Dynamics of Phason Fluctuations in the *i*-AlPdMn Quasicrystal

S. Francoual,[1,2] F. Livet,[1] M. de Boissieu,[1,*] F. Yakhou,[3] F. Bley,[1] A. Létoublon,[4] R. Caudron,[5] and J. Gastaldi[6]

[1]*Laboratoire de Thermodynamique et de Physico-Chimie Métallurgique, UMR CNRS 5614, ENSEEG-INPG, BP 75, 38402 Saint Martin d'Hères Cedex, France*

[2]*Institut Laue Langevin, BP 156, 38042 Grenoble Cedex 9, France*

[3]*ESRF, BP 220, 38043 Grenoble Cedex, France*

[4]*CEA-Grenoble, DRFMC, SP2M, NRS, 17 avenue des Martyrs, 38054 Grenoble Cedex 9, France*

[5]*Laboratoire d'Etude des Microstructures, UMR CNRS 104, ONERA, BP 72 92230 Chatillon, and Laboratoire Léon Brillouin, CEA Saclay, 91191 Gif sur Yvette Cedex, France*

[6]*CRMC2, CNRS, Campus de Luminy, case 913, 13288 Marseille cedex 9, France*

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We report on the study of the dynamics of long wavelength phason fluctuations in the i-AlPdMn icosahedral phase using coherent x-ray scattering. When measured with a coherent x-ray beam, the diffuse intensity due to phasons presents strong fluctuations or speckles pattern. From room temperature to 500 °C the speckle pattern is time independent. At 650 °C the time correlation of the speckle pattern exhibits an exponential time decay, from which a characteristic time τ is extracted. We find that τ is proportional to the square of the phason wavelength, which demonstrates that phasons are collective diffusive modes in quasicrystals, in agreement with theoretical predictions.

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Quasicrystals are long range ordered materials with a symmetry incompatible with translation invariance. Their diffraction pattern exhibits sharp Bragg reflections, with for instance fivefold symmetry in the case of icosahedral phases. In a few systems, quasicrystals can now be obtained as large single grains, with a structural quality similar to the best metallic alloys (see Ref. [1] for an introduction).

Similarly to other aperiodic crystals, quasiperiodicity induces new degrees of freedom and phason modes. This can be understood in the high dimensional description of quasicrystal and aperiodic crystals. In the case of the icosahedral symmetry, the quasicrystalline structure can be embedded in a six-dimensional (6D) space which decomposes in two orthogonal 3D subspaces: the physical space and the perpendicular or complementary space. The periodic 6D lattice is decorated with 3D objects (atomic surfaces) and the 3D quasicrystalline structure is obtained as a section of the periodic decorated lattice. A rigid translation of the cut space along the perpendicular direction will lead to a structure which is not identical, but which is energetically undistinguishable from the previous one. As a rigid translation in physical space leads to three acoustic phonon modes, the invariance of the system free energy under a translation of the cut space in the perpendicular direction leads to phason modes [2]. In a simplified picture, these can be viewed as sin waves propagating in the physical space with a polarization in the perpendicular space.

Aperiodic crystals are usually grouped in three different classes: incommensurately modulated phases, incommensurate composites, and quasicrystals [3]. The nature of long wavelength phason excitation and its atomic realization is different for each class. In incommensurate displacive modulated phases, and when the modulation is a smooth function, a phason wave results in continuous and small atomic displacements. In this case phason modes are collective propagative excitations, and can be measured by inelastic neutron scattering similarly to acoustic phonons. Such collective propagative phason modes have been observed in a few systems: most of the time they are damped excitations with a finite lifetime (see Ref. [4] for a review).

For quasicrystals, because of discontinuities in the atomic surfaces, phason waves result in atomic rearrangements called atomic jumps. Indeed a local distortion of the cut space induces an atomic jump from one position to another one nearby sharing the same local environment. In the case of i-AlPdMn phases, characteristic distances between such sites are of the order of 0.1 nm. Long wavelength phason fluctuations (or phason modes [5]) thus result in correlated atomic jumps, and are predicted to be collective diffusive excitations [2,6]. This means that a given phason wave should decay exponentially with time, with a characteristic time proportional to λ^2, where λ is the phason wavelength. Such behavior has been observed in random tiling simulations [7,8].

Experimentally, uncorrelated local atomic jumps have been observed by quasielastic neutron scattering at high temperature [9], and more recently by high angular dark field scanning transmission electron microscopy (TEM) [10]. Recently, *in situ* high resolution TEM images taken in the decagonal AlCuCo, have evidenced jumps of atom columns, with a time scale of the order 10 s [11].

