, for Al$_{80}$Mn$_{20}$ both experimental and calculated curves are perfectly in phase, while for Al$_{80}$Ni$_{20}$ a phase-shift exists from the second peak. The adjustments of the $i_{NN}(q)$ functions at low $q$ force the calculated $S_{NN}(q)$ function for Al$_{80}$Ni$_{20}$ to tend towards its correct thermodynamic value of 0.046. The most interesting feature is the splitting of the second peak for Al$_{80}$Mn$_{20}$ at positions close to $1.7q_1$ and $2q_1$ ($q_1 = 2.86 \text{Å}^{-1}$) which is well resolved by molecular dynamics and suggestive of local icosahedral order. By contrast, for Al$_{80}$Ni$_{20}$ the calculated

Fig. 6. — Number-number structure factors $S_{NN}(q)$ obtained from neutron diffraction (——) and molecular dynamics (---) for liquid Al$_{80}$Mn$_{20}$.

Fig. 7. — Number-number structure factors $S_{NN}(q)$ obtained from neutron diffraction (——) and molecular dynamics (---) for liquid Al$_{80}$Ni$_{20}$.
curve exhibits a rounded second peak similar to that of the experimental curve. As will be shown in the next section, these features are consistent with the analyses of local symmetries.

3.4 Characterization of the local symmetries. — Two methods of determining and representing the local symmetries in liquid Al_{80}Mn_{20} and Al_{80}Ni_{20} are presented. The first method is based on the Voronoï polyhedron topology statistics and the second method is derived from the calculations of the bond orientational order parameters $Q_l$. The results obtained for the quasicrystal forming liquid Al_{80}Mn_{20} are compared with those calculated in the crystalline $\alpha$-AlMnSi phase [9] and the AlMnSi relaxed icosahedral quasicrystal model [10].

3.4.1 Voronoï polyhedra. — The description of the topology in terms of Voronoï polyhedra was first made in dense random packing models for simple liquids [20]. For random packings of two species with different sizes, the radical plane method proposed by Gellatly and Finney [21] was better adapted and applied to metallic glasses. In Al_{80}Mn_{20} and Al_{80}Ni_{20} liquids, since the two atomic species have close atomic radii, the construction of Voronoï polyhedra is preferentially chosen. As will be shown, the decomposition into radical (Laguerre) polyhedra leads to similar results.

Each Voronoï polyhedron constructed around an atom is defined by a set of integers $(n_3, n_4, n_5, \ldots, n_r, \ldots)$ where $n_i$ represents the number of faces having $i$ edges. Each face of every polyhedron bisects a near neighbour bond and thus the number of faces of the polyhedron defines a number of first neighbours around the central atom. The Voronoï polyhedron statistics in Al_{80}Mn_{20} have been made up from 60 configurations taken among the last 60 000 steps at intervals of 1 000 steps and in Al_{80}Ni_{20} from 100 configurations among the last 100 000 steps at the same interval. The types and percentages of the most frequently observed polyhedra are presented in table II together with those calculated in the icosahedral quasicrystal model and the $\alpha$ phase, we also give the 1% confidence interval on each percentage. Note that for a given configuration, by partitioning into radical polyhedra (using

