Comment on "Atomic jumps in quasiperiodic $Al_{72.6}Ni_{10.5}Co_{16.9}$ and related crystalline material"

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We disagree with a number of statements by Dolinšek *et al.* [Phys. Rev. B **65**, 212203 (2002)] about the specificity of phason dynamics in quasicrystals.

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We are surprised by the lack of foundation of some formulations in a recent paper by Dolinšek *et al.*,[1] which center around two major themes. (1) Phason jumps are stated not to be quasicrystalspecific. It is also suggested that the data on phason dynamics presented up to now would not be unambiguous due to ''interference'' with vacancy diffusion. (2) The authors present NMR data and claim that these would be an unambiguous observation of phason dynamics.

(1) The criticism contained in theme (1) has been based on at least three important confusions: A confusion between the concepts of vacancies and phason sites in quasicrystals (1a), a confusion between regular atomic jumps in $B2$-based τ phases and phason dynamics in quasicrystals (QC's) (1b), and a confusion about what quasicrystal specificity is supposed to mean (1c). All this has been combined in the past to present data from a τ phase (which have no bearing on the issues raised by the authors) as relevant for the physics of QC's.[2,3]

(1a) The confusion about the concepts of vacancies and phason sites is operating on two levels.

(1a-1) It is hinted that the high-temperature data about phason dynamics are not unambiguous as they could also be due to vacancy diffusion. In this context, the authors seem to be well aware of the difference between the two concepts. This also transpires from their introductory statement that no empty lattice site is involved in the concept of a phason flip. It must be clear that there is no ground for an allegation that the dynamical signal observed in Ref. 4 would be due to vacancy diffusion rather than phason hopping. In fact, the Q dependence of the neutron-scattering signal indicates that the atomic motion remains confined in space, while its temperature dependence is unusual and not typical of vacancy diffusion. Furthermore, the diffusion constants that one experimentally observes are much lower than the ones one should reasonably expect on the basis of the observed hopping rates if this hopping were due to vacancy diffusion. Indeed, the hopping is exceptionally fast, while the observed diffusion constants just take values that could be qualified as standard for metallic compounds. The invoked ''remarkable similarity'' between the activation energy of the hopping process and the enthalpy for the formation of a vacancy in pure Al is just a numerical coincidence. We must mention that the numbers quoted from our work are *not* the *activation* energies of the hopping process, but *assistance* energies. Moreover, the value of 0.6 eV quoted for AlCuFe is related with Cu rather than with Al hopping, and the assistance energies we reported for AlPdMn are not remarkably close to 0.6 eV.

(1a-2) The authors claim that it has been shown that d-AlCoNi contains a large amount of ''vacant sites.'' The-''vacant sites'' in question are just phason sites,[5] such that this claim contradicts the introductory statement we mentioned above. That we are dealing here with phason sites rather than with vacancies is not an issue and leaves no space for any confusion of the kind that would seem to emanate from the presentation of the authors. The confusion here is produced by the undifferentiated terminology ''vacant site'' which the authors use for both phason sites and vacancies.

To conclude part (1a) we note that other poorly justified statements have been made by the authors to promote the idea that QC's would contain a large amount of vacancies.[2,3] This shows that this statement has not been deduced by unbiased logical deduction from scientific observation, but that it is a preconceived postulate the authors try to validate. This postulate has a pivotal function in the argument of the authors. It must serve to lend credibility to an analogy they want to impose between $B2$-based crystals (which might contain up to 12% structural vacancies) and QC's (where nothing of that order of magnitude has ever been established). The postulated analogy enforces the confusion (1b) and should permit one to incorporate phason dynamics into a much broader class of trite hopping phenomena (1c).

(1b) The confusion between regular atomic jumps in a $B2$-based phase and phason jumps in a QC is of course linked to the one between vacancies and phason sites. The regular atomic jumps in a $B2$-based phase are towards vacancies, while the phason jumps in a QC are towards phason sites. The authors have tried several times to argue that the regular atomic jumps in a τ phase would be the same physics as phason dynamics. We first discuss their two main arguments (1b-1, 1b-2) and then discuss how these arguments are rooted in an overinterpretation of an analogy between QC's and τ phases.

