Time Scales and Atomic Species in the Phason Dynamics of AlCuFe Quasicrystals

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We present time-of-flight quasielastic neutron scattering data with isotopic contrast on phason hopping in perfect icosahedral $Al_{62}Cu_{25.5}Fe_{12.5}$ quasicrystal powder samples. In total one Fe jump on the time scale $\hbar/2.0 \pm 0.5$ μeV, two Cu jumps ($\hbar/55$ and $\hbar/253$ μeV), and a collective jump phenomenon [$\hbar/(900 \pm 200$ μeV)] involving all atomic species have now been identified. We also explain the unusual temperature dependence of the phason dynamics that has been universally observed in the past. [S0031-9007(97)03263-8]

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Atomic hopping (so-called phason dynamics) [1–4] is important for the physics of quasicrystals (QC) for problems of stability (the random tiling model) [5], diffusion [6], phase transitions between QC and related phases [7], high temperature superplasticity [8], and cross-checking structural models [9]. We have studied this atomic hopping in the past [1–4], mainly by neutron scattering. The most detailed data to date was obtained for jumps of Cu in AlCuFe. However, these data raised several questions: (1) Did the puzzling temperature dependence not suggest that this dynamical signal should be due to a density of states (DOS) rather than to atomic jumps? (2) Why were only copper jumps observed while one would have expected a signal from the other atomic species as well? (3) Why were jumps observed only on a length scale of 4 Å, while all structural models predict a much larger contribution from shorter distances? These problems even sparked off conjectures about "localized vibrations of clusters" [10].

In this Letter we present information that together with the previous data on AlCuFe [1] gives now a well documented picture of the very rich phason dynamics in this QC and answers the three questions evoked above. We report on the observation by TOF neutron scattering of (1) an additional type of Cu jump on the time scale of $\hbar/250$ μeV and on a length scale of less than approximately 2 Å and, (2) a collective jump (involving all atomic species) on even shorter length and time scales. We also present neutron backscattering spectroscopy results, that combined with previously reported Mössbauer spectroscopy data, identify Fe jumps on the time scale of $\hbar/2$ μeV. Finally, we propose a simple model that provides a satisfactory explanation for the strange temperature dependence in terms of a need for an assisting process.

We must mention here that the experiments presented in this Letter are all on the limit of the present day available technology. The main difficulty is that one has to discern small QE signals through the veil of the statistics of the much stronger elastic intensity, with low counting rates. Consequently, it will in general be possible to extract only *average* Q dependences from a line shape analysis of the data [11]. Much more accurate information on the **Q** dependence can be obtained with an AlPdMn single grain sample and will be presented in a future publication. What renders AlCuFe unique, however (e.g., with respect to AlPdMn), is that it allows one (by isotopic contrast methods) to obtain information on the atomic species involved in a jump process.

The backscattering experiments were made with the new spectrometer IN16 [12] at the Institut Max von Laue–Paul Langevin for an incoming wavelength of 6.28 Å using spherically deformed Si(111) analyzers and a setup of five detector angles ($Q = 0.83$, 1.12, 1.38, 1.60, and 1.78 $Å^{-1}$). The width (FWHM) of the corresponding Gaussian energy resolution function was $\Delta E = 1.0$ μeV. Two (powder) samples of $Al_{62}Cu_{25.5}Fe_{12.5}$ were compared, one with natural Cu (18.492 g, ^{nat}Cu sample) and one in which all the Cu was ^{65}Cu (9.859 g, ^{65}Cu sample), with sample transmissions in excess of 95%. The samples were encapsulated between two coaxial Nb cylinders. Three temperatures were measured for the ^{nat}Cu sample (400, 700, and 770 °C), and two temperatures for the ^{65}Cu sample (400 and 770 °C). In fact, the QE signal is generally much smaller than the elastic peak (e.g., only a few % in height). Therefore the *wings* of the resolution function can render the data analysis difficult, even with the excellent resolution of IN16. To prove the presence of QE scattering we subtract a low temperature run (where the hopping dynamics are frozen) from a high temperature run. This must yield a *negative* elastic signal and a *positive* QE signal if the effect is real (see Fig. 1). Standard control experiments using empty cans at 400 and 770 °C, and vanadium at room temperature have been made. The data were fitted with a Gaussian resolution function, a Lorentzian QE signal, and a constant phonon DOS.

