Atomic (phason) hopping in perfect icosahedral quasicrystals $Al_{70.3}Pd_{21.4}Mn_{8.3}$ by time-of-flight quasielastic neutron scattering

Sandrine Lyonnard and Gerrit Coddens*
Laboratoire Léon Brillouin, F-91191-Gif-sur-Yvette Cedex, France

Yvonne Calvayrac and Denis Gratias
Centre d'Etudes de Chimie Métallurgique, CNRS, F-94407-Vitry Cedex, France

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We report neutron-scattering results on atomic hopping in quasicrystals (QC) in the system Al-Pd-Mn. Two distinct atomic jump times have been observed and studied as a function of temperature. The unusual temperature behavior reported previously for 3.9 Å jumps in Al-Cu-Fe (and interpreted as evidence for assisted hopping) is also found here, such that it seems to be universal. We provide a full discussion of all previous quasi-elastic-scattering results in QC, and show that their most reasonable interpretation is in terms of atomic hopping (phason dynamics). The relation of these data to theoretical predictions of fast diffusion and depinning transitions in the phason dynamics is examined.

I. INTRODUCTION

Many very basic issues in our understanding of quasicrystals seem to depend on the existence or otherwise of phason dynamics. Such phasons correspond to atomic jumps.[1] The existence of phasons is, e.g., a prerequisite for the entropic stabilization scenario for quasicrystals, i.e., the so-called random tiling model.[2] The atomic jumps could lead to a very fast diffusion process such as anticipated by Kalugin and Katz.[3] They could also be a mechanism for the high-temperature transitions between quasicrystals and related phases as have been frequently observed in the past.[4] And finally a good knowledge about the atomic jump vectors, including a determination of the atomic species involved, could provide invaluable information for verifying structural models[5] as worked out, e.g., by Le Lann and Devaud[6] for Cu jumps in the icosahedral and rhombohedral phases of Al-Cu-Fe.

In the present paper we report experimental results on atomic hopping in perfect icosahedral quasicrystals (QC's) in the system Al-Pd-Mn. The technique used is time-of-flight (TOF) quasielastic neutron scattering. Comparable results with the same method were obtained previously[1] (mainly) on $Al_{62}Fe_{12.5}Cu_{25.5}$. They revealed the existence of a Lorentzian quasielastic signal that could be interpreted in terms of atomic jumps. We provide the readers who are unfamiliar with the technique of quasielastic neutron scattering with our argumentation for this interpretation in Sec. II. It will transpire that the strongest indications towards this interpretation are given by the very detailed information that can be obtained from contrast variation in the signal intensity by isotopic substitution. We also point out what kind of information can be obtained from the Q and T dependences of the data. In Sec. III we describe the experiments on Al-Pd-Mn. In Sec. IV we report the results, which are further discussed in Sec. V, and finally in Sec. VI we present our conclusions.

II. INTERPRETATION OF THE QUASIELASTIC SCATTERING

A. Experimental results

In the work cited[1] three important results were reported, viz., the Q dependence, the T dependence, and the isotope dependence of the quasielastic signal. The Q dependence should in principle give information on the local or nonlocal character of the process and on the characteristic distances, the T dependence should give information on the characteristic energies of the process, and the isotope dependence on the atomic species involved.

(1) *The Q dependence of the data.* The width Γ of the quasielastic signal does not change with the momentum transfer Q, while its intensity shows a first maximum at about 1.2 $Å^{-1}$. This suggests that it is a local hopping process that is observed, involving a jump distance of about 3.9 Å. This Q dependence is the opposite of what one would expect to give evidence of the existence of a diffusion process as proposed by Kalugin and Katz,[3] since this would imply an intensity that is constant with Q and a width varying as DQ^2 in the long-wavelength limit (with D the diffusion constant). Nevertheless, diffusion cannot be entirely excluded on the basis of these results. In fact the scattering signal is predominantly coherent. Knaak *et al.*[7] obtained a similar absence of evidence for diffusion in the coherent neutron-scattering signal from the fragile glass-forming *liquid* $(KNO_3)_{0.6}[Ca(NO_3)_2]_{0.4}$. By adding traces of water to the compound the signature of diffusion could be established by the incoherent scattering from the protons. The reason is that coherent scattering probes correlations between configurations instead of the dynamics of individual atoms.[8] If the initial and final configurations are indistinguishable, then the diffusion will not show up in the coherent scattering data. One should also realize that in the model of Kalugin and Katz[3] the relation between the *local* jump rate and the *long-range* diffusion constant is not given. Of course the tiling models used are naive in the sense that they are monoatomic

and that in more realistic quasicrystal models a tile flip could involve a complicated simultaneous move of several atoms. But even in this simplified approach one can easily convince oneself that a large number of tile flips is required to move an atom over a small distance. E.g., in the octagonal tiling model used in Ref. 3 the paths that are particularly effective in moving the atom far away from its initial position require a well-defined sequence of jumps (as has been worked out explicitly in the work of Trub and Trebin[9]). Other jumps can upset the strong order of configurations that is necessary for the development of the sequence, and sidetrack the process by (more or less temporarily) washing out the possibility of some steps on the right path. Moreover, Penrose lattice points with high local symmetry are particularly stable against tile-flip-induced motion, such that the diffusing atom has to avoid such points. This suggests that the diffusion could be slow even if the jump process is fast. A similar conclusion was reached by Gähler[10] based on a computer simulation on a square-triangle tiling. He was able to show that the atomic motion can be strongly enhanced by assistance from vacancy formation.[11] A Monte Carlo study on self-diffusion in random-tiling quasicrystals has been performed recently by Jarić and Sørensen.[12] Rüdinger and Trebin[13] have found that in the (monoatamic) three-dimensional Ammann-Kramer-Penrose tiling the diffusion occurs along two separated sublattices and thus has two components. Unfortunately, no data on self-diffusion by the technique of tracer elements have been reported up to now for the system Al-Cu-Fe. Nakajima *et al.*[14] measured the self-diffusion of ^{54}Mn in an $Al_{72}Pd_{20}Mn_8$ quasicrystal between 723 and 1022 K, and found that it was three orders of magnitude lower than in crystalline Al and two orders of magnitude lower than in the crystalline alloy $Al_{60}Pd_{25}Mn_{15}$. Such experiments are, however, difficult and require further confirmation.