In this Letter we present the first measurement of collective phason dynamics in quasicrystals, using coherent x-ray scattering.

Long wavelength phason fluctuations give rise to diffuse scattering tails close to Bragg peaks in a way similar that acoustic phonons lead to thermal diffuse scattering (TDS). The diffuse scattering intensity distribution can be computed using the theory of generalized elasticity of icosahedral phases which is essentially that of phonon and phason fluctuations in the long wavelength or hydrodynamical limit [12]. In this framework, five elastic constants are defined, the two phonon Lamé coefficients, the two phason elastic constants $K1$ and $K2$ and a phonon-phason coupling term $K3$. Neutron and x-ray diffuse scattering experiments in the i-Al-Pd-Mn quasicrystal have revealed characteristic anisotropies which can be explained considering only the $K1$ and $K2$ phason elastic constants [13–15], the TDS contribution being negligible [15]. From the temperature dependence of the diffuse scattering it has been suggested that it is related to pretransitional fluctuations, phason fluctuations being frozen in at room temperature [16,17]. The intensity distribution of the diffuse scattering $S(\mathbf{Q} + \mathbf{q})$, where $\mathbf{Q}$ is the Bragg peak position, is thus a signature of a phason fluctuation with wave vector $\mathbf{q}$.

We have studied phason dynamics by means of coherent x-ray scattering and time correlation spectroscopy. This technique [18–20] allows one to measure slow dynamics (10^{-3} to 1000 s) at the atomic scale. When a coherent beam is used to measure the diffuse scattering, the $\mathbf{q}$ dependence of the intensity does not show any longer a smooth variation (resulting from an ensemble average) but rather displays strong intensity fluctuations called speckle pattern. Any time dependence of phason fluctuations will show up in the time dependence of the speckle pattern measured at a position $S(\mathbf{Q} + \mathbf{q})$. More precisely, we compute the intensity correlation function defined as

$$F_{\mathrm{cor}}(\mathbf{q}, t) = \langle I(\mathbf{q}, t')I(\mathbf{q}, t + t')\rangle_{t'} / \langle I(\mathbf{q}, t')\rangle^2_{t'}. \qquad (1)$$

We have the relation $F_{\mathrm{cor}}(\mathbf{q}, t) = [1 + \beta g(\mathbf{q}, t)]$ where β is the partial coherence of the beam and $g(\mathbf{q}, t)$ is the time dependence of the phason fluctuation.

In the present experiment we used a single crystal ($3 \times 3 \times 1$ mm^3) oriented with a fivefold axis perpendicular to the surface, extracted from a large single grain of the i-AlPdMn phase grown by the Czochralski method [21]. It was annealed for 8 d at 780 °C under ultrahigh vacuum and slowly cooled down to room temperature. After annealing, the sample surface displayed flat terraces, with typical sizes of the order 0.1 mm. The x-ray beam was set inside the terraces to avoid parasitic interferences effects and we worked in reflection geometry. The sample was heated up in a furnace under secondary vacuum (10^{-5} mbar).

The coherent beam (energy 8 keV) was produced by the focusing optics of the ID20 beam line (ESRF) following the setup described in [22]. The coherence of the beam was defined by a 10 μm pinhole located just before the sample. The speckle pattern was recorded on a directly illuminated 2D CCD camera located at 1.85 m from the sample position. It acted as a 2D photon detector, using a droplet algorithm [23]. The partial coherence of the setup β, was found equal to 0.05 and 0.03 for low and high angle Bragg reflections.

The fivefold reflection with N/M indices 7/11 was set in diffraction condition (indexing is carried out following Ref. [24]) . As previously observed, the rocking curve around this reflection was extremely narrow, with a full width at half maximum (FWHM) equal to 0.005°, illustrating the high sample quality. Diffuse scattering measurements were carried out by rotating the sample θ angle. With the sample orientation we used, the central position of the CCD corresponds to a phason wave vector $\mathbf{q}$ propagating along the $(\tau, -1, 0)$ direction, i.e., perpendicular to the fivefold axis. Measurements were performed for different temperatures and $\mathbf{q}$ values. To follow the intensity correlation time dependence, a series of 500 images with a time acquisition between 1 and 5 s were recorded. The stability of the entire setup allowed measuring correlation times from 2 to 1000 s.

