Reply to "Comment on 'Atomic jumps in quasiperiodic Al$_{72.6}$Ni$_{10.5}$Co$_{16.9}$ and related crystalline material'"

Janez Dolinšek[1] and Jean-Marie Dubois[2]

[1]*J. Stefan Institute, University of Ljubljana, Jamova 39, SI-1000 Ljubljana, Slovenia*

[2]*LSG2M (UMR 7584), Centre d'Ingénierie des Matériaux, Ecole des Mines, Parc de Saurupt, F-54042 Nancy Cedex, France*

We clarify the issues raised in the preceding Comment [Phys. Rev. B **68**, 216201 (2003)] on the NMR-observed atomic dynamics in quasicrystals and related crystalline material.

This is our Reply to the Comment[1] on the above-noted paper[2] (hereafter referred to as I). In the Comment the author suggests that the magnetism of the decagonal *d*-AlNiCo quasicrystalline phase offers an alternative explanation of the dynamical nuclear magnetic resonance (NMR) signal observed in I. Below we consider this possibility. The NMR spectra of the investigated *d*-AlNiCo taken at two magnetic fields are displayed in Fig. 1(a). Solid circles represent the frequency-swept spectrum in a field 6.34 T (the "high-field" spectrum), whereas open circles represent the field-swept spectrum for the center field 2.35 T (the "low-field" spectrum). In both cases the origin of the frequency scale is taken at the ^{27}Al resonance frequency of the AlCl$_3$ aqueous solution. Three resonances are observed in the spectrum, ^{27}Al, ^{59}Co, and ^{63}Cu, where the last resonance originates from the copper in the probe head. The ^{27}Al (spin $I = 5/2$) spectrum exhibits a structure of a broad "background" line corresponding to first-order quadrupole-perturbed $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$ satellite transitions and a narrow, high-intensity central line ($1/2 \leftrightarrow -1/2$), quadrupole-perturbed in second order. A related structure applies also to the ^{59}Co ($I = 7/2$) spectrum. The electric-quadrupole origin of the large inhomogeneous broadening of the satellites is evident from its field independence. This is best seen on the positive frequency side of the ^{27}Al central line, where the satellite intensities of the high- and low-field spectra perfectly match. On the negative side this is less evident, as the ^{59}Co and the ^{27}Al spectra partially overlap and their satellite intensities between both central lines are superimposed (this is more pronounced in the low field, where the two resonances are closer together). The ^{27}Al spectrum extends in total over the frequency interval of about 8 MHz. Since this corresponds to $4\nu_Q$, this gives an estimate of the quadrupole coupling constant $\nu_Q \approx 2$ MHz, a very large value. The broadening of the ^{27}Al central line (that is quadrupole-perturbed in second order) shows, on the other hand, magnetic-field dependence [Fig. 1(b)]. The low-field central line (extending in total over 500 kHz) is about 2.5 times broader than the high-field one (extending over 200 kHz), in agreement with the second-order quadrupolar broadening that is inversely proportional to the external magnetic field. This factor of about 2.5 is consistent with the ratio 2.7 of the magnetic fields. Thus, the electric quadrupole broadening is by far dominant also on the central line. Further, the nonmagnetic nature of the *d*-AlNiCo is demonstrated by three effects: (i) the ^{59}Co spectrum [Fig. 1(a)] is centered about its Larmor frequency (63.7 MHz in the high field), demonstrating that cobalt is in a nonmagnetic state; (ii) the shift of the peak position of the ^{27}Al central line from the AlCl$_3$ frequency, and (iii) its full width at half height (FWHH) are independent of temperature (Fig. 2) between 300 and 4 K. In the presence of localized magnetic moments, even a diluted amount, both the shift and the width should exhibit a $1/T$ increase on cooling. These results give clear evidence that (1) the *d*-AlNiCo sample is nonmagnetic and (2) that the inhomogeneous broadening of
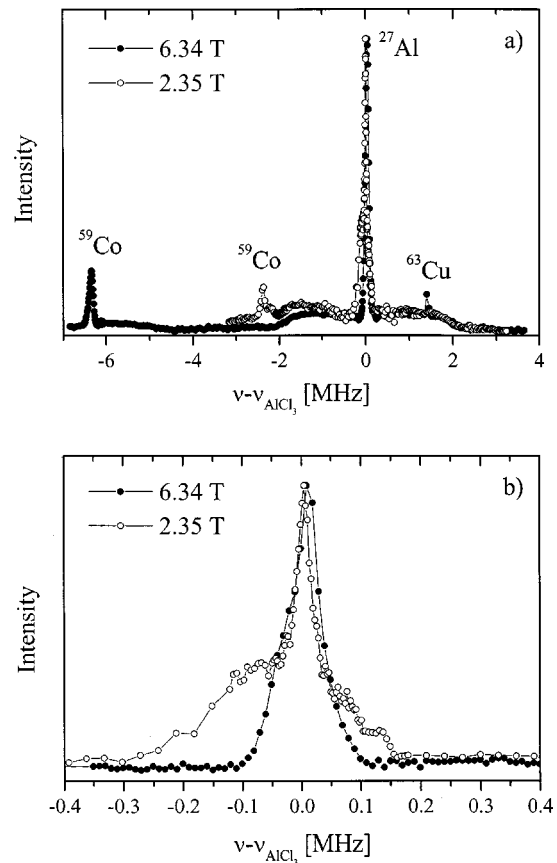