(2) *The temperature dependence* of the signal observed in our previous work[1] is unusual. The quasielastic intensity rises with temperature while the width does not change noticeably within the accuracy of the experiments. As explained previously this could be the signature of the existence of an assisting process in the spirit of the work of Gähler. In fact, the energy of 755 meV extracted from the Arrhenius plot for the intensity is of the right order of magnitude for Al vacancy formation in pure Al.[15]

(3) *The isotope dependence.* Finally it has been shown by isotopic substitution that the signal observed was entirely due to Cu motion.

B. Arguments in favor of hopping

The latter is a very strong result: It excludes (a) explanations of the signal in terms of a density of states of vibrational modes as these should include all types of atoms, (b) a possible magnetic origin of the signal (as it follows the Cu *nuclear* cross section), (c) a possible artifact it (such as, e.g., the presence of hydrogen in the niobium sample holder or a multiphonon effect), and (d) a possible partial melting of the sample (which would also involve all other types of atoms).

Only a well-defined set of phenomena can actually give rise to quasielastic scattering:[16,17] rotational diffusion of molecules, localized jumps of atoms, e.g., in double-well potentials, translational diffusion, paramagnetism, and possibly a low-energy density of states of exotic modes. Due to the previous remark, the only possible conclusion is that the signal stems from atomic jumps, leaving open the question of whether these give rise to long-range translational diffusion or otherwise. For some of the four previously mentioned points (a)–(d) further arguments can be given to strengthen our case but they are less direct and more involved than the one based on the proportionality of the signal with the Cu cross section. E.g., magnetic scattering gives rise to a form factor in the intensity which is very different from the one that was observed in Ref. 1. The temperature dependence of the intensity is also hard to reconcile with the assumption of a vibrational density of states.[18] The perfectly icosahedral phase is not in thermal equilibrium with a liquid such that diffraction data on our samples should have shown if there had been partial melting.[21]

It must be clear that there are no molecules that could rotate in quasicrystals. Even if it is very likely that the existence of clusters plays an important role in the structure and stability of quasicrystals,[22–24] these clusters are not isolated entities that could turn like molecules such as the well-known examples C_{60}, CH_4, and NH_3, for which the intramolecular binding forces are much stronger than the intermolecular forces. The atoms of a cluster in a quasicrystal are in fact as strongly linked to the surrounding atoms as to other atoms of the same cluster and sometimes clusters even overlap. There is also simply no space for rotation. In the model of Katz and Gratias[5] there are configurations of seven Cu atoms distributed according certain rules over the vertices of a dodecahedron, with the other vertices remaining empty. Some of the atomic jumps in this system lead to a change of configuration that could be obtained by a rotation if there were no steric hindrance. However, it is not this rotation that takes physically place, but the atomic jump. In view of this fact, Andreoni[25] called such rotations *pseudorotations*. Admittedly, coherent neutron scattering would not be able to distinguish between these two possibilities, whereas incoherent neutron scattering would.

Of course, all the previous arguments do not mean that our results of Ref. 1 are not surprising. The jump rate observed ($\Gamma = 55\ \mu$eV) is very fast[26] and it is legitimate to ask why no signal was observed from the other types of atoms. It was assumed that this could be for one or more of the following reasons: (1) The Al cross section is too low to make it possible to observe the Al dynamics. (2) The jumps of the Al and Fe atoms could be outside the energy and/or Q windows of the spectrometer used. We can mention here that in the same sample $Al_{62}Fe_{12.5}Cu_{25.5}$ a second, shorter atomic jump, also entirely related to the Cu cross section, has been found now. This work is in progress. Finally, we recently also observed Fe jumps on the time scale of 160 ps ($\Gamma = 4\ \mu$eV) in $Al_{62}Fe_{12.5}Cu_{25.5}$ by a specially designed Mössbauer experiment.[27] The conventional Mössbauer experiment of Janot *et al.*[19] was unable to detect this quasielastic signal directly for reasons of contrast and resolution. Nevertheless, the presence of jumps showed up indirectly as a very rapid anomalous decrease of the elastic intensity above 600 °C. By a beautiful analysis of the transverse Doppler effect in data taken under essentially identical experimental condi-

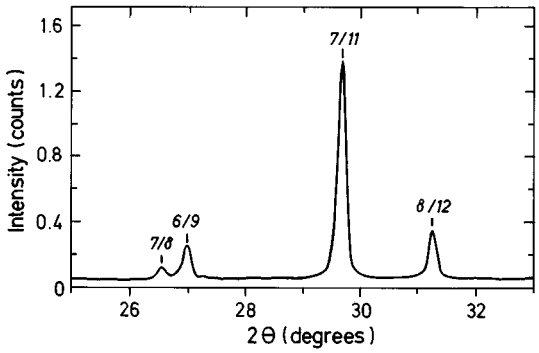

FIG. 1. X-ray-diffraction pattern of the Al-Pd-Mn powder taken with $\lambda = 1.7889$ Å Co $K\alpha$ radiation, and showing the [7/8], [6/9], [7/11], and [8/12] Bragg peaks.

tions de Araújo *et al.* were able to show that this anomaly is in agreement with an interpretation in terms of atomic hopping and not in agreement with an interpretation in terms of vibrations.[28]

III. EXPERIMENTAL PROCEDURES

The nominal composition of our *powder* samples was $Al_{70.3}Pd_{21.4}Mn_{8.3}$. They have been checked for magnetism with a superconducting quantum interference device (SQUID) magnetometer by F. Hippert. Assuming $s=5/2$ these results show that less than 1% of the Mn atoms are magnetic.[29] This is important, as the presence of paramagnetic quasielastic scattering would severely complicate the study of the hopping phenomena.[30] Room-temperature quasielastic-neutron-scattering tests confirm the absence of such a paramagnetic signal (which should have its strongest contribution at $Q=0$ due to the magnetic form factor). A powder diffraction diagram of the sample is shown in Fig. 1. It was taken with $\lambda = 1.7889$ Å Co $K\alpha$ x rays. As discussed previously,[1] it is important, to avoid all-out confusion, that the sample does not show nonintrinsic phason strain.[31]

The quasielastic-neutron-scattering experiments were done on the time-of-flight spectrometer MIBEMOL of the Laboratoire Leon Brillouin in Saclay. The Al-Pd-Mn alloy is a perfect icosahedral quasicrystal; i.e., there are no phase transitions to crystalline approximant states at low temperatures. The experiments were made with about 10 g of Al-Pd-Mn encapsulated in a single-crystal sapphire (Al_2O_3) cylinder of 10 mm inner diameter, 60 mm height, and 0.5 mm thickness, inside a thin niobium container and mounted under vacuum in a furnace allowing a temperature regulation within 1 °C. The use of sapphire is dictated by our concern to preserve the quality of the sample; all other materials react with the sample at high temperature.