<table>
<thead>
<tr>
<th>Liquid Al_{80}Mn_{20}</th>
<th>Relaxed icosahedral quasicrystal model</th>
<th>Cubic $\alpha$-AlMnSi phase</th>
<th>Liquid Al_{80}Ni_{20}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1320K - MD</td>
<td>((n_3, n_4, n_5, n_6)) pcT</td>
<td>((n_3, n_4, n_5, n_6)) pcT</td>
<td>((n_3, n_4, n_5, n_6)) pcT</td>
</tr>
<tr>
<td>(0,3,6,4)</td>
<td>4.1±0.2</td>
<td>0.6±0.2</td>
<td>(0,3,6,4)</td>
</tr>
<tr>
<td>(0,1,10,2)</td>
<td>4.05±0.25</td>
<td>6.2±0.2</td>
<td>(0,3,6,5)</td>
</tr>
<tr>
<td>(0,2,8,4)</td>
<td>3.8±0.2</td>
<td>5.8±0.2</td>
<td>(0,2,8,4)</td>
</tr>
<tr>
<td>(0,2,8,2)</td>
<td>2.8±0.2</td>
<td>5.6±0.2</td>
<td>(0,2,8,2)</td>
</tr>
<tr>
<td>(0,0,12)</td>
<td>2.3±0.2</td>
<td>3.1±0.2</td>
<td>(0,2,8,4)</td>
</tr>
<tr>
<td>(0,3,6,5)</td>
<td>2.0±0.15</td>
<td>2.8±0.15</td>
<td>(0,3,6,4)</td>
</tr>
<tr>
<td>(0,1,10,3)</td>
<td>1.8±0.2</td>
<td>2.7±0.2</td>
<td>(0,1,10,3)</td>
</tr>
<tr>
<td>(0,2,8,5)</td>
<td>1.7±0.15</td>
<td>2.6±0.15</td>
<td>(0,2,8,5)</td>
</tr>
<tr>
<td>(0,3,6,3)</td>
<td>1.6±0.15</td>
<td>2.5±0.15</td>
<td>(0,3,6,3)</td>
</tr>
<tr>
<td>(0,2,8,3)</td>
<td>1.6±0.2</td>
<td>2.5±0.2</td>
<td>(0,2,8,3)</td>
</tr>
<tr>
<td>(1,2,6,3,1)</td>
<td>1.5±0.1</td>
<td>2.1±0.1</td>
<td>(0,2,8,1)</td>
</tr>
<tr>
<td>(0,0,12)</td>
<td></td>
<td></td>
<td>(0,0,12)</td>
</tr>
</tbody>
</table>

Table II. — Types and percentages of the most frequent Voronoï polyhedra found in the simulated Al_{80}Mn_{20} and Al_{80}Ni_{20} liquids, in the relaxed icosahedral quasicrystal model and in the cubic $\alpha$-AlMnSi phase. The common polyhedron types between liquid Al_{80}Mn_{20} and the other phases are exposed in heavy characters.
atomic radii equal to 2.82 Å and 2.5 Å for Al and transition metal atoms respectively) we obtain the same types of the most frequently observed polyhedra with similar percentages.

The population of atoms with icosahedral symmetry characterized by the pentagonal dodecahedron (0, 0, 12) is of 13% in the α-phase, 5.6% in the icosahedral model, 2.3% in liquid Al$_{80}$Mn$_{20}$ and only 0.2% in Al$_{80}$Ni$_{20}$. Moreover, among the polyhedra listed in table II, seven of them are observed in both the liquid Al$_{80}$Mn$_{20}$ and the icosahedral model; by taking the corresponding lowest percentages, we find that at least 17% of the atomic sites have the same local symmetry. In contrast, only two types of polyhedra found in the α-phase are also observed in the liquid Al$_{80}$Mn$_{20}$ representing 6.1% of atomic sites.

Even if the proportion of (0, 0, 12) polyhedra in the liquid Al$_{80}$Mn$_{20}$ is small, the importance of local icosahedral order must not be underestimated, especially in comparison with the almost zero proportion found in Al$_{80}$Ni$_{20}$. By counting the first neighbours of the atomic sites with icosahedral symmetry, 22% of the 864 atoms are engaged in such order and in average the icosahedra are connected two by two. Consequently, there is no chain of icosahedral clusters, as it was proposed in the liquid eutectic AgGe to explain the small angle neutron scattering signal [22].

The three polyhedron types constructed in the crystalline phase Al$_3$Ni [23], the nearest compound from the liquid composition Al$_{80}$Ni$_{20}$, are the following ones: (0, 3, 6, 5), (0, 3, 6) and (0, 3, 6, 8) with respective frequencies of 50%, 25% and 25%. The (0, 3, 6) polyhedron type constructed around Ni atoms characterizes a trigonal prismatic neighbourhood. According to table II, only the (0, 3, 6, 5) polyhedron also belongs to the list of the first 11 polyhedra found in the liquid Al$_{80}$Ni$_{20}$ but with a frequency of 1.3% still lower than in Al$_{80}$Mn$_{20}$. The types of bond-orientational order in the Al$_3$Ni compound have, therefore, almost completely disappeared in the liquid Al$_{80}$Ni$_{20}$. Indeed, there are more similarities between the two liquid structures, since at least 8% of the atomic sites have similar local symmetries. The distribution of the polyhedron types much more spread out in Al$_{80}$Ni$_{20}$ than in Al$_{80}$Mn$_{20}$ indicates essentially that the local topological order in liquid Al$_{80}$Ni$_{20}$ is less defined than in Al$_{80}$Mn$_{20}$.