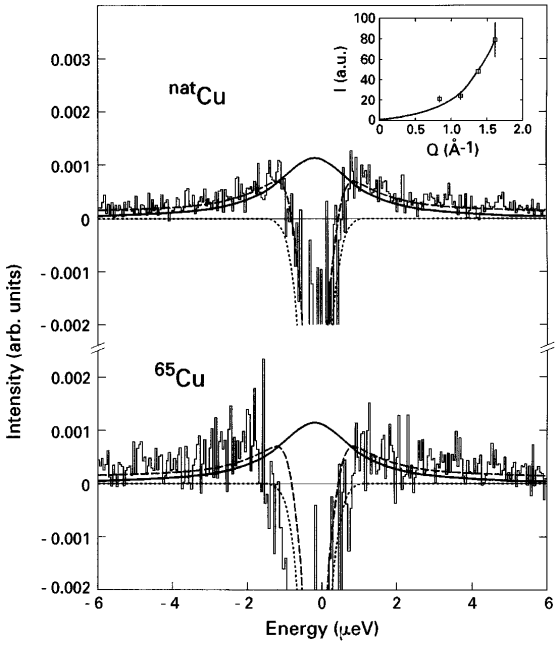

FIG. 1. IN16 spectrum of AlCuFe with ^{nat}Cu (top) and ^{65}Cu (bottom) at 770 °C, after subtraction of the 400 °C data; $Q = 1.12$ Å^{-1}. The fit of the ^{nat}Cu data has been superimposed on both data sets. The total Cu cross section in a ^{65}Cu sample is 1.81 times as strong as in a ^{nat}Cu sample. The Q dependence of the QE intensity is also shown (inset).

The results can be summarized as follows: (1) There is a QE signal with a width of $\approx 2.0 \pm 0.5$ μeV, in both the natural and the ^{65}Cu sample. Comparison with the empty can (770–400 °C) difference spectra, where this signal is absent, makes it beyond doubt that it is not an artifact. After normalization to the same sample mass the signals from the two samples (natural and isotopic) have essentially the same QE intensity. This shows that the Cu atoms do not participate in the observed dynamics. As we already obtained some evidence for hopping on the same time scale by ^{57}Fe Mössbauer spectroscopy [4], and as the ^{nat}Fe neutron scattering cross section is much stronger than the Al cross section, this is a very strong indication that this signal is due to Fe hopping. (2) An inspection of the negative and positive areas in Fig. 1 shows that the QE intensity trivially accounts for the drop in the Debye-Waller factors reported in Ref. [10], laying bare the absence of an experimental basis that could justify embarking on cluster themes. (3) The QE intensity has a structure factor. (Figure 1 shows that its maximum is situated beyond the Q range available, which sets an upper limit on the jump distance of 2.9 Å). The width of the signal does not vary with Q within the limits of precision. Thus both features plead for an interpretation in terms of local hopping (as opposed to diffusion). (4) Our information on the T dependence is very crude but exhibits the same qualitative behavior as has been observed for other types of jumps (see below).

The TOF experiments were done with the spectrometer MIBEMOL [12] at the Laboratoire Léon Brillouin with incident wavelengths λ of 5 Å ($\Delta E = 160$ μeV) and 4 Å ($\Delta E = 300$ μeV) on the same two samples. The 320 ^{3}He detectors were grouped in nine banks with scattering angles 2θ of 40.1, 47.1, 55.1, 63.1, 73.6, 88.6, 104.6, 120.0, and 137.2°. At $\lambda = 5$ Å runs were made at 770, 700, 625, 400, and 300 °C for the ^{65}Cu sample, and at 770 and 300 °C for the ^{nat}Cu sample. The samples were put into cylindrical sapphire containers.