The incoming wavelength of the neutron bursts determines the resolution and the Q range of the experiment. A preliminary test with an incoming wavelength $\lambda = 8$ Å, a corresponding elastic resolution ΔE of triangular shape and 40 μeV full width at half maximum (FWHM), and a corresponding $Q_{\max} = 1.49$ Å^{-1} gave no evidence of a quasielastic signal from room temperature (RT) up to 816 °C. It confirmed that one has to go far out in Q space to see the jumps. As a consequence we chose to make the experiment with the lowest values of λ one can reach without too much deterioration of the resolution. High values for the incoming wavelength are also recommended in order to minimize the occurrence of spurious peaks in the data due to stray Bragg scattering (as illustrated below in some of our data). A first series of runs was performed with $\lambda = 5$ Å [$Q_{\max} = 2.342$ Å^{-1} and $\Delta E = 82$ μeV half width at half maximum (HWHM)] and a second one with $\lambda = 4$ Å ($Q_{\max} = 2.927$ Å^{-1} and $\Delta E = 161$ μeV HWHM).

The experimental conditions were the same in both cases. The 332 ^{3}He neutron detectors were positioned in groups at scattering angles $2\theta = 17.5°$, 26.0°, 40.1°, 47.1°, 55.1°, 63.1°, 73.6°, 88.6°, 104.5°, 120°, and 137.4°. (Only the last five groups showed detectable quasielastic scattering in the experiments.) The data were completed by empty-can measurements at high temperature and RT (for background subtraction), and by a vanadium run at RT (for calibration of the detectors efficiencies and the instrument resolution function). When the sample is removed from the beam and inserted again later, its position and orientation are not necessarily perfectly reproducible. One could imagine that this may introduce artifacts due to coherent scattering and texture effects in the niobium and sapphire sample containers. To make sure that our data would not be affected by such spurious effects, in the $\lambda = 4$ Å study all temperature runs were made one after the other without touching the sample. In the 5 Å studies, two sets of data with possibly different orientations for the sample holders can be distinguished, but they were cross-checked by performing the 816 °C scans in both series. Moreover, the empty-can spectrum of the sapphire and niobium containers is clean (i.e., flat) between -5 and 1 meV in the 4 Å runs and between -1.62 and 0.7 meV in the 5 Å runs, such that the quasielastic data cannot be contaminated by coherent or texture effects from the sample holders. The corrected and normalized spectra were analyzed by fitting them with three components convoluted to the resolution function $\mathscr{R}(Q,\omega)$ as follows:

$$\left[A_0(Q)\,\delta(\omega)+A_1(Q)\,\frac{1}{\pi}\,\frac{\Gamma}{\omega^2+\Gamma^2}+A_2(Q,\omega)\right]\otimes\mathscr{R}(Q,\omega). \tag{1}$$

The Dirac measure contribution describes the elastic scattering. $A_2(Q,\omega)\propto e^{-\langle u^2\rangle Q^2}Q^2 g(\omega)n(\omega,T)/\omega^2$ is a Debye term used to take into account the low-energy phonon density of states. This Debye term is essential to render proper account of the phonon background. (While it is flat as an energy distribution, it is not flat as a TOF distribution.) In the previously reported data on the Al-Cu-Fe system the shape of the phonon and multiphonon background could be described by assuming a linear dependence, as the Q range spanned in these experiments was much smaller than in the present ones. (The low-energy phonon density of states follows a Q^2 law such that it is much more intense in the present experiments.) In the $\lambda = 5$ Å data such linear fits still reproduce more or less the right values for the intensities $A_1(Q)$, but the widths Γ are systematically underestimated by a factor of 2. In the $\lambda = 4$ Å data the phonon background

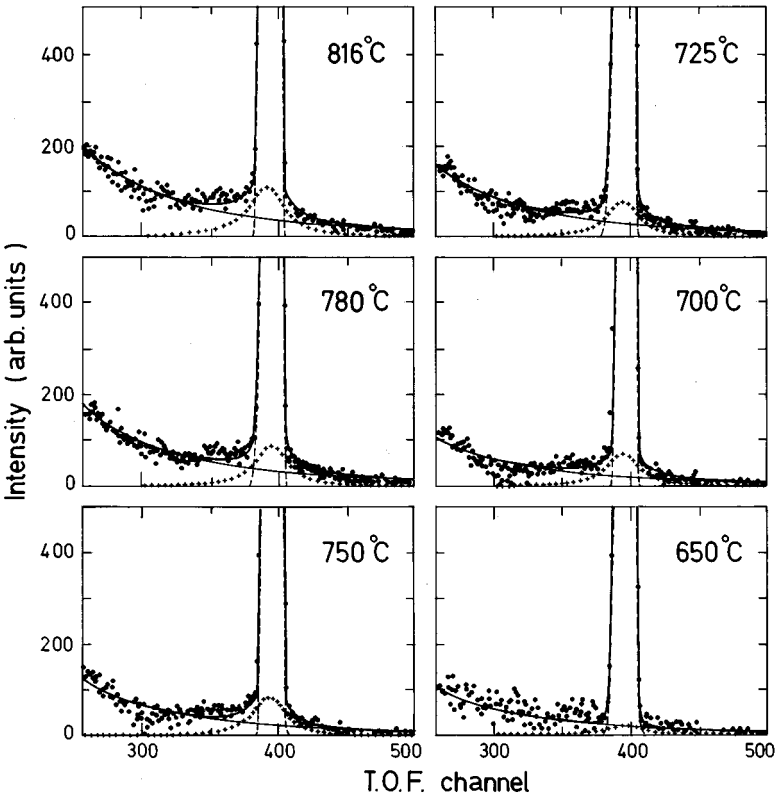

FIG. 2. T dependence at $Q=2.34$ Å^{-1} in the $\lambda=5$ Å data.

is so strong that it can no longer be fitted with a linear dependence. The Lorentzian component with intensity $A_1(Q)$ at the foot of the elastic peak is the signature of the hopping process. It is interpreted in terms of jumps of relaxation time $\tau=\hbar/\Gamma$, where Γ is the HWHM. The intensity of the elastic peak is typically 100 times stronger than the quasielastic one, which makes the data analysis very difficult, especially if the width of the quasielastic signal is not much larger than the resolution.[32] It is necessary to exclude the elastic peak from the fits in order not to bias the value of $A_1(Q)$. Before presenting the experimental results, it is worth making a remark. Unfortunately, no isotopic substitution can be used to improve the intensity of the hopping signal, as was done in the previous TOF experiments on Al-Cu-Fe.[1] In fact, the contrast between the various Pd isotopes is negligible.[33] This also means that we cannot discriminate the atoms and determine which species is jumping.