(1b-1) One line of argument used is the similarity of jump times. But there is more to the similarity of the physics than a similarity of relaxation times. It is not because two signals look similar that they cover similar physics: What is more similar to a relaxation time with an activation energy than another relaxation time with an activation energy? But in many experimental techniques, relaxation times and activation energies are all the hard data resume to.

(1b-2) The second line of argument has consisted in twice presenting wrong proofs that a $B2$-based τ phase and a QC would be linked by a modulation.[6,7] As a corollary the atomic jumps in a τ phase could also be called phasons. These proofs are in very obvious contradiction with a famous

classical paper by Duneau and Oguey[8] that conclusively shows that it is not possible to define a 1-1 mapping between the atomic positions of a crystalline phase and those of a quasicrystal (within a certain physical context). The impossibility to consider a QC as a modulated phase was also demonstrated in several other well-known papers.[9] Duneau and Oguey established that a 1-1 mapping between a QC and a crystal (permitting one to perceive the QC as a modulated phase whose basic lattice is the crystal) can only exist if the acceptance window of the projection method is able to tile the perpendicular space without overlaps or empty spaces. As the acceptance window for an icosahedral lattice (which is a triacontrahedron) does not tile the three-dimensional perpendicular space, there is no mapping between an icosahedral QC and a crystal.

(1b-3) The quest for such proofs was inspired by some analogies reported by Van Tendeloo *et al.*[10] between the construction rules for τ phases AlCuNi and those for a Fibonacci chain. The τ phases can be denoted as τ_n where n is a Fibonacci number. Their structure can be constructed from two fundamental plane stackings that we may denote as L and S, and whose contents we will specify later on. Repeat units for the phases are defined as

$$\tau_2 \Rightarrow S,$$

$$\tau_3 \Rightarrow L,$$

$$\tau_5 \Rightarrow LS = \tau_3 \tau_2,$$

$$\tau_8 \Rightarrow LLS = \tau_3 \tau_5,$$

$$\tau_{13} \Rightarrow LLSLS = \tau_8 \tau_5,$$

$$\tau_{21} \Rightarrow LLSLLSLS = \tau_8 \tau_{13},$$

$$\tau_{34} \Rightarrow LLSLLSLSLLSLS = \tau_{21} \tau_{13}.$$

By presenting matters this way, we obtain the strongest similarity possible to the construction of the one-dimensional Fibonacci chain, in the sense that this is as far as one can go in suggesting on the basis of similarities in the formalisms that we could be dealing with a kind of one-dimensional QC.[11] In this spirit, one can even imagine that there could be a unique composition leading to an infinite unit τ_∞ that would be an aperiodic sequence, while all finite repeat units would define approximants. τ phases would then appear to be related to QC's and at least they would have the same status as approximants. In reality, only a few τ phases have been observed, and the hypothetical aperiodic sequence (τ_∞) has never been obtained.

The construction rule for the τ phases does not define a QC, even if one could evoke a kind of cut method to define the letter sequences. The essential point is that in the Fibonacci chain the letters L and S are coding interatomic distances, while in the τ phases they rather serve to code a first-order description of the architecture in terms of some recurring configurations of stacked atomic layers that are piled up along the [111] direction [This description is rather loose: The choice between Cu and Ni is not even specified (see below).] The situations are thus very different. In fact, the interatomic distances in the τ phases always take the same value a, except when a vacancy occurs, in which case we have a distance $2a$. The τ phase is thus defined on a periodic lattice, not on a quasilattice as the Fibonacci chain. In conclusion, for the Fibonacci chain the cut method defines two possible interatomic distances, while for the crystalline τ phase it defines only one interatomic distance a. We could perhaps say that the periodic lattice of a τ phase has a ''modulation'' of its decoration or its occupation, although it would remain to be proved that the word modulation has here the same meaning as in the case of incommensurately modulated phases. The letter sequence (or the cut method) in the τ phases is thus a decoration rule, not a distance rule as in the QC. We are dealing with two totally different construction rules that can accidentally be both coded by two-letter sequences, with frequencies given by Fibonacci numbers in one case and by the golden ratio τ in the other case. The coding of the hypothetical τ_∞ phase is even different from the one of the Fibonacci chain.