3.4.2 Bond-orientational order parameters. — Another way of characterizing the local symmetries has been developed by Steinhardt et al. [2] to study the bond-orientational order in Lennard-Jones supercooled liquids. To every bond joining a central particle to one of its neighbours, they associate a spherical harmonic:

$$Q_{lm}(r) = Y_{lm}(\theta(r), \phi(r)),$$

where $\theta$ and $\phi$ are the polar angles of the bond represented by the vector $r$.

To each atom surrounded by $N$ near neighbours, correspond average values of $Q_{lm}(r)$:

$$\bar{Q}_{lm} = \frac{1}{N} \sum_{i} Y_{lm}(\theta, \phi).$$

Since $\bar{Q}_{lm}$ changes for a given $l$ if one rotates the coordinate system, Steinhardt et al. had the idea to calculate the second-order invariants such as:

$$Q_{l} = \left[ \frac{4 \pi}{2l + 1} \sum_{m=-l}^{l} |\bar{Q}_{lm}|^2 \right]^{1/2}$$

and they found that the sequences $\{Q_{l}\}$ were characteristics of cluster symmetries. For instance, clusters with icosahedral symmetry exhibit nonzero bond-orientational order parameters for $l = 6, 10, 12$. Here, the bond-orientational order parameters which will
characterize the symmetries of the simulated liquids will be finally obtained by averaging the values of \( Q_f \) over all the particles of different equilibrium configurations.

To calculate the parameters \( Q_f \), we need to define the number \( N \) of near neighbour atoms in equation (5). We restrict the analysis of \( Q_f \) to the local scale, i.e. for the Al\(_{80}\)Mn\(_{20}\) and Al\(_{80}\)Ni\(_{20}\) simulated liquids we consider around any atom all the neighbours within the first coordination shell of radius \( r_{\text{min}} \). The value of \( r_{\text{min}} \) is chosen such that the average number of first neighbours is close to 12 (\( r_{\text{min}} \) is equal to 3.75 and 3.7 Å for Al\(_{80}\)Mn\(_{20}\) and Al\(_{80}\)Ni\(_{20}\) respectively, and corresponds roughly to the position of the first minimum in the Fourier transform of \( S_N(q) \)). In the icosahedral and \( \alpha \) phases, \( r_{\text{min}} \) is taken equal to 3.7 Å giving coordination numbers of 12.2 and 12.7 respectively. Figure 8 shows the histogram of \( Q_f \) versus \( \ell \) up to \( \ell = 12 \) for liquid Al\(_{80}\)Mn\(_{20}\) and Al\(_{80}\)Ni\(_{20}\), the relaxed icosahedral quasicrystal and the \( \alpha \)-phase. For each \( \ell \) number, \( Q_f \) are the values averaged over the 864 particles of the liquid structures, the 10 028 particles of the quasicrystal model and the 138 atoms of the \( \alpha \)-phase. For the liquids, the values of \( Q_f \) corresponding to the random initial configuration are shown together with close calculated from the equilibrium configurations which are the values averaged over 6 configurations taken among the last 60 000 steps at intervals of 10 000 steps for Al\(_{80}\)Mn\(_{20}\), and 10 configurations among the last 100 000 steps at the same interval for Al\(_{80}\)Ni\(_{20}\). Most of the values for the perfect 13-atom icosahedral cluster fall out of the range of figure 8 and are not shown (for \( \ell = 6, 10, 12 \) the \( Q_f \)'s are equal to 0.663, 0.363 and 0.585).

![Fig. 8](image-url)

Fig. 8. — Second-order invariants \( Q_f \) for the initial and equilibrium configurations of the simulated Al\(_{80}\)Mn\(_{20}\) and Al\(_{80}\)Ni\(_{20}\) liquids, the relaxed icosahedral AlMnSi quasicrystal model and the \( \alpha \)-AlMnSi phase.

