Diffuse Scattering and Phason Elasticity in the AlPdMn Icosahedral Phase

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The diffuse scattering located close to Bragg reflections has been measured on a single grain of the AlPdMn icosahedral phase using elastic neutron scattering. This diffuse scattering is mainly due to phason disorder. The intensity distribution and anisotropic shape can be reproduced in the framework of the elastic theory of quasicrystals using only the two phason elastic constants whose ratio is found to be equal to -0.5.

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The atomic structure and physical properties of quasicrystals have been the focus of many experiments since the discovery of the "perfect" quasicrystal in the AlCuFe [1] and AlPdMn [2] systems. These quasicrystals are characterized by well defined long-range quasiperiodic order with resolution-limited Bragg peaks [3–5], similar to what is obtained with the best metallic alloys. The quality of these grains is such that dynamical diffraction can take place on a macroscopic scale [6]. Although the AlPdMn icosahedral phase presents very good long-range quasiperiodic order, it was shown recently that some diffuse scattering is located close to the Bragg reflections [7].

Structural descriptions of icosahedral alloys are most conveniently done in a higher dimensional space where the structure is periodic. Here, the atomic structure of icosahedral phases is described by a six-dimensional cubic lattice that may be decomposed into two subspaces: $E_{\|}$, the physical space, and $E_{\perp}$, the complementary or perpendicular space (see Ref. [8] for an introduction). The six-dimensional lattice is decorated by three-dimensional objects, called atomic surfaces, lying in the perpendicular space.

Previously, we [7] found that the integrated intensity of the diffuse scattering was scaled as $I[1 - \exp(-B_{\perp} Q_{\perp}^2)]$, where I is the Bragg peak intensity, $Q_{\perp}$ the perpendicular component of the reciprocal vector, and $B_{\perp}$ a perpendicular Debye-Waller factor. This is what is expected from bounded fluctuations of the atomic surfaces in the perpendicular direction. The rms fluctuations of the atomic surfaces were found to be about 2 Å, which has to be compared to 20 Å, the average diameter of atomic surfaces. Such fluctuations in the perpendicular direction lead to a distribution of "phason" defects. A study of the shape of the diffuse scattering will give information about the spatial distribution of the phason defects.

We report, in this paper, measurements of the intensity distribution and shape anisotropy of the diffuse scattering located close to the Bragg reflections. As described in detail below, most of the diffuse scattering is due to phason disorder and can be interpreted within the framework of the hydrodynamic theory of quasicrystals.

Phason degrees of freedom arise as a consequence of the noncrystallographic symmetry of quasicrystals [9]. In the simplest case, a phason defect corresponds to an atomic jump from one position to another one nearby having a similar local environment. Such atomic jumps have been observed in icosahedral AlCuFe above 600 °C [10]. A distribution of phason strain leads to a broadening of Bragg reflections [9,11]. Bounded random fluctuations of the atomic surfaces in the perpendicular subspace do not destroy the long-range order, i.e., there are still Bragg peaks, with a reduced intensity, and some diffuse scattering shows up. This is the case for random tiling models in which phason fluctuations lead to a configurational entropy [12,13]. It is conjectured that in a random-tiling-like phase the entropy density varies quadratically as a function of the phason strain [12,13]. This was demonstrated in the case of the square and triangle tilings [14] and checked numerically on two-dimensional [15] and three-dimensional [16] models. Even if a quasicrystal is energetically stabilized representing a ground state, it was shown numerically that above some critical temperature the system is in a random-tiling-like phase or unlocked phase [17]. Because of the squared gradient dependence of the entropy, the elasticity theory of quasicrystals can be formulated in the long wavelength or hydrodynamic limit [9,18]. For icosahedral quasicrystals, the elastic free energy may be written as the sum of three terms: a phonon term depending on the phonon strain tensor, a phason term depending on the phason strain tensor, and a coupling term which couples phonon and phason distortion. Group theoretical arguments show that the free energy depends on five independent elastic constants as $F = F_{\mathrm{phon}}(\lambda + \mu) + F_{\mathrm{phas}}(K_1, K_2) + F_{\mathrm{coup}}(K_3)$, where λ and μ are the Lamé coefficients, K_1 and K_2 the phason elastic constants, and K_3 the phonon-phason coupling term [9,13]. In such a framework the diffuse scattering due to phonon or phason disorder can be computed [19].