IV. RESULTS

A. 5 Å data

First, we present the results obtained with $\lambda=5$ Å. The runs were made at RT and 270, 550, 650, 700, 750, and 816 °C.

Figure 2 shows the temperature dependence in the TOF representation after empty-can subtraction and vanadium normalization. It is given for the highest (elastic) Q value, i.e., $Q_{\rm el}=2.34$ Å^{-1} (for the last group of detectors). The quasielastic signal appears around 500 °C and increases regularly until 816 °C. It is polluted on the left hand side by a little bump, the maximum of which is located in channel 355 and does not move with temperature, as evidenced in Figs. 3(a) and 3(b). It corresponds to the interception of the transverse acoustic phonon emanating from the [14/21] Bragg peak. It is located at $Q=2.47$ Å^{-1} and $\hbar\omega=222$ μeV. To eliminate the bump, we tried to subtract the 550 °C data instead of the empty-can measurement, as they show only marginal quasielastic scattering. But the resulting elastic peak signal is negative because of the Debye-Waller factor, and no fit can be done in such bad conditions. We kept thus the conventional method for background correction.

The fitting procedure for this temperature dependence is divided into two steps. First, we exclude the elastic peak and leave all the parameters free to determine the width Γ. Figure 3(f) shows that Γ is constant within the experimental precision. Then we fix Γ to its mean value of 200 μeV, and fit again to find the temperature dependence of the intensity. Figure 3(e) shows an unexpected Arrhenius-like behavior. Its depinning energy is not very well determined by the data, due to the large error bars (related to the small intensities) and to the small temperature range of the Arrhenius plot. Figure 3(e) shows the plot for a slope of 271 meV. For a simple model of jumps in a double-well potential one would expect the quasielastic intensity to be constant with the temperature and the width varying according to $\hbar/\Gamma=\tau=\tau_0\exp[-E_a/kT]$, where E_a is the activation energy.[16] It seems to be contrary to that observed in Figs. 3(e) and 3(f); viz., the width is constant while the intensity varies. To emphasize this contrast between the observed and the expected behavior we will use the terminology *depinning energy* rather than *activation energy* to refer to the slopes of these Arrhenius plots.

This temperature dependence has been interpreted as characteristic of cooperative motion, i.e., assisted hopping. It has already been observed in Al-Cu-Fe, where a depinning energy of 750 meV has been found, excluding *a priori* assis-

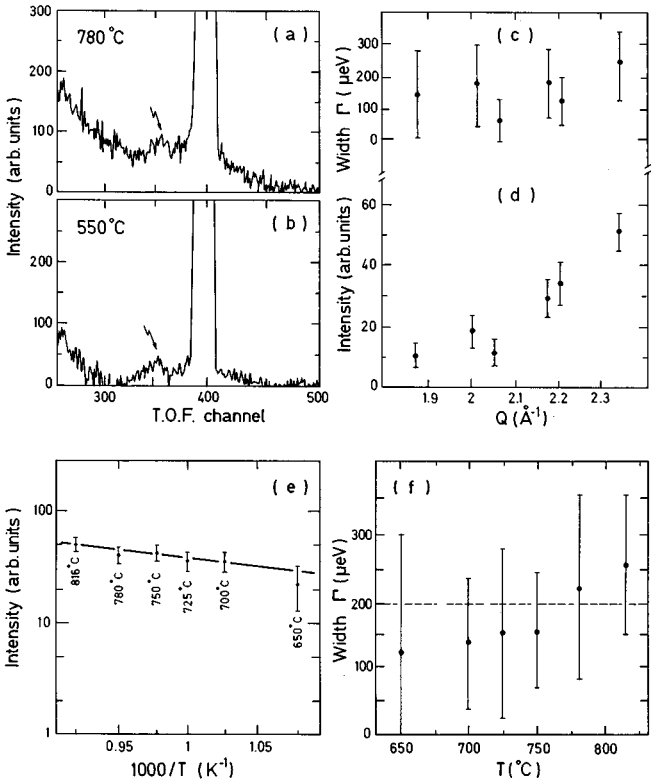

FIG. 3. Results of the $\lambda = 5$ Å runs. The transverse acoustic phonon connected to the [14/21] Bragg peak hinders the data analysis. It is shown at 816 °C (a) and 550 °C (b); (c) Q dependence of the Lorentzian width Γ at 816 °C; (d) Q dependence of the quasielastic intensity $A_1(Q)$ at 816 °C; (e) Arrhenius plot for the quasielastic intensity; (f) temperature dependence of Γ.

tance from phonons. In the case of Al-Pd-Mn, the depinning energy is much more compatible with such a kind of scenario.

Figures 3(c) and 3(d) give the Q dependence of the quasielastic signal at high temperature (816 °C). The Lorentzian appears around $Q = 1.755$ Å^{-1} but the signal is too weak to be fitted. It is only significant for the three groups of detectors correponding to $Q = 1.99$ Å^{-1}, $Q = 2.18$ Å^{-1}, and $Q = 2.34$ Å^{-1}. As three points are not sufficient to describe the Q dependence, an experiment was made at $\lambda = 5.3$ Å ($\Delta E = 70$ μeV HWHM) to complete these data. An empty-can measurement, a vanadium run, and a sample run at 816 °C were performed in the same experimental conditions as before. The three last groups of detectors gave a quasielastic signal strong enough to be fitted, and we added three new points at $Q = 1.87$ Å^{-1}, $Q = 2.05$ Å^{-1}, and $Q = 2.21$ Å^{-1}. Between the two experiments the sample and the temperature regulation were not touched. All the runs lasted 20 h and were fitted exactly in the same way as explained above. It ensures us that the second experiment at $\lambda = 5.3$ Å is consistent with the first one at $\lambda = 5$ Å.