The building brick S stands for a plane stacking sequence Al-Cu/Ni-Al-vac (where Al stands for a layer occupied by Al atoms, Cu/Ni stands for a layer occupied by either Cu or Ni atoms, and vac for a layer with vacancies) while the building brick L stands for Al-Cu/Ni-Al-Cu/Ni-Al-vac. We may note that a change of configuration $LS \leftrightarrow SL$ does not correspond to simple atomic jumps: Cu/Ni atoms would have to leapfrog Al atoms in order to achieve it. As a more physical process, in the τ phases we can have regular atomic hopping, which simply corresponds to athermal-vacancy kinetics on a periodic lattice, but this hopping has no relation whatsoever with the short-distance phason dynamics of a QC, which, in principle, does not require the presence of any (thermal or athermal) vacancy. The possibility of phason hopping in one-dimensional QC's is a direct consequence of the existence of two different interatomic distances L and S which define the short hopping distance $L-S$. As there is only one interatomic distance on the periodic lattice of a τ phase, the claim that phason hopping in a τ phase would exist cannot be right. It was already pointed out by Van Tendeloo *et al.* that at high temperatures the vacancy positions in the τ phases become disordered. It was thus obvious right from the start that high-temperature hopping would be observed in the τ phase studied by the authors, and that it could be very fast due to the exceptionally large concentration of vacancies. [Note that the observation that the vacancies order on lowering the temperature shows very clearly that the NMR signals reported by the authors have nothing to do with jump dynamics (See below)].

(1c) Contrary to the statements of the authors, there has never been an error in the literature in the sense that someone would have claimed that fast atomic jumps could only exist in QC's. Nobody would understand a possible QC specifity of phason dynamics in the singular, restrictive sense of exclusivity the authors want to give to it. Such a concern of uniqueness is just not in order and poses a wrong issue. In fact, phasons correspond to atomic jumps in double-well potentials whose minima are separated by a distance shorter than the interatomic distances. Nobody claims that such double-well potentials giving rise to atomic jumps would be

a rarity in condensed-matter physics. The example of the hydrogen bond has been well known for a long time. One of the original features of QC's is that the presence of these short-distance double wells is an integrated part of the quasilattice. Conceptually, a simple $B2$-based lattice with vacancies does not imply the existence of short-distance double wells. It would thus appear that examples of signals from $B2$-based phases do not capture the essence of the nonuniqueness of the dynamics of such double-well potentials. In fact, in the $B2$-based phases the jumps are not fast due to the short jump distances but to the huge concentration of athermal vacancies.

(2) A much more urgent concern about uniqueness than the one of fast atomic jumps in QC's is the one of the interpretation of the NMR data. In fact, there is a total lack of proof for the attribution of the low-temperature NMR signal to hopping dynamics, as reflected in the caution of the authors' statement that the data are *compatible* with phason dynamics. This remark applies to both the τ phase and the QC data. We must develop here three points. The attribution is not justified as NMR data alone rarely allow us to make such definite assignments (2a). Furthermore the authors simply have not considered the possibility of alternative interpretations, even though there could be many (2b). Finally, there are robust physical reasons to think that the assignment is wrong (2c).

(2a) NMR data alone very rarely are able to produce the kind of detailed identifications as proposed in the paper. They do not provide much information about characteristic distances as they do not yield Q-dependent information. Identifying which atomic species is moving is also not straightforward. The Al NMR signals might just indicate that a neighbor of an Al atom is moving. The present NMR data do stand alone: The time scales accessed are quite remote from the time scales that can be accessed by other techniques such that cross checking or use of complementary information to validate the claims is not possible. Due to all these limitations the interpretation of the NMR signals require a caution that was not observed by the authors.