In the present experiment we used a 2 cm^3 single grain grown by the Czochralski method [20]. It had an overall mosaicity smaller than 0.05° and a chemical composition given by $Al_{68.2}Pd_{22.8}Mn_9$. Measurements were carried out on the 4F2 triple axis located on the cold source of the Orphée reactor (Laboratoire Léon Brillouin, Saclay). All scans were done with an incident wave vector equal to 1.64 $Å^{-1}$ and a double graphite filter to suppress higher harmonics. In this configuration, the energy resolution is 0.055 THz, and the resolution in reciprocal space is on the order of 0.01 $Å^{-1}$ with an almost circular shape in the diffracting plane. The high energy resolution allowed the separation of the usual thermal diffuse scattering due to phonons, from the elastic diffuse scattering. Tests carried out by masking part of the sample showed that the diffuse scattering arises from all the sample.

One of the main difficulties in studying the diffuse scattering located near strong Bragg reflections is the large intensity difference that is encountered between the Bragg peak and diffuse scattering (their ratio is of the order of 10^4). A precise knowledge of the instrumental resolution is thus necessary if one desires to disentangle the Bragg peak contribution from the diffuse scattering. Various tests on perfect crystals and on different reflections of the quasicrystal showed that the resolution function is Gaussian with the contribution from the Bragg peak becoming negligible for a distance $q > 0.04$ $Å^{-1}$ from the Bragg point. Moreover, for this wave vector, all phonons are excluded from the elastic energy window. The diffuse scattering has been measured at room temperature, around various points in a twofold scattering plane (Fig. 1). Results are presented for q values larger than 0.04 $Å^{-1}$.

Within the framework of the hydrodynamic theory, Jaric and Nelson [19] describe a way of computing the diffuse scattering due to thermalized or quenched-in phason (and phonon) disorder. In the present measurement at room temperature, phason disorder is likely to be frozen in. However, they showed [19] that the diffuse scattering may be computed in a manner similar to what is done for equilibrium phason disorder. Let us consider that only phason disorder contributes to the diffuse scattering (i.e., $K_3 = 0$ and there is no contribution from elastic phonon distortions). If $\mathbf{Q}$ is a reciprocal lattice vector, with components $\mathbf{Q}_{\parallel}$ and $\mathbf{Q}_{\perp}$ in parallel and perpendicular space, the diffuse scattering intensity measured at a position $\mathbf{q}$ away from this Bragg peak can be derived from the elasticity theory as [19]

$$I(\mathbf{Q}_{\parallel} + \mathbf{q}) = \mathbf{Q}_{\perp} C^{-1} \mathbf{Q}_{\perp} I_{\mathrm{Bragg}}\,, \qquad (1)$$

where I_{Bragg} is the Bragg peak intensity and C is the phason part of the hydrodynamic matrix which depends on $\mathbf{q}$ and the two phason elastic constants K_1 and K_2. From this relation one can deduce the following characteristics for the diffuse scattering: (i) along a given direction $\mathbf{q}$ it decays as $1/q^2$; (ii) for Bragg reflections along the same direction in reciprocal space the diffuse scattering scales as $I_{\mathrm{Bragg}} Q_{\perp}^2$; and (iii) the overall icosahedral symmetry of the diffraction pattern is preserved.

Figure 2 shows transverse scans taken around the fivefold reflections A and B (Fig. 1) with $Q_{\perp}$ values equal to 0.7 and 0.17 $Å^{-1}$, respectively. The solid line is a fit of the $1/q^2$ decay to the data. For the B reflection, where there is a large diffuse scattering intensity, measurements are reported from 0.04 to 0.6 $Å^{-1}$, corresponding to more than 2 orders of magnitude in intensity. This $1/q^2$ decay has been found for all measured reflections and for any direction in reciprocal space. In the same figure

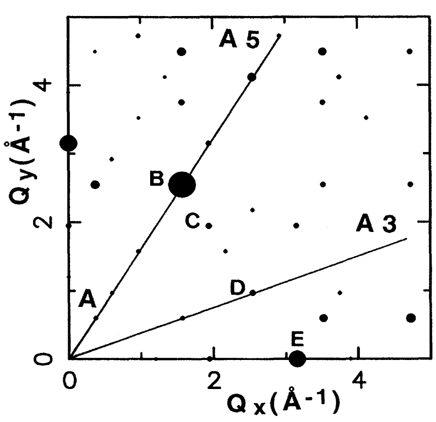

FIG. 1. Twofold scattering plane of the i-AlPdMn phase. The area of the spot is proportional to the intensity of the reflection. The diffuse scattering has been measured, in this plane, around the labeled reflections. $A5$ and $A3$ denote fivefold and threefold symmetry axes.