The $\lambda = 5$ Å data set was completed with a vanadium run for detector normalization purposes. The phonon DOS of the QC hampered strongly the data analysis of the QE scattering signal (see Fig. 2). Therefore the 300 and 400 °C data, which do not contain QE scattering, were used as background runs, such that at least a part of this DOS could be subtracted out, which rendered the fits somewhat more tractable. These low T data were also used in order to determine the elastic line shape. The fits were performed in several steps [2]. First, the spectra at all angles were summed up and the QE line width Γ was determined to be 253 ± 53 μeV. We excluded the elastic peak from this refinement [2]. Afterwards, we kept Γ fixed and analyzed the Q and T dependence of the QE intensity. The results are as follows: (1) The *average* [11] Q dependence obtained at 770 °C is shown in Fig. 3. It shows that the first maximum of the structure factor of the 253 μeV jump lies beyond the available Q range; this puts an upper limit on the jump distance of 1.9 Å. (2) A comparison of the QE intensities at 770 °C in the two samples shows that the signal is entirely due to Cu motion

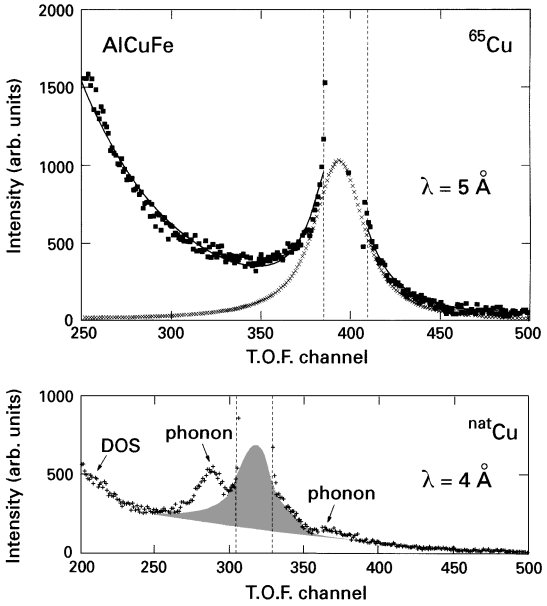

FIG. 2. QE signals at 770 °C in the 5 Å run (top) on the ^{65}Cu sample, and in the 4 Å run (bottom, on a different TOF scale) on the ^{nat}Cu sample obtained on MIBEMOL.

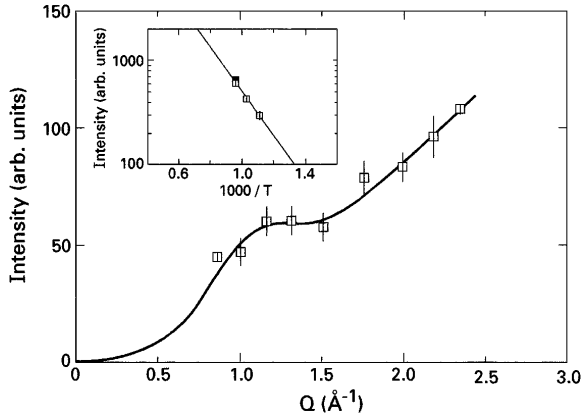

FIG. 3. Q dependence of the QE intensity obtained with the ^{65}Cu sample at 770 °C, after subtraction of the low T data. The small local maximum around 1.2 Å^{-1} corresponds to the 3.9 Å jump ($\Gamma \approx 55$ μeV) reported previously [1,11]. Inset: Arrhenius plot of the QE intensities (after subtraction of the low T data) obtained with the ^{65}Cu sample (open squares), and the ^{nat}Cu sample (full square) [multiplied by $\sigma_{tot}(^{65}Cu)/\sigma_{tot}(^{nat}Cu) = 1.81$]. The intensities are normalized to the same sample mass.