(2b) The only thing we really know with certainty is that there is some slow (local) relaxation with a low activation energy. There are many other processes than atomic jumps which can produce similar signals, i.e. we argue that the low temperature region is not as exempt of the possibility of ''interfering'' dynamics as the authors suggest. We illustrate this by discussing three possibilities in principle, viz. small atomic shifts (2b-1), tunneling states (2b-2), and magnetism (2b-3).

(2b-1) The idea of a small local shift of the Al atom in response to a slowly fluctuating or diffusing strain field that includes its environment is equally compatible with the data. We observe here a neglected possibility of explanations in terms of small, nonphasonic atomic shifts, whose amplitudes explore a continuum rather than a discrete set.

(2b-2) One can think of still other phenomena that could be compatible with the data. Without wanting to reinterpret the NMR data accordingly, we may mention that one type or another of slow dynamics remaining unfrozen at even lower temperatures is observed in many systems, including QC's, e.g., in the form of tunneling states.[12] Above a few degrees K the coherent tunneling may cross over to a thermally activated process. It has still not been proven experimentally that tunneling states in QC's are not phasons. This illustrates the difficulty of making the assignments we already mentioned. In glasses tunneling states are conceived as small simultaneous shifts in the positions of groups of atoms bringing about a transition between slightly degenerate configurations. The precise detailed geometrical picture of the motions involved in such processes remains unknown. This kind of lack of information is a recurrent theme in slow dynamics and due to the physical limitations of the available experimental techniques. From this discussion on tunneling states we may distillate the idea of the alternative explanation proposed under (2b-1).

(2b-3) The suggested uniqueness of interpretation of the NMR data is also contradicted by other NMR data of the authors. In fact, in Ref. 13 they observed a temperature behavior of an NMR signal that was not compatible with their interpretation of it in terms of phason dynamics. The AlPdMn phase can be magnetic, a fact that offers seeds for an alternative explanation.[14] In a subsequent paper they stated[15] that this scenario could not be proved, and concluded that the origin of the signal was not understood, but probably due to the unusual magnetic properties of Mn atoms. They also stated that the data from AlPdRe are of a different origin than those from AlPdMn, despite possible similarities in the time scales. This illustrates that other phenomena that are not frozen can exist at low temperatures and hamper the interpretation of the data. It also illustrates the point (1b-1).

(2c) We already mentioned that the observation of an order-disorder transition by Van Tendeloo *et al.* rather precludes the interpretation of the NMR data in the τ phase in terms of hopping. The authors have established the existence of similar signals in QC's and $B2$-based AlNiCu, which despite all possible claims definitely does not support phason dynamics. If following them we discard interference from vacancy motion, we are faced with the problem of elucidating the origin of an NMR signal in the $B2$-based phase that is not due to phasons nor to vacancy hopping. If there is any conclusion to be drawn from the apparent similarity of the results in the two samples, then it would be that the odds are against an interpretation of the QC signal in terms of phason hopping. But the authors counterbalanace this evidence by introducing two postulates: An observation of phason dynamics would be expected at low temperatures (2c-1) and $B2$-based phases contain phasonlike features (2c-2).

(2c-1) The accepted notion is that phason dynamics is *not* expected to be active at low temperatures. All available experimental data indicate that phasons freeze. The neutron data show that this freezing does not consist in an exponential increase of the jump time with decreasing temperature, but in an exponential decrease of the number of atoms that jump (with any relaxation time) at all. This indicates that observing phason dynamics at a given temperature is not just a matter of the time scale window that is accessible to the experimental technique. We may note that the theory of Jarić and Nelson for diffuse scattering[16] is based on the ansatz that phason dynamics is frozen, which is also at variance with

this postulate. In this context the assignment of the authors would also call for a complete rethinking of matters that have been directly linked to the validity of the random tiling model.

(2c-2) The second postulate is presented as a conclusion of the paper instead of a premiss, and serves to justify the claim that phasons are not as QC specific as is often believed. The pertinence of these issues has been discussed under points (1b) and (1c).

In conclusion, Dolinšek *et al.* have established the existence of some slow low-temperature motion in QC's and in AlCuNi. It is not possible to make a reliable assignment for their NMR signals, but not justified to associate them with phason dynamics.

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