Figure 3(c) shows that the Lorentzian width seems to be constant with Q. Its mean value is nearly equal to the 200 μeV found above with the temperature analysis. The quasielastic intensity is reported in Fig. 3(d). For isolated hopping in the simple model of the double-well potential with a distance d between the two minima, the intensity $A_1(Q)$ is expected to follow a spherical Bessel law, $A_1(Q) = \frac{1}{2}[1 - j_0(Qd)]$, the maximum of which would give d. It is not possible in our data to say if there is a first maximum between the two lowest points at $Q = 1.87$ Å^{-1} and $Q = 2.05$ Å^{-1} or not. A test at $\lambda = 6$ Å ($\Delta E = 47$ μeV) was made to explore specifically this region, but the intensities were too weak to be adjusted. We can only say that if there is a maximum, it corresponds to jump distances of the order of 2.5 Å. For larger Q values, the intensity increases until the last value of Q available in the experiment, without reaching any second maximum. This means that the Q range is too short and is the reason why we decided to undertake the second series of runs at $\lambda = 4$ Å.

B. The 4 Å data

The $\lambda = 4$ Å runs were made at 500, 550, 600, 650, 680, 710, 740, 770, and 794 °C.

Figure 4 shows the temperature dependence after empty-can subtraction and vanadium normalization, for the last group of detectors corresponding to $Q_{max} = 2.93$ Å^{-1}. As predicted by the hopping models, the quasielastic signal is stronger at $\lambda = 4$ Å than the one observed at $\lambda = 5$ Å. It appears at 500 °C and its intensity grows along the way up to 794 °C. Figure 5 shows that we observe again the same characteristic T dependence; i.e., the width seems to be constant (around 700 μeV) and the intensity follows an Arrhenius-like behavior, with a depinning energy of 177 meV, indicating a possible assistance by phonons.

The data are fitted with *one* quasielastic component at the foot of the elastic peak. Nevertheless, the relaxation time observed here is different from the one evidenced by the preceding experiment at $\lambda = 5$ Å. It is possible and even likely that the two different relaxation times occur simultaneously, such that in principle all fits should have taken into account more than one Lorentzian to describe the whole hopping process. But in reality the problems of phonon background and stray Bragg peaks discussed below become too bad at 4 Å to allow one to identify the slow times revealed in the 5 Å runs, and in the 5 Å runs the resolution is too good to provide the contrast needed to see the very fast jumps observed in the 4 Å runs. (The 200 μeV jump should have shown up at $Q_{el} = 2.48$ Å^{-1} if the quality of the 4 Å data were good enough.[34])

Figures 6 and 7 show a qualitative temperature dependence for the two lower groups of detectors, i.e., at $Q_{el} = 2.48$ Å^{-1} and at $Q_{el} = 2.72$ Å^{-1} respectively. The form of the quasielastic signal is distorted in both sets of data. At $Q_{el} = 2.48$ Å^{-1} (Fig. 6) a spurious little peak on the right hand (neutron energy loss) side of the elastic line rides on the hopping signal. It is probably due to a Bragg peak from Al-Pd-Mn that is scattered a second time (but incoherently) somewhere in the instrument, as occurs at all scattering angles. No fits can be made under such conditions, even when taking into account only the neutron energy gain side of the data, whose quantitative behavior looks identical to the one observed at Q_{max}. One can only say that the intensity is increasing with temperature. At $Q_{el} = 2.72$ Å^{-1} (Fig. 7) a very broad and asymmetric signal is observed between the Debye phonon density of states and the elastic peak. It is located approximately around $Q = 3$ Å^{-1} and $\hbar\omega = 2.28$

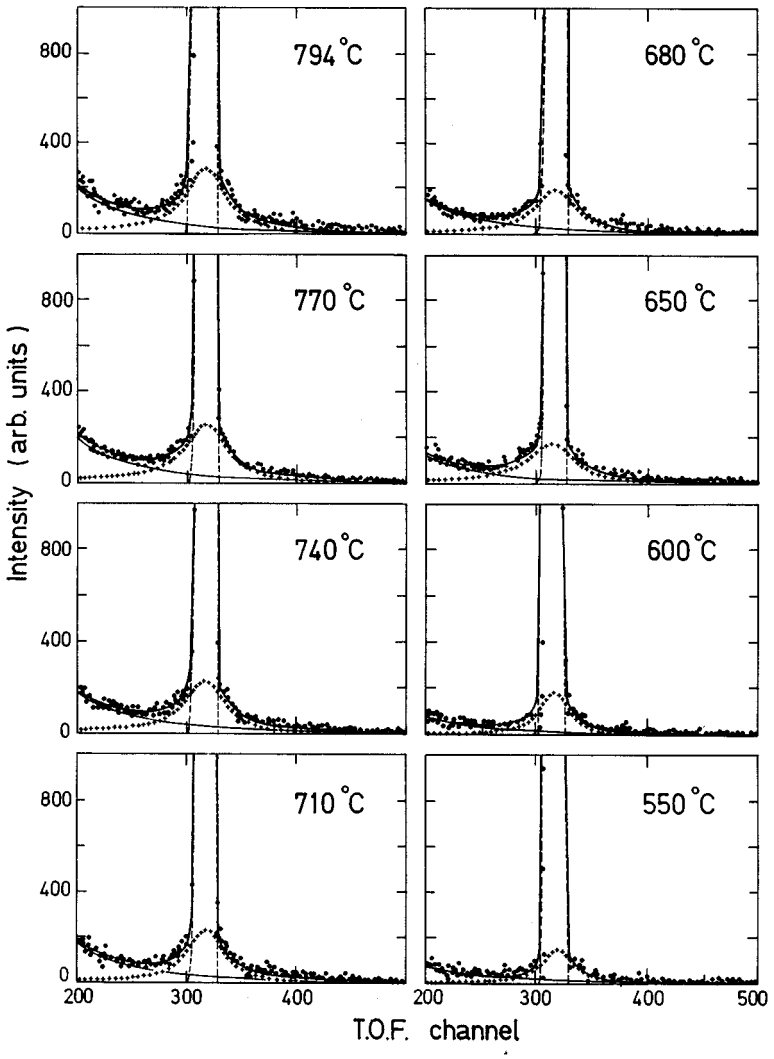

FIG. 4. Results from the $\lambda = 4$ Å runs. T dependence at $Q = 2.93$ Å^{-1}.