Except for \( \ell = 10 \), the even values of \( Q_f \) for the quasicrystal model and the \( \alpha \)-phase stand between those for the liquids and the 13-atom icosahedral cluster. For any \( \ell \) number, the changes in \( Q_f \) between the initial and equilibrium states are larger for Al\(_{80}\)Mn\(_{20}\) than for Al\(_{80}\)Ni\(_{20}\), such that the equilibrium values for Al\(_{80}\)Mn\(_{20}\) are approaching closer to the values of the icosahedral model or the \( \alpha \)-phase. In particular, the icosahedral symmetry is more
developed in Al$_{80}$Mn$_{20}$ than in Al$_{80}$Ni$_{20}$, as suggested by the strong difference between the equilibrium values of $Q_0$.

3.5 Molecular dynamics simulations of Al$_{80}$Mn$_{20}$ and Al$_{80}$Ni$_{20}$ supercooled liquids. — In order to follow the changes in the local symmetries when decreasing the temperature, molecular dynamics simulations of supercooled liquids, Al$_{80}$Mn$_{20}$ and Al$_{80}$Ni$_{20}$, were performed at 1 000 K (i.e. 0.8 $T_m$) using the same interatomic potentials as shown in figure 3. We started from the final 864-particle configuration obtained at 1 320 K by molecular dynamics and we associated a new Gaussian distribution of velocities such that the kinetic energy corresponds to a temperature of 1 000 K. For the two alloys, 100 000 molecular time steps were performed at constant temperature and pressure; the pressure being chosen equal to that obtained by simulation at 1 320 K. The enthalpy of the system $(E_p + PV)$ has attained its equilibrium value after 60 000 steps for Al$_{80}$Mn$_{20}$ and 40 000 steps for Al$_{80}$Ni$_{20}$.

The Voronoi polyhedron statistics were compiled from 50 independent equilibrium configurations taken among the last 50 000 ones at intervals of 1 000 steps for Al$_{80}$Mn$_{20}$ and 70 configurations among the last 70 000 at the same interval for Al$_{80}$Ni$_{20}$. In table II are presented the most frequently observed types of Voronoi polyhedra in the undercooled liquids together with those found in a dense random packing model of amorphous iron [24]. It is remarkable that the five most frequent types of polyhedra are identical in the undercooled liquid Al$_{80}$Mn$_{20}$ and in the amorphous iron model. It is worth recalling that in this amorphous iron model, Srolovitz et al. have shown through the calculations of local structural parameters that, on the one hand, all the polyhedra presented a degree of ellipsoidal deviation from the spherical symmetry of the environment, and on the other hand, the (0, 0, 12) polyhedra were located in the most compressive regions [24].

Now, by comparing the results given in tables II and III, we can observe that for Al$_{80}$Mn$_{20}$ the five most frequent types of polyhedra found at 1 000 K are identical with those found at higher temperatures. In contrast, for Al$_{80}$Ni$_{20}$ the statistics are quite different since two new

Table III. — Types and percentages of the most frequent Voronoi polyhedra found in the simulated undercooled liquids of Al$_{80}$Mn$_{20}$ and Al$_{80}$Ni$_{20}$, and in a random packing model of amorphous iron [24]. The common polyhedron types between the undercooled liquid Al$_{80}$Mn$_{20}$ and the other phases are expressed in heavy characters.