In agreement with simulations, the observed diffuse scattering on the CCD exhibits a weak anisotropy with an almost ellipsoidal shape slightly elongated along the vertical axis of the CCD. The counting rate on a single pixel was too low to get good statistics, the intensity correlation function of Eq. (1) was thus calculated by averaging on successive circular shells centered on the $(\tau, -1, 0)$ axis. This allowed obtaining several q values for each position of the CCD. In the following we present results for q values close enough to the $(\tau, -1, 0)$ direction so that they are representative of phason fluctuations propagating along this direction. This direction is the one of maximum diffuse intensity which is dominated by the slowest mode.

At room temperature and for temperatures up to 500 °C, the intensity correlation function does not show any time dependence. As shown in Fig. 1 the function is constant and equal to $1 + \beta$.

Above 500 °C, the autocorrelation function did show a slow time evolution. Results obtained at 650 °C, and for two different q values of the phason wave vector are displayed in Fig. 2. A reasonable fit to the data is achieved using an exponential time decay $g(q, t) = \exp[-t/\tau(q)]$ from which a characteristic time is deduced [25]. As shown in Fig. 2, the time decay is decreasing as q is increasing. This is qualitatively what is expected for a diffusive process, since τ varies as q^{-2} in this case. A better estimate of this dependence is illustrated in Fig. 3 , where the characteristic time τ for various values of q is plotted as a function of q^{-2}. Although data are scattered, there is a clear linear dependence. From this a phason diffusive constant D_{phason}, defined as $\lambda^2 = D_{\mathrm{phason}}\tau$, where λ is the phason excitation wavelength, can be evaluated and is found to be equal to $1.5 \times$

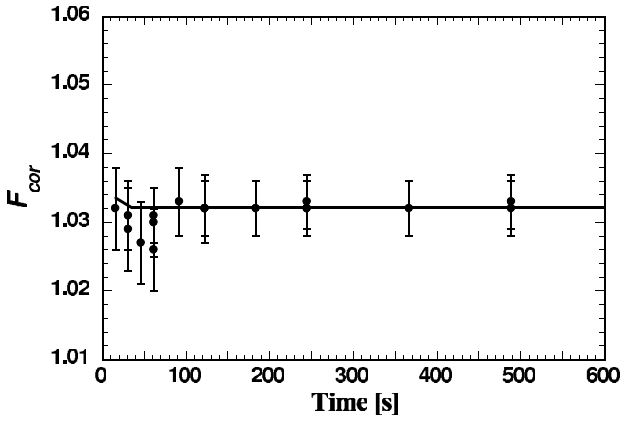

FIG. 1. Time dependence of the intensity correlation function measured at 400 °C for a phason wave vector equal to 0.17 nm^{-1}.

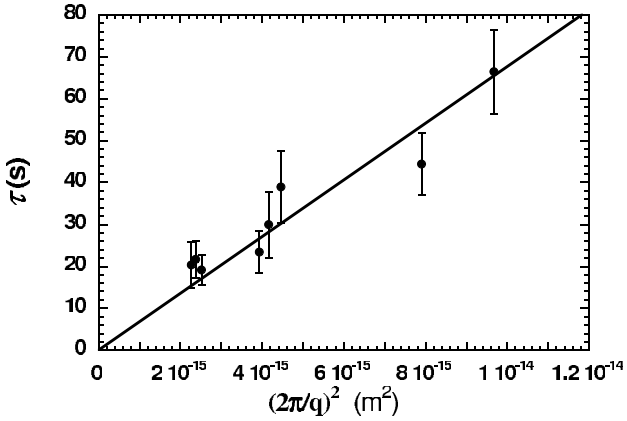

FIG. 3. Evolution of the characteristic time τ as a function of λ^2, measured at 650 °C. There is a linear dependence from which the phason diffusion constant can be extracted.

10^{-16} m^2 s^{-1}. Note that this value is estimated from data corresponding to relatively large phason wavelengths between 50 and 100 nm.

A few measurements were also carried out at 600 °C. At this temperature phason fluctuations are much slower. An estimate of the phason diffusive constant was difficult, because characteristic times are now close to the maximum value which can be measured. Nevertheless, we find that characteristic times are between 5 to 10 times larger than at 650 °C. From these measurements it is obviously not possible to extract an Arrhenius plot. Nevertheless, if we make the assumption that phason fluctuations are energy activated processes, we can estimate the activation energy to be of the order $3(\pm 1)$ eV.