meV. It is due to coherent scattering from phonons; in fact the transverse acoustic phonons[35] emanating from the [18/29] and [20/32] Bragg peaks are both intercepted by the instrument at this point in reciprocal space, and their polarizations are making them active in this scattering geometry. The orientation of the resolution ellipsoid with respect to these branches at this point in **Q** space is rather unfavorable (i.e., defocusing). The Q resolution of the time-of-flight spectrometer is coarse as the group of detectors spans roughy 6.5° in 2θ. The combined effect results in a very broad signal that disappears at low temperature (due to the Bose factor). If it were due to quasielastic scattering it would have required a fit with a very broad Lorentzian ($\Gamma \sim 1500$ μeV).

Except for the last group of detectors, the data are very hard to fit. As a consequence, no Q dependence and no jump distance can be extracted from the experimental data. The only information the data give is qualitative: The phason signal appears beyond $Q = 2$ Å^{-1} and increases with Q. The maximum of intensity is located at a higher Q value, but in experiments at lower incident wave lengths it becomes increasingly difficult to avoid spurious peaks due to stray Bragg intensity and to separate the quasielastic scattering from the phonon background. However, experiments on a single crystal could significantly improve on the problems encountered in Fig. 6 and Fig. 7, as a proper orientation of the crystal combined with an adequate **Q**-vector selection should be able to provide a strong discrimination against these disturbing background effects.

V. DISCUSSION

A. Unusual temperature dependence

As a first remark it can be stated that the unusual T dependence of the quasielastic signal seems to be quite universal. It is observed here for two different jumps in Al-Pd-Mn. It was also observed for two different jumps in Al-Cu-Fe. As for the case of the Cu neutron-scattering data on Al-Cu-Fe the presence of a T dependence in the intensity is evidence for an assisted jump process. In Al-Cu-Fe the nature of the assisting process, which has an energy of 750 meV, is not clear. One possibility that was suggested was based on the possibility of breathers.[36] A search by inelastic neutron scattering with an incoming energy of 1 eV on the spectrometer HET of the ISIS facility at Rutherford Appleton Laboratory did not give evidence for the existence of collective modes with such energies[37] in Al-Cu-Fe. Both room- and high-temperature runs were attempted for the case where the breathers would need a softening of the lattice before they

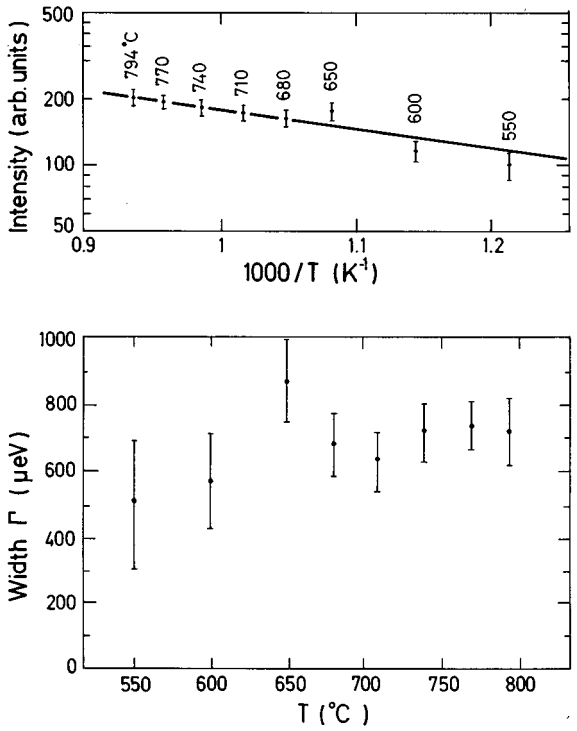

FIG. 5. Results from the $\lambda = 4$ Å runs. T dependence of Γ and $A_1(Q)$ deduced from the fits shown in Fig. 4.

could be created. However, the incident energy in these experiments is very high, such that the data can be considered to a high degree of accuracy as taken in the impulse approximation. Hence they might be unable to yield clues about the existence or otherwise of such collective effects such as breathers which are spread out over a large region in space. Because this argument shows that the breathers could be elusive to inelastic neutron scattering, we are forced to adopt the conservative viewpoint that in Al-Cu-Fe an identification of the 750 meV activation term with the energy required to create an aluminium vacancy seems quite reasonable. The situation looks very different for our data in Al-Pd-Mn. The activation energy of 177 meV for the jumps observed at 3 $Å^{-1}$ is here not inconsistent with the possibility of an assistance by phonons. Optical phonons in Al-Pd-Mn have been observed by Boudard *et al.* on a triple-axis spectrometer[38] and by Suck[30] on a TOF spectrometer. These data do not reach out to 177 meV (those of Ref. 30 were obtained at room temperature, and in Ref. 38 the scans did not reach out far enough in energy), but it would be interesting to check if a signature of a coupling between the hopping and the phonons could be evidenced in the temperature dependence of the phonon spectra. Since many types of jumps have been observed now in various QC's it would be extremely valuable to have measurements of the number of vacancies and their activation energies. In the case of Al-Pd-Mn, where large single-grain samples are available, this could in principle be obtained from a comparison of the microscopic lat-

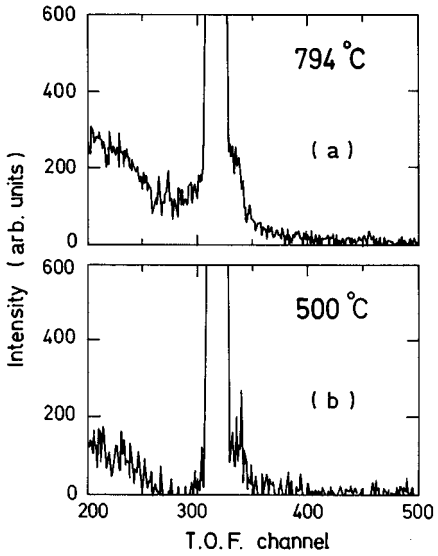

FIG. 6. Results from the $\lambda = 4$ Å runs. T dependence at $Q = 2.48$ $Å^{-1}$. The spurious peak in TOF channel 335 hampers the data analysis of the quasielastic scattering. It does not occur in the empty-can run and is probably due to stray Bragg scattering.