(see inset, Fig. 3). (3) The T dependence is unusual, as has been systematically observed for other jump signals in the past (both in AlCuFe and in AlPdMn) [1,2]: The QE intensity follows an Arrhenius law with an activation energy of 390 meV, while, within the limits of precision, the width can be considered to remain constant (see inset, Fig. 3).

We can now propose [13] an explanation for this surprising T behavior, based on the model depicted in Fig. 4, whose description in the case of assistance by Al jumps could sound as follows: A Cu atom can hop between two sites A and B with a (fast) relaxation time τ, provided site C is not occupied by an Al atom, which is then in some place in the "reservoir" symbolized by site D. The presence of an Al atom in site C blocks the hopping of the Cu atom. In general, the Al atom will wait a long time to jump

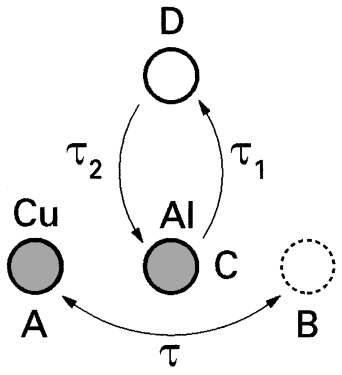

FIG. 4. The Cu atom in A can jump to B only if the Al atom in C is not in its way (i.e., if it has jumped to D). The various relaxation times are indicated.

away from site C, and come back very quickly to it. In terms of vacancies: A vacancy will pass a long time (τ_1) in exploring many possible other lattice sites before visiting site C, but it will leave C again very quickly with a relaxation time τ_2. In this particular example of assistance the physics of the vacancy diffusion process imply thus that $\tau_1 \gg \tau_2$. The calculation of this model is tedious but straightforward [13] and reproduces correctly the anomalous behavior. However, we are not able to specify the *actual* assisting process(es).

At 4 Å runs were made at 770, 700, and 300 °C for the ^{65}Cu sample, and at 770 and 700 °C for the ^{nat}Cu sample. Because of the Q^2 dependence, the phonon DOS is even stronger in these data (see Fig. 2). This and the presence of coherent phonon peaks renders the data analysis very difficult. Only at two angles were the data of sufficient quality to allow for line shape analysis, and to obtain a crude estimate for Γ by fitting the high temperature difference spectra between the ^{65}Cu and ^{nat}Cu samples. At $Q = 1.88$ Å^{-1} the mass corrected intensity ratio $J(^{65}Cu)/J(^{nat}Cu)$ (close to 0.55) is in agreement with the observation from the 5 Å data that the signal is entirely due to Cu motion. However, at $Q = 2.93$ Å^{-1}, the intensity ratio indicates that all atomic species are contributing to the signal (as it is close to 0.73), with a width of $\Gamma \approx 900 \pm 200$ μeV. The most plausible interpretation of this *collective* signal is that it corresponds to the observation on a local length scale of very fast hopping, mainly of Al, the contributions from the other atoms being a mere relaxational response to the environmental changes induced by the Al hopping. This Al hopping may lead to the phason-mediated diffusion process anticipated by Kalugin and Katz. No such fast phenomena have been shown to occur so far by tracer diffusion experiments [14], but these concerned only the Fe atoms. With a concentration of 62% in the sample the Al should be more apt to built a fast diffusion mechanism upon the local jumps we observed, as there is no reason to believe that they would be confined by some cage effect within structural elements. In fact, any type of atomic "cluster" one would like to discern in the structure can be dismantled or assembled locally by a few atomic jumps.