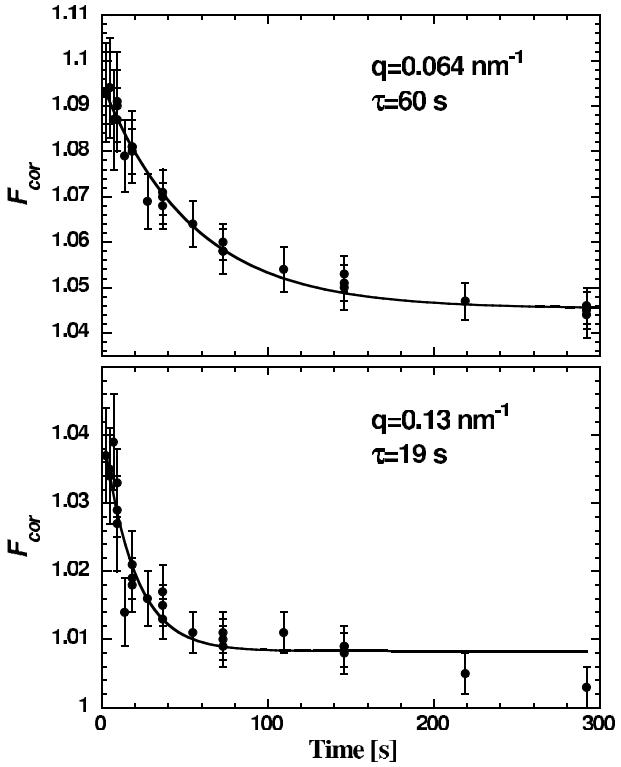

FIG. 2. Time dependence of the intensity correlation function measured at 650 °C for two different phason wave vectors propagating along the $(\tau, -1, 0)$ direction. The solid line is an exponential time decay fit to the data. Corresponding q and characteristic time τ values are indicated on the different panels.

We found that a phason with a 100 nm wavelength has a characteristic time decay of the order 60 s at 650 °C and 5 times larger at 600 °C. Since phason fluctuations can be regarded as correlated atomic jumps, the atomic diffusion process will tend to suppress them. Recently atomic diffusion in the i-AlPdMn phase has been carefully investigated. Above 450 °C, diffusion coefficients for Pd and Mn atoms are very similar to what is known in periodic intermetallic alloys, with a vacancy mediated diffusion. In the i-AlPdMn phase, Mn atoms are slow diffusers with a diffusion coefficient D_{Mn} equal to about 10^{-14} m^2 s^{-1} at 650 °C, and an activation energy of the order 2 eV [26]. From this we can estimate that a Mn atom will span an average distance equal to eight phason wavelengths during the corresponding phason characteristic time. Both diffusion constants (Mn and phason) are thus consistent.

Our results are in agreement with mechanical spectroscopy experiments carried out on oriented large single grains of the i-AlPdMn phase [27]. By measuring the internal friction, Feuerbacher *et al.* have observed a signal corresponding to collective atomic motion and an activation energy of 4 eV. It was interpreted as an evidence for collective phason fluctuations.

Phason fluctuations are believed to play an important role in the growth process and in the mechanical properties of quasicrystals. In the i-AlPdMn phase, plastic deformation is possible through dislocations movements for temperatures larger than 600 °C. Because of the quasiperiodic long range order, the distortion field around a dislocation contains an elastic phonon part and a phason

one. When a dislocation is moving, a highly localized phason strain (named phason wall) is left behind (see Ref. [28] for a recent review). *In situ* high resolution TEM has shown that these phason walls anneal out very rapidly above 650 °C [29]. This is in agreement with the time scale found in the present study. Indeed phason fluctuations will "relax" the highly localiszed phason strain on time scale of the order a few tens of seconds, thus preventing the observation of phason walls at high temperature.

The phason diffusion constant was measured along a single direction, perpendicular to a fivefold axis. Since the phason diffuse scattering intensity displays strong anisotropies, we also expect a phason diffusion constant anisotropy. Roughly speaking, since the $K2/K1$ ratio is close to the threefold instability, we expect to have a small diffusion constant for threefold phason modes and a larger one for fivefold and twofold ones. In some sense, this is equivalent to the acoustic phonon dispersion curve for which longitudinal sound velocity is larger than the transverse one. In the present case, Fig. 3 can be viewed as a phason dispersion curve. This is similar to what is observed in order-disorder incommensurate systems [30].