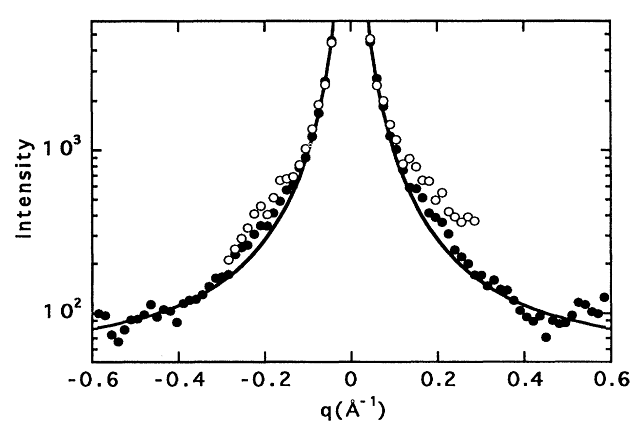

FIG. 2. Transverse elastic scans taken around the reflections A (open circle) and B (full circle), lying along a fivefold axis. The solid line is the $1/q^2$ decay. The diffuse scattering of reflection A has been renormalized as described in the text. Note the logarithmic scale for intensity.

the diffuse scattering measured around the A reflection has been renormalized to the data for the B reflection in order to account for the $I_{\mathrm{Bragg}} Q_\perp^2$ dependence. As can be seen in Fig. 2, both curves superimpose quite well, demonstrating the $Q_\perp$ dependence of the diffuse scattering. Similar rescaling for reflections along the twofold axis gave a rather good agreement.

Figures 3(a)–3(d) shows isointensity contours of the diffuse scattering measured around the Bragg reflections B, C, D, and E in a twofold scattering plane. Horizontal and vertical axes Q_x and Q_y are parallel to a twofold axis. In the four panels, contours are in the range 0 to 1000 counts, allowing a direct quantitative comparison of the diffuse scattering intensity. Note that the diffuse scattering at each reciprocal lattice point has a very different shape, demonstrating that it is indeed due to the sample and does not arise from instrumental resolution or mosaic effects. It might seem surprising that the diffuse scattering around reflections B and C [Figs. 3(a) and 3(b)] have such a different anisotropy. Indeed these reflections have almost the same vector $\mathbf{Q}_\parallel$ (Fig. 1). However, their perpendicular components are almost orthogonal, reflection B having perpendicular space coordinates of (0.14, −0.085), while reflection C has coordinates (−0.45, −0.45). This is, once again, a clear demonstration that the diffuse scattering is related to phason disorder. Note also the large difference in diffuse scattering intensity between reflections C and D [Figs. 3(b) and 3(c)] although these reflections have the same Bragg peak intensity. This is because reflection C has a $Q_\perp$ value about 3 times that of reflection D. Finally, Fig. 3(d) presents the diffuse scattering around the twofold reflection E. In the icosahedral phase there is a mirror plane along the $Q_y = 0$ direction. As can be seen, the diffuse scattering obeys this symmetry element as expected from theory.

It should be possible to reproduce the anisotropic shape of the diffuse scattering using relation (1). The only adjustable parameter is the ratio K_2/K_1 of two phason elastic constants. Figures 3(e)–3(h) show the diffuse scattering shapes predicted by the model when the ratio K_2/K_1 is equal to −0.52. The agreement between the model and the experiment is surprisingly good. The comparison can be made more quantitative for scans along a given direction by fitting the $1/q^2$ decay. The overall agreement is satisfactory [21] and can be seen, for instance, by looking at Figs. 3(b), 3(c), 3(f), and 3(g). The strong diminution of diffuse scattering when going from reflection C to D is well reproduced. To go further in the analysis would certainly require the introduction of phonon elastic distortions and of the phason-phonon coupling term.

It is interesting to compare the experimental ratio of the phason elastic constant with the onset of hydrodynamic instability calculated by Ishii [22] and Widom [23] (see also [13]). When the ratio K_2/K_1 is equal to −0.75 the matrix inverse in expression (1) diverges, leading to a vanishing of the Bragg reflections. When approaching this instability point, the computed diffuse scattering

