Correlated Simultaneous Phason Jumps in an Icosahedral Al-Mn-Pd Quasicrystal

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A triple-axis neutron-scattering experiment has been performed on a large single-grain sample of an icosahedral Al-Mn-Pd quasicrystal. The scattering plane in reciprocal space was a binary plane of the quasicrystal. The intensities of the quasielastic signals collected were compared with model calculations assuming isolated single-particle jumps along two-, three-, and fivefold axes of the quasicrystal. The agreement turned out to be unsatisfactory. We were able to explain the experimental data only by assuming the existence of *correlated simultaneous* jumps of several atoms.

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Both quasicrystals and incommensurately modulated crystals (IC) can be derived from a common description based on an embedding in a higher-dimensional superspace that contains a periodic lattice of so-called atomic surfaces [1,2]. This hyperspace crystallography leads also to the possibility of an attractive analogy within the realm of lattice dynamics based on the introduction of the notion of "phasons" [3] in addition to the usual phonons [4]. Here we stumble onto a first real difficulty. Once we go beyond one-dimensional structures there are very important differences in the topology of the atomic surfaces between QC and IC [5,6]. Generally speaking, the atomic surfaces in QC are not continuous. Therefore phasons in QC are not *collective propagating modes* as in IC but rather atomic jumps, that can be visualized by configuration flips within Penrose-like tiling models. Ensuing experimental studies confirmed this picture [7–9]. In our current understanding an atomic jump is a *stochastic single-particle process*. The phonon heat bath produces a fluctuating environment that from time to time will open a low-energy gateway that is prosperous for a jump. Starting from this conceptual image that thrives on disorder it is hard to imagine an orderly concerted choreography of simultaneous jumps of two or more atoms. A rigid slide of the entire cut in superspace can thus not be a realistic notion in QC, and phasons in QC and IC should correspond to very different, antipodal types of dynamics. Tile flips in real, *i.e., not monoatomic* structural models entail in general several simultaneous atomic jumps. It was therefore inferred that the elementary phason building brick would rather be the atomic jump than the tile flip [10].

The aim of the present Letter is to point out the necessity of a refinement to the common-sense based paradigm sketched above, as in recent triple-axis neutron-scattering experiments on a large single-grain sample of the icosahedral phase Al-Mn-Pd we came across some evidence that seems to challenge it. In fact, we found a **Q**-dependence of the quasielastic signal that we are able to explain only by assuming that two (or more) atoms jump simultaneously keeping their separation vector fixed. Preliminary data of this long-standing triple-axis study have been published as short conference communications [8], but their analysis was partial and must be considered as superseded. The present data were obtained with a different, substantially larger sample. This resulted in much better statistics and unambiguous results for the fits. Phason dynamics have a bearing on many other issues in QC, such as stability, diffusion, growth, phase transitions between QC and related phases, high temperature superplasticity and crosschecking structural models, but here we will address only the crucial evidence for the simultaneous correlated jumps.

The quasielastic-neutron-scattering experiments were performed with the cold-neutron double-monochromator triple-axis spectrometer 4F2 of the LLB in the fixed $k_f = 1.64$ Å^{-1} ($\Delta E = 100$ μeV) and $k_f = 1.97$ Å^{-1} ($\Delta E = 200$ μeV) configurations. The loci of some of the constant-Q energy scans in the binary scattering plane of the QC are indicated in Fig. 1, which also shows the intensities of the most prominent Bragg peaks. If possible, operating in the vicinity of the latter should be avoided

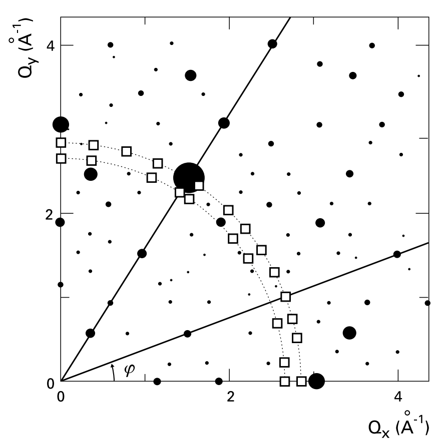

FIG. 1. Binary scattering plane. The sizes of the full circles represent the intensity of the Bragg peaks. The locations of the various constant-Q scans discussed in this Letter have been drawn: They were all made in the $k_f = 1.64$ Å^{-1} configuration. The angle φ is defined with respect to Q_x.