In conclusion, we have studied phason dynamics in the i-AlPdMn phase by coherent x-ray scattering and photon correlation spectroscopy. By measuring the time dependence of the speckle pattern observed in the phason diffuse scattering, we can determine the time dependence of equilibrium long wavelength phason fluctuations at various temperatures. Slow time dependence is observed for temperatures larger than 500 °C. At 650 °C phason fluctuations decay exponentially with time. The characteristic time is of the order 60 s for phason fluctuations propagating along the $(\tau, -1, 0)$ direction and having a wavelength of 100 nm. We find that the characteristic decay time is proportional to the square of the phason wavelength. This demonstrates that phason fluctuations are collective diffusive excitations, as predicted by theory. The phason diffusive constant D_{phason}, is found to be equal to 1.5×10^{-16} m^2 s^{-1}. At 600 °C the phason diffusive constant is 5 times smaller, i.e., phason fluctuations characteristic time decays are 5 times larger. This corresponds to an activation energy of phason fluctuation of the order 3 eV.

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*Electronic address: boissieu@ltpcm.inpg.fr

[1] C. Janot, *Quasicrystals: A Primer* (Oxford Science Publication, Oxford, 1992).
[2] P. A Kalugin, A. Y. Kitayev, and L. S. Levitov, J. Phys. (Paris), Lett., **46**, L601 (1985); P. Bak, Phys. Rev. Lett. **54**, 1517 (1985); D. Levine *et al.* Phys. Rev. Lett. **54**, 1520 (1985).
[3] T. Janssen, O. Radulescu, and A. N. Rubtsov, Eur. Phys. J. B **29**, 85 (2002).
[4] R. Currat and T. Janssen, Solid State Phys. **41**, 201 (1988).
[5] The name phason has been used with at least three different meanings in the quasicrystalline community (see [3] for a complete discussion on this point). A phason jump refers to the atomic jump which results from a local cut space distortion. A phason strain corresponds to a slope change of the cut space: it produces Bragg peak shift or broadening. Finally phason modes are similar to phason excitations discussed in aperiodic crystal. To avoid any confusion we call them (long wavelength) phason fluctuations.
[6] T. C. Lubensky, S. Ramaswamy, and J. Toner, Phys. Rev. B **32**, 7444 (1985).
[7] L. H. Tang, Phys. Rev. Lett. **64**, 2390 (1990).
[8] L. J. Shaw, V. Elser, and C. L. Henley, Phys. Rev. B **43**, 3423 (1991).
[9] G. Coddens *et al.*, Europhys. Lett. **23**, 33 (1993); G. Coddens *et al.*, Phys. Rev. Lett. **83**, 3226 (1999).
[10] E. Abe, S. J. Penycook, and A. P. Tsai, Nature (London) **421**, 347 (2003).
[11] K. Edagawa, K. Suzuki, and S. Takeuchi, Phys. Rev. Lett., **85**, 1674 (2000).
[12] M. V. Jaric and D. R. Nelson, Phys. Rev. B**37**, 4458 (1988); Y. Ishii, Phys. Rev. B **45**, 5228 (1992); M. Widom, Philos. Mag. Lett. **64**, 97 (1991).
[13] M. de Boissieu *et al.*, Phys. Rev. Lett., **75**, 89 (1995).
[14] M. Capitan *et al.* Phys. Rev. B**60**, 6398 (1999).
[15] A. Létoublon *et al.*, Philos. Mag. Lett. **81**, 273 (2001).
[16] M. Boudard *et al.*, Europhys. Lett. **33**, 199 (1996).
[17] M. de Boissieu *et al.*, Philos. Mag. A **78**, 305 (1998).
[18] M. Sutton *et al.*, Nature (London) **352**, 608 (1991).
[19] *Dynamic Light Scattering*, edited by W. Brown (Clarendon Press, Oxford, 1993).
[20] S. Brauer *et al.* Phys. Rev. Lett. **74**, 2010 (1995).
[21] M. Boudard *et al.*, Philos. Mag. Lett. **71**, 11 (1995).
[22] A. Létoublon *et al.* Europhys. Lett. **54**, 753 (2001).
[23] F. Livet *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. A **451**, 596 (2000).
[24] J. W. Cahn, D. Shechtman, and D. Gratias, J. Mater. Res. **1**, 13 (1986).
[25] For a given phason wave vector there are three modes with different polarization and a priori three different time constants. However, with the present experimental geometry, the slowest mode gives the main contribution to the signal so that only one decay time can be considered.
[26] Th. Zumkley *et al.*, Phys. Rev. B **54**, R6815 (1996); R. Blüher *et al.* Phys. Rev. Lett., **80**, 1014 (1998).
[27] M. Feuerbacher *et al.*, Philos. Mag. Lett. **74**, 81 (1996).
[28] P. Guyot *et al.*, Scr. Mater. **49**, 1 (2003).
[29] U. Messerschmidt and M. Bartsch, Scr. Mater. **49**, 33 (2003).
[30] D. Durand *et al.*, Phys. Rev. B **43**, 10 690 (1991).