We have also studied a number of related phases. An investigation with an incident wavelength λ of 7 Å($\Delta E = 77$ μeV) at 790 °C in the cubic β-$Al_{50}Cu_{25}Fe_{25}$ did not yield any QE signal [1]. The same is true of $\lambda = 5$ Å and $\lambda = 7$ Å searches at 680 °C in the cubic approximant phase [15] α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$. Finally, we studied the reversible first order transition between the microcrystalline rhombohedral low T and the icosahedral high T phase in $Al_{62.5}Cu_{26.5}Fe_{11}$, by neutron and X-ray diffraction and TOF QE neutron scattering. Because of the hysteresis effects we were able to obtain the same sample at 705 °C once in the rhombohedral phase and once in the icosahedral phase. The QE signal (which we measured only on MIBEMOL with $\lambda = 5$ Å) is *identical*

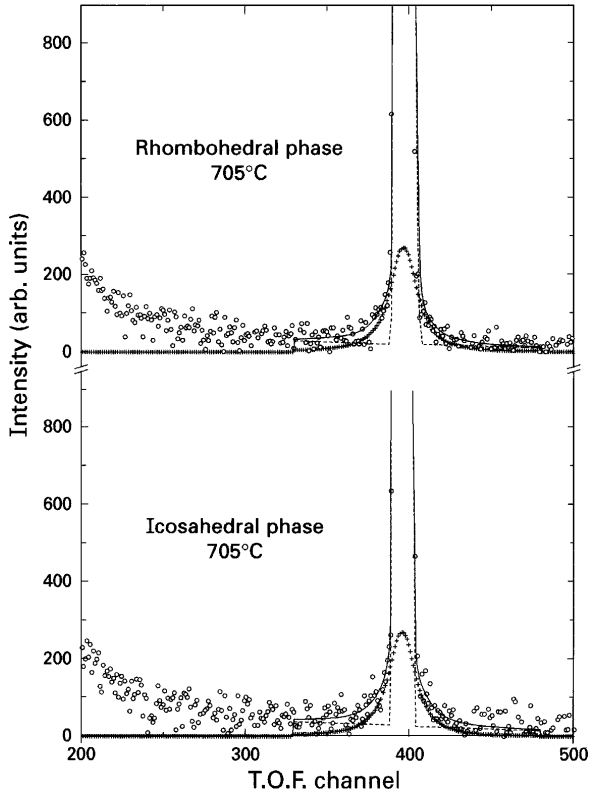

FIG. 5. QE signals at 705 °C in a 5 Å run on the rhombohedral sample (top), and on the icosahedral sample (bottom).

in the two phases, with a width Γ of 64 $\pm$ 35 μeV (see Fig. 5). These results show that the fast atomic hopping process is characteristic of local QC order. The signal was too weak to allow a determination of its Q dependence.

The main conclusion from our work is that the atomic hopping of Al, Cu, and Fe in AlCuFe occurs on three well separated time scales. The higher the concentration of an atomic species in the sample, the faster its jump rate is. This is quite natural as chemical disorder is expensive in the energy balance. The higher the concentration of an atomic species is in the sample, the more structural sites will be available for the jumping atom to accept it. The separated time scales reinforce the arguments [2] in favor of the interpretation of these dynamical signals in terms of hopping. Any exotic vibrational DOS would rather have included all atomic species. (The latter argument cannot be used to attribute the collective $\Gamma = 900$ μeV signal to hopping. In this case our arguments are more indirect. We should mention here that in AlPdMn relaxation times have been observed on roughly the same time scales [2]. The analogous 700 μeV wide signal in AlPdMn exhibits a structure factor with a first maximum around 3 Å^{-1} rather than a Q^2 dependence).

The fact that we observed only one long jump distance in the past is due only to the limited Q window covered by the spectrometer in these experiments. It is fortunate that the shorter jump distances are still observable with shorter wavelengths, i.e., coarsened energy resolution.

And finally we proposed an explanation for the bizarre T behavior in terms of assisted hopping.

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