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in the scans as the wings of the resolution function tend to flood the quasielastic intensity if the elastic signal is too strong and the unwanted background of coherent signals from acoustic phonons which scales with the intensity of the Bragg peaks can really jeopardize the data. The choice of the binary plane allows us to explore all types of symmetry axes (twofold, threefold, and fivefold) of the QC in one setup. The 3-cm^3-sized single-grain sample has been grown by the Czochralsky method. It had the stoichiometric composition $Al_{70.4}Mn_{8.6}Pd_{21.0}$. It has been checked by neutron diffraction that it was not contaminated by other individuals or other phases. A curved-analyzer setting has been used in order to increase the counting rates without appreciable losses in Q resolution [11]. A (002) pyrolytic graphite filter was used on the scattered beam in order to suppress higher-order contaminations. Typical data-acquisition times were of the order of 8 h per scan. Spectra were taken at 800 and 400 °C. The latter data served as background checks. In fact, a subtraction of the 400 °C run from the 800 °C run yields a negative contribution in the elastic region (due to the Debye-Waller factor), while one observes a positive quasielastic signal, which proves that it is not due to the wings of the resolution function. Such low-temperature runs further confirm that there is no paramagnetic scattering polluting the data as can also be inferred from magnetization measurements with a superconducting quantum-interference device [12]. Background scans as a function of temperature were also made at fixed points $(\omega, \mathbf{Q})$ in reciprocal space in order to monitor the contribution of the incoherent phonon background. This background is not necessarily isotropic in a single-grain sample due to the coupling factor $\mathbf{Q} \cdot \mathbf{e}_p$, where $\mathbf{e}_p$ is the polarization vector of the phonon. The complete triple-axis study comprised many more scans than shown in Fig. 1. Its results with further details on experimental conditions and data analysis will be published elsewhere [13].

A typical data set is featured in Fig. 2 together with a fit based on a Lorentzian quasielastic signal convoluted with the Gaussian resolution function. Also included in this fit are the elastic peak and a linear incoherent phonon background. The $\mathbf{Q}$-dependence of the quasielastic intensity for $Q = 2.85$ Å^{-1} is displayed in Fig. 3. It is strongly anisotropic. In a simple single-particle model in the white-noise approximation [14] for atomic jumps between two sites separated by a jump vector $\mathbf{d}$ the quasielastic intensity should follow an (incoherent) structure factor $S_{q.e\ell}(\mathbf{Q}) = \frac{1}{2}[1 - \cos(\mathbf{Q} \cdot \mathbf{d})]$. If this jump occurs along a m-fold axis of the QC, then there are $30/m$ symmetry-related jump vectors $\mathbf{d}_j$, such that one can expect

$$S_{q.e\ell}(\mathbf{Q}) = \sum_{j=1}^{30/m} \frac{1}{2}[1 - \cos(\mathbf{Q} \cdot \mathbf{d}_j)]. \qquad (1)$$

This equation can represent three models, with $m = 2$, $m = 3$, and $m = 5$ for jumps along twofold, threefold, and fivefold directions, respectively. If the direction of the jump is not along a symmetry axis, then the sums will have to extend over the whole icosahedral group. (This corresponds to the case $m = 1$). The quasielastic and elastic intensities obey a sum rule such that the incoherent elastic structure factor is obtained from Eq. (1) by changing the sign in front of the cosine term:

$$S_{e\ell}(\mathbf{Q}) = \sum_{j=1}^{30/m} \frac{1}{2}[1 + \cos(\mathbf{Q} \cdot \mathbf{d}_j)]. \qquad (2)$$