<table>
<thead>
<tr>
<th>Undercooled liquid Al$<em>{80}$Mn$</em>{20}$</th>
<th>Undercooled liquid Al$<em>{80}$Ni$</em>{20}$</th>
<th>Random packing model of amorphous iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n$_3$,n$_4$,n$_5$,n$_6$, ) pct</td>
<td>(n$_3$,n$_4$,n$_5$,n$_6$, ) pct</td>
<td>(n$_3$,n$_4$,n$_5$,n$_6$, ) pct</td>
</tr>
<tr>
<td>(0,1,10,2) 6.9±0.3</td>
<td>(0,3,6,4) 3.1±0.2</td>
<td>(0,1,10,2) 13</td>
</tr>
<tr>
<td>(0,3,6,4) 5.7±0.3</td>
<td>(0,2,8,4) 2.5±0.2</td>
<td>(0,3,6,4) 8.8</td>
</tr>
<tr>
<td>(0,1,12) 7.6±0.2</td>
<td>(0,3,6,5) 1.9±0.15</td>
<td>(0,0,12) 8.7</td>
</tr>
<tr>
<td>(0,3,6,5) 8.8±0.25</td>
<td>(0,1,10,2) 1.8±0.15</td>
<td>(0,2,8,4) 7.6</td>
</tr>
<tr>
<td>(0,2,8,2) 3.8±0.25</td>
<td>(0,2,8,2) 1.8±0.15</td>
<td>(0,2,8,4) 4.3</td>
</tr>
<tr>
<td>(0,1,10,3) 3.6±0.2</td>
<td>(1,3,4,5,1) 1.5±0.1</td>
<td>(0,3,6,3) 6.2</td>
</tr>
<tr>
<td>(0,3,6,5) 2.5±0.2</td>
<td>(0,3,6,3) 1.4±0.1</td>
<td>(0,0,12,2) 3.2</td>
</tr>
<tr>
<td>(0,2,8,5) 2.5±0.2</td>
<td>(1,2,6,3,11) 1.4±0.1</td>
<td>(0,1,10,4) 2.2±0.2</td>
</tr>
<tr>
<td>(0,1,10,4) 2.2±0.2</td>
<td>(0,2,8,5) 1.3±0.1</td>
<td>(0,0,12) 0.7±0.1</td>
</tr>
<tr>
<td>(1,0,9,3) 2.0±0.2</td>
<td>(0,3,7,4,1) 1.3±0.1</td>
<td></td>
</tr>
</tbody>
</table>
types of polyhedra, (0, 1, 10, 2) and (0, 2, 8, 2), appear at 1000 K among the five most frequent ones. Moreover, icosahedral symmetry increases significantly for Al₈₀Mn₂₀ and starts to develop in Al₈₀Ni₂₀. On the whole, for Al₈₀Mn₂₀ the main types of local symmetry found at 1323 K are preserved at lower temperatures, while for Al₈₀Ni₂₀ the atomic rearrangements are more significant.

The second-order invariants were averaged over 5 configurations taken among the last 50,000 ones at intervals of 10,000 steps for Al₈₀Mn₂₀ and 7 configurations among the last 70,000 ones at the same interval for Al₈₀Ni₂₀. Figure 9 shows the effect of temperature on the invariants $Q_\ell$, which except for $\ell = 5$ is similar for the two alloys: i.e. when decreasing the temperature, the $Q_\ell$-values of the supercooled liquids are approaching closer to the values corresponding to the icosahedral phase model. In particular, the increase of $Q_6$ for $\ell = 6$ is well pronounced in agreement with the higher percentages of atoms with icosahedral symmetry.

Fig. 9. — Effect of the temperature on the second-order invariants $Q_\ell$ for the simulated Al₈₀Mn₂₀ and Al₈₀Ni₂₀ liquids. The $Q_\ell$ values for the initial random configuration are also presented.

4. Reverse Monte Carlo simulations of liquid Al₈₀Mn₂₀ and Al₈₀Ni₂₀.

In section 3, we have seen that the liquid configurations simulated by molecular dynamics yielded a good, but not perfect, representation of the experimental functions. Consequently, information on the local symmetries extracted from these configurations contains some unaccuracy difficult to estimate.

A way of generating configurations which allows a good representation of diffraction data is the so-called reverse Monte Carlo method [25]. If we start with the final configuration obtained by molecular dynamics and let $g_{ij}(r)$ be the pair correlation functions of a configuration at a given step, a new configuration is generated by random motion of one particle among the 864 particles with a maximal displacement chosen equal to 0.1 Å.
If the particle in motion approaches any other particle within a distance smaller than the lower cutoff distances \( r^0_{ij} \), taken equal to the first values for which the experimental \( g^E_{ij}(r) \)'s are non-zero, the new configuration is automatically rejected. Otherwise, the new configuration with the new pair correlation functions \( g'_i(r) \)'s is accepted using a standard \( \chi^2 \) test such as:

\[
\chi^2 = \sum_{ij} \sum_{k=1}^n \frac{(g^E_{ij}(r_k) - g_{ij}(r_k))^2}{\sigma^2_{ij}}
\]

and

\[
\chi'^2 = \sum_{ij} \sum_{k=1}^n \frac{(g^E_{ij}(r_k) - g'_{ij}(r_k))^2}{\sigma^2_{ij}}
\]

where \( n \) is the number of \( r \) points and \( \sigma_{ij} \) are the errors on the experimental curves \( g^E_{ij}(r_k) \). If \( \chi' < \chi \), the new configuration is accepted; if \( \chi' > \chi \), it is accepted with a probability that follows a normal distribution. The process is repeated until \( \chi^2 \) decreases to an equilibrium value and then oscillates about it.