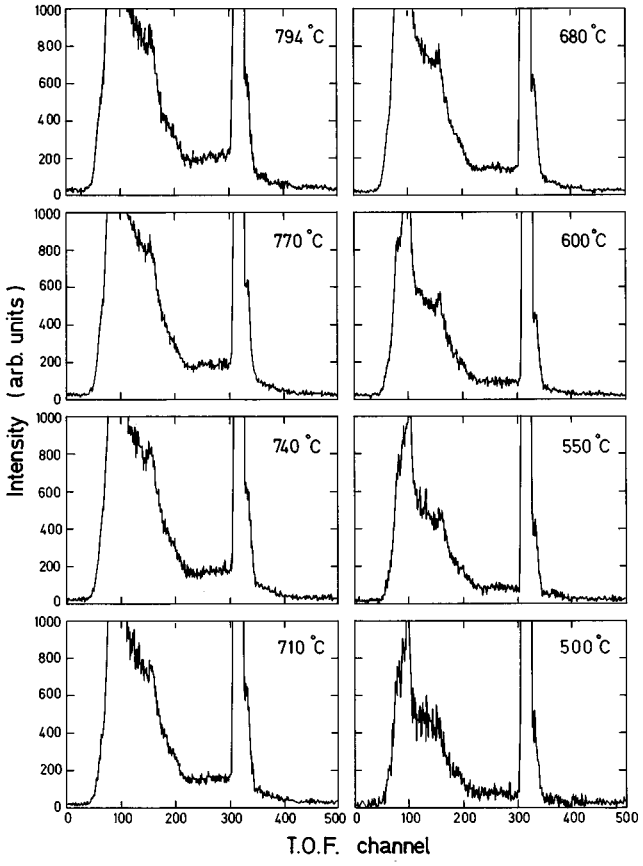

FIG. 7. Results from the $\lambda = 4$ Å runs. T dependence at $Q = 2.72$ $Å^{-1}$. The broad feature around TOF channel 240 precludes the data analysis of the quasielastic scattering. It is due to coherent scattering from transverse acoustic phonon branches originating from the [18/29] and [20/32] Bragg peaks.

tice constant (as measured in a diffraction experiment) with the macroscopic thermal expansion coefficient.[39] Positron annihilation experiments are able to provide some information on these values as well.[40,41]

B. Relation with the fast diffusion process proposed by Kalugin and Katz

A second and important question that is raised by our data is the problem of fast diffusion. The presence of a signal at 780 °C despite the very low value for the diffusion constant obtained in Ref. 14 makes this now a burning issue. It underlines the problem of the **Q** dependence of our data that was spelled out above and the need for a confirmation of the tracer diffusion results. Such experiments are planned.[42] One possibility might be that the percolation transition anticipated by Kalugin and Katz does not correspond to the superplasticity transition,[43] but to the melting of the quasicrystal, as already discussed by Coddens and Bellissent.[44] In fact the fraction of hopping atoms has often been found to be about 20% close to the melting point. The superplasticity transition could then correspond to the depinning transition of the phasons. It has been a long-standing matter of speculation (see, e.g., Ref. 45) if there could be such a depinning phase transition in quasicrystals. This very important issue is almost impossible to settle experimentally by neutron-scattering experiments due to the vanishing quasielastic intensities when the temperature is lowered. The extrapolation of the T dependence of Γ down to lower temperatures in the Mössbauer experiments on Al-Cu-Fe *could provide now strong experimental evidence against or in favor of such a phase transition as probed by the Fe atoms*. Another way to approach this problem could be a very precise measurement of the elastic intensity of the *intrinsic* diffuse scattering as a function of temperature in order to check if there is an indication of a phase transition.

VI. CONCLUSION

In the present paper we have provided a full discussion of all the arguments that have lead us to the conclusion that the most reasonable interpretation of quasielastic signals in quasicrystals is in terms of atomic hopping. We have reported the results of an experimental study by quasielastic neutron scattering on Al-Mn-Pd. We have shown evidence of the existence of two atomic jump times and studied their temperature dependence. We have discussed the difficulties that arise in relating the quasielastic data to the self-diffusion mechanism proposed by Kalugin and Katz and the possibilities of assistance to the jump process that is suggested by the experimental data. We have detailed the arguments underlying our viewpoint that there is no link between the quasielastic scattering and the phenomenon of phonon localization, pointing out what, in our opinion, the real mechanism for localization ought to be. By this study we have also obtained a firm basis for future research, which may consist in a triple-axis experiment on a large single-grain sample in order to obtain (1) better information on the $\Gamma = 700$ μeV quasielastic signal at lower Q values than 3 Å^{-1} by getting rid of the background problems illustrated in Fig. 6 and Fig. 7, (2) information on the jump *vectors* by a comparison with simplified model calculations, and (3) more Q information on the $\Gamma = 200$ μeV signal by looking at it in regions where the $\Gamma = 700$ μeV signal is absent.

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APPENDIX: A COMMENT ON LOCALIZED VIBRATIONS FROM CLUSTERS

In Refs. 19,20 it was proposed that our quasielastic scattering data should be reinterpreted within a scheme of localized vibrations from clusters. We are giving here the reasons why we cannot agree with this suggestion.

(1) The only experimental data given in Ref. 19 are Debye-Waller or Lamb-Mössbauer[46] factors, which translate a sudden drop of the diffuse (elastic) scattering above 870 K. For sure such a drop marks the onset of some type of dynamics above a certain observation threshold, but it constitutes only indirect evidence: When the temperature rises, the inelastic intensity increases at the expense of the elastic peak, and this elastic effect can be monitored. There is thus a sum rule that relates the elastic intensity to the integrated inelastic intensity. But these integral-type elastic data do not contain information on the spectral shape of the inelastic events or on their energy. In assigning such data to a specific dynamical process (corresponding *a priori* to a well-defined energy) one should thus be extremely cautious and conservative.