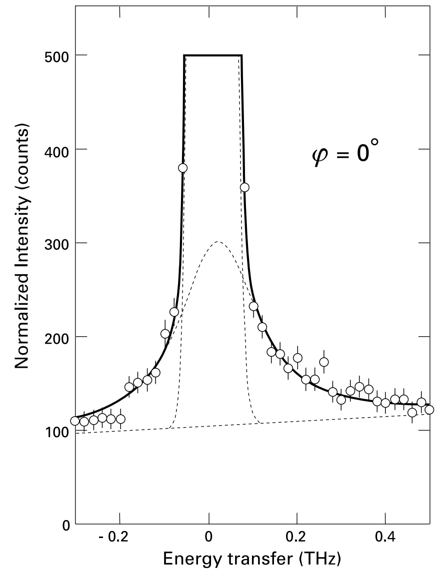

FIG. 2. Typical constant-Q scan with fit. The data shown here correspond to $|Q| = 2.85$ Å^{-1} and $\varphi = 0°$.

The incoherent elastic structure factor is quite useless in view of practical applications as the scattered intensities are predominantly determined by the coherent neutron scattering cross sections. For the quasielastic intensity this coherence is not a source of problems as long as we stick to uncorrelated single-particle behavior. Both elastic and quasielastic intensities are in principle attenuated by the Debye-Waller factor. The quasielastic structure factors embodied by Eq. (1) all exhibit an isotropic first local maximum in Q. This remains true if the direction of the jump is not a symmetry axis. This is quite at variance with the experimentally observed data which do not display such a spherical shell of maximum intensity, and on the contrary exhibit their strongest anisotropy at low Q. We should point out that this discrepancy cannot be waved away by invoking arguments that the signal could be narrower at lower Q and as such would have been missed by too coarse a resolution of the spectrometer. Previously reported [9] time-of-flight experiments with very good energy resolution on powder samples unequivocally preclude such a loophole. We should point out that none of the three models expressed by Eq. (1) can reproduce the peak/valley-ratios that occur in Fig. 3, as is easily

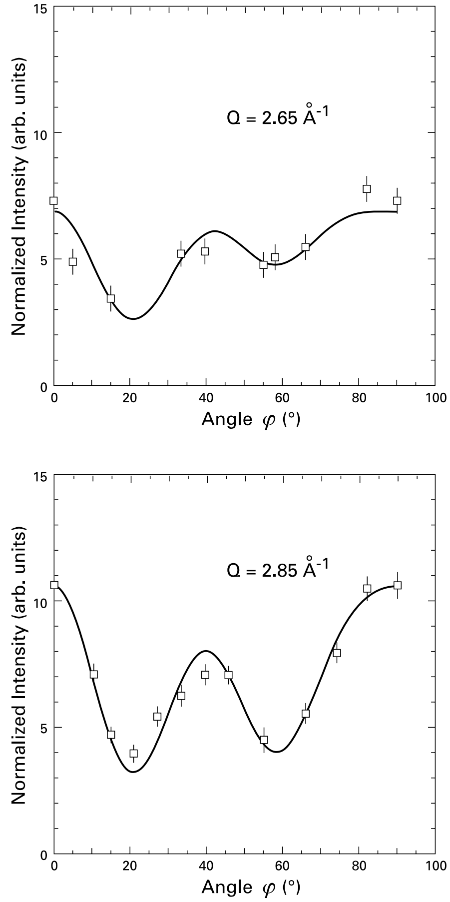

FIG. 3. Quasielastic intensities for $|Q| = 2.65$ Å^{-1} and $|Q| = 2.85$ Å^{-1}. A fit with model function (2) is also shown. (Data collected with a second sample, both in $k_f = 1.64$ Å^{-1} and $k_f = 1.97$ Å^{-1} setups, bear out the reproducibility of these results).