The \( g_{ij}(r) \) functions are calculated with a path of 0.1 Å up to \( L/2 \) (\( L \) being the size of the box, equal to 24.6 Å for \( \text{Al}_{80}\text{Mn}_{20} \) and 24.3 Å for \( \text{Al}_{80}\text{Ni}_{20} \)). The lower cutoff distances are equal to 2.2 Å for the three pairs in \( \text{Al}_{80}\text{Mn}_{20} \), and 2.1 Å for \( \text{AlAl} \) and \( \text{NiNi} \) pairs and 1.5 Å for \( \text{AlNi} \) pairs in \( \text{Al}_{80}\text{Ni}_{20} \). The experimental errors \( \sigma_{ij} \) are assumed constant; for the two alloys they are equal to 0.02 for \( g_{\text{AlAl}}(r) \) and 0.04 for \( g_{\text{AlMn}}(r) \) and \( g_{\text{MM}}(r) \) (\( M = \text{Mn} \) or \( \text{Ni} \)).

The convergence is attained after about 65,000 accepted moves. Figures 10 and 11 show the calculated pair correlation functions, which are averaged over eight configurations taken
among those generated after 65 000 to 300 000 accepted moves. The agreement with the experimental curves is perfect for the AlAl and AlM pairs, and in comparison with the curves generated by molecular dynamics is clearly better for the MnMn and NiNi pairs.

The statistics of the Voronoï polyhedra established from the same configurations as those used for the calculations of the $g_{ij}(r)$ functions are presented in table IV. Due to the limited number of configurations, the 1% confidence intervals on the percentages are wider than those found in the MD configurations. For the two liquids, most polyhedra which were among the ten most frequently occurring polyhedra in the MD configurations are always present (indicated in bold characters) in table IV) with respective percentages systematically lower. For Al$_{80}$Mn$_{20}$ we observe a significant decrease of the fractions of the (0, 1, 10, 2) and (0, 0, 12) polyhedron types. For Al$_{80}$Ni$_{20}$ the percentage of (0, 0, 12) polyhedra, already very weak in the MD configurations, also decreases in the RMC configurations. It appears that the most compressive regions, where from Srolovitz et al. [24] the 13-atom icosahedra are located, tend to decrease in the configurations generated by reverse Monte Carlo.

Table IV. — Types and percentages of the most frequent Voronoï polyhedra found in the Al$_{80}$Mn$_{20}$ and Al$_{80}$Ni$_{20}$ liquid configurations generated by the reverse Monte Carlo method. The polyhedra common with the polyhedra the most frequently observed in the Al$_{80}$Mn$_{20}$ and Al$_{80}$Ni$_{20}$ liquids simulated by molecular dynamics are expressed in heavy characters.