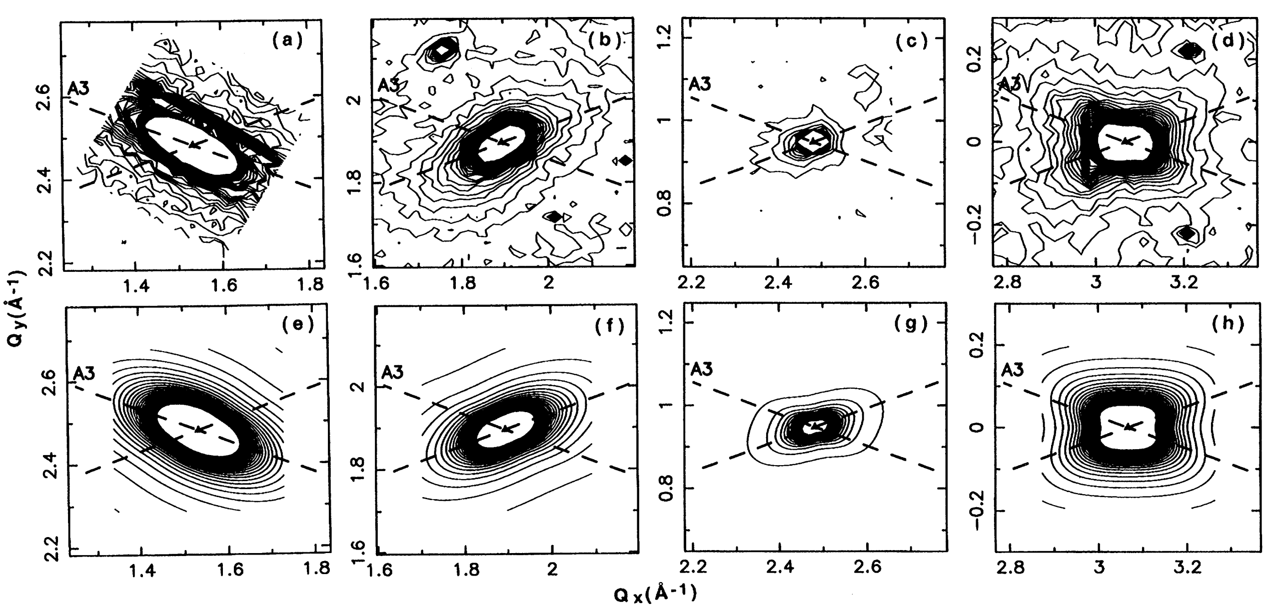

FIG. 3. Comparison of the diffuse scattering measured around Bragg reflections B, C, D, and E (a)–(d) and computed with the phason elastic constant K_2/K_1 equal to −0.52 (e)–(h). The figures present isointensity contours from 0 to 1000 counts. The model has been put on the same relative scale. Both the anisotropy and the intensity of the diffuse scattering are reproduced by the model. The dashed lines $A3$ are parallel to a threefold axis.

shows strong streaks along the threefold axes [22,23]. Note that recently a modulated icosahedral phase was discovered for an alloy composition very close to that of the quasicrystal [24]. Around each Bragg reflection of the icosahedral lattice, there is a star of satellite reflections lying along the threefold axis, precisely what is expected from the stability argument. This indicates either a strong dependence of the ratio K_2/K_1 with the chemical composition, similarly to what has been conjectured in the AlCuFe system [4,13], or the occurrence of a first order transition. In the first case, one would have a "softening" of the phason elastic constants when going towards the chemical composition of the modulated phase. Lowering the temperature would lead to a transition from an icosahedral phase to a threefold modulated phase. For the present sample, the temperature transition would be too low for the transition to be achieved kinetically (say, for instance, $T_c = 500\,^\circ\mathrm{C}$). The observed phason disorder, at room temperature, would thus result from a freezing of pretransitional phason fluctuations.

Another possibility is the case where the quasicrystal is energetically stabilized. At sufficiently high temperature the quasicrystal is in a random-tiling-like phase. In the low temperature region, the free energy is no longer quadratic in the phason variable [13], and the diffuse scattering has not yet been computed. Our results would suggest that we are still in a random-tiling-like phase at room temperature, which might seem surprising; nevertheless, both scenarios predict a very different temperature dependence for the diffuse scattering. Such experimental studies are in progress.

In conclusion, we have studied the diffuse scattering located close to the Bragg reflections in a perfect icosahedral AlPdMn phase. Its anisotropic shape and intensity dependence are reproduced by considering only the two phason elastic constants K_2 and K_1 whose ratio is equal to -0.5. The present results are in agreement with squared gradient behavior of the free energy as a function of the phason strain, as proposed in the random tiling picture of quasicrystals. The phason disorder corresponds to the superposition of long wavelength fluctuations (between 10 and 150 Å) in the sample, leading to correlated phason jumps. This is of importance for the understanding of the formation of quasicrystal and modeling of their atomic structure.

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