(2) In Ref. 19 an explanation in terms of the onset of *localized vibrations from hierarchical clusters* was proposed. (As mentioned above, a deeper analysis reveals[28] that the Mössbauer data are not compatible with an interpretation in terms of vibrations.) The same authors *now* interpret similar *elastic*-neutron-scattering data in Al-Pd-Mn as evidence for the onset of ''phason dynamics.''[47] Without further backing by inelastic-scattering data both attributions remain guesses.

(3) Our inelastic-scattering data show conclusively that the elastic effects should be associated with atomic hopping and not with cluster vibrations. In fact, our Mössbauer experiments described in Ref. 27 have shown that at 785 °C 20% of the Fe atoms are jumping on the time scale of 160 ps: Based on an analysis of the weak points of the experiment described in Ref. 19 we were able to design an improved experimental setup and to observe a quasielastic signal with a width Γ of 4 μeV. On the other hand, the phonon density of states in our time-of-flight measurements does not show an abnormal temperature dependence that could explain the strong effect in the Debye-Waller factor observed. This is also true of the HET experiments, such that inelastic scattering in the meV range (as from cluster vibrations) can be excluded as the cause of the Debye-Waller effects. The elastic effects correspond thus to the onset of quasielastic scattering. Experimental arguments why the quasielastic intensity cannot be identified as due to cluster vibrations have been given in the Introduction and in Ref. 27. de Araújo

et al.[28] have come to the same conclusions by following a completely different route.

(4) The data of Ref. 19 thus do not constitute experimental evidence for cluster vibrations. The basic idea underlying the claim in Ref. 19 is that acoustic phonons become localized by interactions with clusters at the length scale of about 10 Å. It was argued that this is pertinent based on the behavior of the phonon spectra obtained in triple-axis scans: A broading shows up when both the width and the wavelength of the phonons correspond to this scale. In the following we would like to clarify this point. In fact, localization of phonons *does* occur in quasicrystals, and it *is* evidenced by the broadening of the acoustic phonons, *but it is not related to the Debye-Waller factor data* of Ref. 19. Moreover, the localization occurs in the meV region instead of the μeV region, and the underlying mechanism is most probably related to the lack of periodicity rather than to the presence of (hierarchical) clusters.

We can justify these statements by additional theoretical arguments based on a discussion of the physics of localization (which does not imply a temperature threshold or an abnormal thermal population factor that could explain the sudden additional drop in the Debye-Waller factors).

The cluster argument is not new as it is very akin to an explanation invoked by some authors for the so-called boson peak, a universal feature in glasses that shows up both in neutron- and Raman-scattering data. The explanation of the boson peak in glasses remains a hotly debated issue, but we can nevertheless use estimates of the order of magnitude for the effect of sound wave localization that were derived within the context of this debate. Theoretical estimates, combined with the well-known values for the sound velocities in $Al_{63}Fe_{12}Cu_{25}$, show in fact that the 10 Å diameter cluster vibrations invoked have energies in the meV instead of the μeV range (called very confusingly high energy in Ref. 19). Using, e.g., the formulas given by Sokolov *et al.*,[48] viz., $\omega_p = \mathscr{C}_p (v_p/c\mathscr{D})$ and $v_t = 3650$ m/s, $v_\ell = 7700$ m/s,[49] we obtain energies of 13 and 22 meV. (In the equations v_t and v_ℓ are the transverse and longitudinal sound wave velocities, c is the speed of light, and $\mathscr{D}$ is the cluster diameter. If the polarization p is longitudinal, $\mathscr{C}_\ell = 0.85$; if it is transverse, $\mathscr{C}_t = 0.70$.) Experimental evidence on the boson peak in various glasses also exhibits energies in the meV region; e.g., the boson peak is found around 1.5 meV in the fragile glass former salol[50] and between 4 and 8 meV in silica,[51] which is a strong glass.[52]

This discussion places the possible vibrations from clusters of 10 Å diameter in the meV region. On the other hand the triple-axis data show that localization of the phonons also occurs in the meV region, but despite this coincidence, the localization does not occur on clusters. The reason herefore is that the clusters invoked very often overlap such that they cannot be seen as more or less isolated entities that would be almost disconnected from the rest of the structure.[53] The real argument is that propagation of phonons in crystals is good since neighboring sites have identical environments due to periodicity, and this allows for perfect transmission of the vibrational amplitudes from site to site by a resonance mechanism. Any deviation from periodicity will thus affect the quality of this propagation.[49]

(5) Finally we would like to stress that large *isolated* clusters could have low-energy modes, but there is not a single plausible argument to claim that these will survive an embedding in condensed matter. The various suggestions of Refs. 19,20 have thus to be dismissed.

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*Also at: Neutron Scattering Project, I.I.K.W., University of Antwerp, B-2610-Wilrijk, Belgium. Electronic address: teddy@bali.saclay.cea.fr

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from time-of-flight neutron scattering experiments on the rhombohedral → icosahedral transition in $Al_{62.5}Cu_{26.5}Fe_{11}$ [S. Lyonnard, G. André, R. Bellissent, Y. Calvayrac, and G. Coddens (unpublished)] that transformations to approximant phases do not affect the jump behavior. This result is easily understood if one realizes that the jumps are observed on a local scale and that in the related phases the short-range order is identical (Ref. 6). But of course we would like to have always a sample as perfect as possible.

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the data in Ref. 1 does not even extend to the first observable [6/9] Bragg peak (at 1.66 $Å^{-1}$) in the system such that multiple scattering involving Bragg peaks is trivially excluded. One has also suggested (Ref. 19) segregation of Cu atoms into grain boundaries as a possible mechanism for the quasielastic scattering, but there is no experimental ground for such guesses, especially since 20% of the copper atoms should be involved.

[53] The reason invoked for the clusters being responsible for the localization is the hierarchy argument. This argument [C. Janot (unpublished)] is one of self-similarity and tries to draw an analogy with localization in fractals [see, e.g., K. Yakubo, T. Nakayama, and R. Orbach, Rev. Mod. Phys. (1994)]. But localization in fractals is primarily due to the poor bond connectivity rather than to self-similarity, as a Bravais lattice is also self-similar. Self-similarity induces such poor bond connectivity only if the Hausdorff dimension is smaller than the Euclidean dimension. The Hausdorff dimension of quasicrystals is 3, and the connectivity puts them on the same footing as crystals, such that the self-similarity argument is as good to predict localization in quasicrystals as it would be in crystals.