<table>
<thead>
<tr>
<th>Liquid Al$<em>{80}$Mn$</em>{20}$</th>
<th>1320K - RMC</th>
<th>Liquid Al$<em>{80}$Ni$</em>{20}$</th>
<th>1320K - RMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n3,a4,a5,a6,)</td>
<td>pct</td>
<td>(n3,a4,a5,a6,)</td>
<td>pct</td>
</tr>
<tr>
<td>(0,3,6,4)</td>
<td>3.1±0.7</td>
<td>(0,3,6,4)</td>
<td>1.5±0.4</td>
</tr>
<tr>
<td>(0,2,8,4)</td>
<td>2.6±0.5</td>
<td>(0,2,8,4)</td>
<td>1.1±0.5</td>
</tr>
<tr>
<td>(0,2,8,2)</td>
<td>2.4±0.6</td>
<td>(1,2,6,3,1)</td>
<td>1.1±0.5</td>
</tr>
<tr>
<td>(0,1,10,2)</td>
<td>2.2±0.2</td>
<td>(1,3,4,5,1)</td>
<td>1.1±0.6</td>
</tr>
<tr>
<td>(0,3,6,5)</td>
<td>1.7±0.4</td>
<td>(1,3,4,4,1)</td>
<td>1.2±0.5</td>
</tr>
<tr>
<td>(1,3,4,5,1)</td>
<td>1.6±0.4</td>
<td>(0,4,5,4,1)</td>
<td>1.2±0.3</td>
</tr>
<tr>
<td>(0,3,6,3)</td>
<td>1.5±0.7</td>
<td>(1,3,5,4,2)</td>
<td>0.9±0.5</td>
</tr>
<tr>
<td>(1,2,6,3,1)</td>
<td>1.4±0.7</td>
<td>(0,3,6,5)</td>
<td>0.9±0.4</td>
</tr>
<tr>
<td>(0,3,6,6)</td>
<td>1.3±0.7</td>
<td>(0,3,7,4,1)</td>
<td>0.8±0.4</td>
</tr>
<tr>
<td>(0,4,5,4,1)</td>
<td>1.3±0.5</td>
<td>(1,2,6,4,1)</td>
<td>0.8±0.4</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(0,0,12)</td>
<td>1±0.3</td>
<td>(0,0,12)</td>
<td>0.04±0.05</td>
</tr>
</tbody>
</table>

Figure 12 presents the histograms of $Q_i$, these values are averaged over the same configurations as those previously used for the determination of the Voronoï polyhedra, in comparison with the histograms corresponding to the random configuration and the MD equilibrium configurations. We observe the same behaviour for the two alloys, i.e. globally the values of the RMC configurations are closer of the $Q_i$'s of the random configurations than the $Q_i$'s of the MD configurations. These results are consistent with the larger dispersion of the Voronoï polyhedron found in the RMC configurations than in the MD configurations.

Consequently, it turns out that the configurations generated by RMC are sensitively more disordered than the equilibrium configurations obtained by molecular dynamics. Even if the amount of icosahedral order has decreased in liquid Al$_{80}$Mn$_{20}$ after the RMC simulations, these simulations confirm the existence of a premonitory local icosahedral order in liquid Al$_{80}$Mn$_{20}$ in comparison with liquid Al$_{80}$Ni$_{20}$, which could explain the formation of the icosahedral Al$_{80}$Mn$_{20}$ phase.
5. Conclusion.

For both liquid alloys Al\textsubscript{80}Mn\textsubscript{20} and Al\textsubscript{80}Ni\textsubscript{20}, the rather good agreement between the experimental partial pair correlation functions and those calculated by the molecular dynamics technique gives some reliability in the interatomic potentials derived from our neutron diffraction experiments.

The characterization of the local symmetries from the calculation of the invariants of spherical harmonics and especially from the construction of the Voronoi polyhedra allows us to confirm the existence of a local icosahedral order in the quasicrystal forming liquid Al\textsubscript{80}Mn\textsubscript{20}. Even if it concerns only a small percentage of atoms, equal to 2.3 \%, it is nevertheless significant in comparison with the percentage about ten times smaller found in Al\textsubscript{80}Ni\textsubscript{20} which forms no quasicrystal.

The molecular dynamics simulations of the undercooled liquids show that for Al\textsubscript{80}Mn\textsubscript{20} the most frequently occurring local symmetries observed above the liquidus line are not only preserved at 0.8 \( T_m \) but also more pronounced. For Al\textsubscript{80}Ni\textsubscript{20}, the atomic rearrangements are more considerable, since new symmetries appear among the most frequent ones, and in particular the icosahedral symmetry starts to develop.

The improvement of the agreement between the experimental partial pair correlation functions and those calculated by the reverse Monte Carlo method leads to Al\textsubscript{80}Mn\textsubscript{20} and Al\textsubscript{80}Ni\textsubscript{20} configurations which are, in average, more disordered than those generated by molecular dynamics. Nevertheless, they present the same most frequently observed symmetries as those obtained in the molecular dynamics configurations, yet with lower percentages.

Acknowledgments.

We are indebted to Dr M. A. Howe and Dr R. L. McGreevy for providing the reverse Monte Carlo programs.
References