verified by plotting their angular intensity profiles for various values of Q. This means that one needs another type of model. By some serendipity we found out that the data in Fig. 3 are described by Eq. (2) for $m = 3$ and $d = 3.85$ Å. Among the (idle) lines of thought we followed in our attempts to come to grips with this alienating finding we can mention models as proposed in [15,16] and down-sized versions of Elser's escapement model [10,17,18]. A full account with many details will be given in a forthcoming paper [13]. These models feature seven atoms on a dodecahedron. The atoms can jump between first neighbor sites but should always obey two rules: (1) Two atoms should never be first neighbors, and (2) two atoms should never occupy opposite sites on the dodecahedron. This model has been analyzed and solved numerically in Ref. [16]. The method applied can be used both for coherent and incoherent signals. The atomic jumps in this model occur along twofold directions. The refinement with respect to Eq. (1) with $m = 2$ is that this model involves complicated correlations between successive jumps. The final result for the calculated intensities is also a mere refinement of that for Eq. (1) and does not alter its gross features. Elser's model is a further refinement that consists of combining two such configurations in an interlock. When the atoms are able to jump on one of the dodecahedra, the jumps on the other one are blocked and vice versa. Whether a dodecahedron is silent or otherwise is determined by another atom that jumps between two sites situated in between the two dodecahedra. The experimental evidence is cogent: all models featuring single jumps or correlated sequences of single jumps are missing the point. The failure to represent our data by such models helped us to realize where the minus signs in front of the cosines in Eq. (1) come from. Each time an atom jumps from A to an empty site B, the neutron-scattering contrast between A and B is inverted, which amounts to a π flip of its phase. Therefore, the only way to obtain a plus sign is by designing a model that preserves the contrast despite the occurrence of the jump. This can be achieved only by admitting that two atoms in A and B are jumping simultaneously to A' and B', respectively, whereby the vectors AB and $A'B'$ are equipollent. This leads to expressions of the type $S_{q.e\ell}(\mathbf{Q}) = \sum_{j=1}^{30/m} \frac{1}{2}[1 - \cos(\mathbf{Q}\cdot\mathbf{d}_j)][1 + \cos(\mathbf{Q}\cdot\mathbf{s}_j)]$, where the correlation vector $\mathbf{s}_j$ is analogous to the separation vector AB. The $[1 - \cos(\mathbf{Q}\cdot\mathbf{d}_j)]$ parts are responsible for the first radial maximum, while the $[1 + \cos(\mathbf{Q}\cdot\mathbf{s}_j)]$ terms entail a modulation of this local maximum that otherwise would have been an isotropic spherical shell.

At once, this means that phasons in QC could nevertheless have some collective character, making them (unexpectedly) more similar to the propagating phason modes that are typical of IC. It should be mentioned that such a feature of simultaneous jumps occurs as an unavoidable consequence of the specific decoration of the atomic surfaces in many structural models. This happens, among others in models designed by Beraha *et al.* [19], and Zeger and Trebin [20]. As pointed out above, such collective motion clashes with our *Weltanschauung*, as we were strong believers of the heat-bath-driven scenario outlined above [21]. We must admit in all fairness that already before us a number of colleagues had expressed the opinion that phason dynamics in QC could have a collective aspect [22,23]. In fact, Rivier mentioned it explicitly in connection with the model of Zeger and Trebin. Trebin has evoked an image of a wave of collective jumps as an elastic response of the quasiperiodic medium to a periodic external source of deformation, e.g., in a vibrating-reed experiment. Such an elastic response must then be governed by the phason elastic constants.

We must signal that the description of the data by Eq. (2) breaks down at higher Q values, where we are unable to explain the observed intensities [13]. At 2.65 and at 2.85 Å^{-1} we are so lucky to find ourselves in the small-Q limit, where the largest characteristic distance within the dynamics can be discerned in an isolated fashion, free from the obfuscating presence of signals corresponding to shorter length scales.

In conclusion, we have made neutron triple-axis experiments on phason hopping in a large single-grain quasicrystal and discovered a very unusual Q-dependence of the quasielastic signal. We think that this novel result constitutes an important step towards the elucidation of the physical nature of phasons in QC.

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