FIG. 1. (a) NMR spectra of the decagonal Al$_{72.6}$Ni$_{10.5}$Co$_{16.9}$ single-grain quasicrystal in two magnetic fields (solid circles: frequency-swept spectrum in a field 6.34 T; open circles: field-swept spectrum in a center field 2.35 T). (b) Central lines on an expanded frequency scale. The origin of the frequency scale is chosen at the ^{27}Al resonance of the AlCl$_3$ aqueous solution.
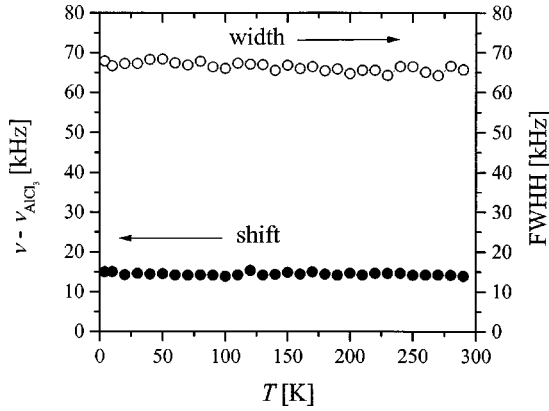
FIG. 2. Temperature dependence of the shift of the ^{27}Al central line peak position and its FWHH from 300 to 4 K (in the field 6.34 T).

the ^{27}Al central line is of the electric quadrupole origin, so that the possible magnetic origin of the dynamic NMR signal studied in I by the Carr-Purcell (CP) spin-echo technique can be discarded. The dynamic NMR signal is due to atomic motion (with kHz frequencies) in a spatially inhomogeneous electric field gradient. Here we mention that both substances investigated in I (the d-AlNiCo and AlCuNi) are diamagnetic.

In quasicrystals (QC's) containing magnetic atoms, such as Mn in AlPdMn or Fe in AlCuFe (where magnetic atoms in both substances are diluted), these moments produce local magnetic fields that introduce additional magnetic inhomogeneous broadening. The diffusive atomic motion in this additional inhomogeneous local magnetic field would just add to the spin-echo destruction, thus amplifying the diffusion echo attenuation. Experimentally we observed the same dynamical NMR signal (spin-echo destruction) due to atomic motions in the nonmagnetic systems d-AlNiCo (Ref. 2), AlCuNi (Ref. 2), and i-AlPdRe (Ref. 3) as well as in the magnetic i-AlPdMn (Ref. 4). Our analysis of the NMR signals was made in terms of the "effective" diffusion constant D_ω, which is a product of the true diffusion constant D and the frequency gradient square $(\nabla\omega)^2$, so that the additional magnetic contribution to the gradient just changes the value of D_ω (which is a fact of marginal importance, as the gradient $\nabla\omega$ is anyhow not known). What we analyze in our studies is the temperature dependence of D_ω, which, in a rough model, is assumed to follow that of the true diffusion constant D. We found consistently that D_ω exhibits weak temperature dependence in all samples studied [below 300 K in d-AlNiCo and AlCuNi in I and below 400 K in i-AlPdMn (Ref. 4)], demonstrating low-activation-energy character of the detected motions in the studied temperature range. In all cases D_ω showed a tendency towards a stronger T dependence above room temperature (see Fig. 3 of I and Fig. 3 of Ref. 4), indicating an increase of the activation energy. The raw experimental data of all samples are thus consistent.

On the basis of the above considerations, we can claim reliably that with NMR we detected slow, low-E_a, diffusive atomic dynamics at low and intermediate temperatures. As in a solid, the diffusion motion takes place by jumping over

lattice sites; it is also straightforward to assume that these processes are low-E_a, diffusive atomic jumps. The slow-motion frequencies of these jumps in the kHz range cannot be associated with usual atomic vibrations, which are at much higher frequencies. As correctly pointed out in the Comment, NMR is not specific on the jump distances and on which atomic species is jumping (what is observed is the relative motion of the resonant nuclei with regard to the rest of the lattice). From this point of view it is correct to say that the NMR-detected atomic jumps are *not* directly proven to be phason jumps. We are aware of that, but since the properties of the detected jumps—low-E_a and diffusive character—are also the properties attributed to phason jumps, we use in I instead of a direct claim "phason jumps" a more cautious statement "*compatible* with phason jumps." This is different from our earlier work on i-AlPdMn,[4] where we still used the direct claim. The reason there was the remarkable similarity between the temperature dependences of D_ω observed in the i-AlPdMn (Fig. 3 of Ref. 4) to the T dependence of the predicted Kalugin-Katz diffusion constant (Fig. 5 of Ref. 5) of the QC-specific phason-assisted diffusion. However, later observations in I that similar atomic jumps exist also in non-QC materials indicate that the data of Ref. 4 may have been overinterpreted.

A highly relevant issue is the fact that the existence of low-T atomic dynamical processes in icosahedral [i-AlCuFe (Ref. 6), i-AlLiCu (Ref. 7), and i-ZnMgY (Ref. 8)] and decagonal [d-AlNiCo (Ref. 9)] QC's was reported independently also by sound velocity experiments. These experiments relate the detected motions to the tunneling states (two-level tunneling states (TLS's) are mentioned, hence motion in double-well potentials). There is no direct evidence that the low-T TLS's are related to the high-T dynamics observed by neutrons. However, in the Comment it is correctly pointed out that it has still not been proved experimentally that tunneling states in QC's are not phasons. As phason jumps are thermally activated processes, also performed in double-well potentials, this offers seeds to consider the following link between the high-T and low-T dynamics. Phason jumps are by definition low-activation-energy processes, so that one may consider that some thermally activated hopping in double wells at high T survives to low T by transforming into tunneling. This crossover is an exciting question, and, in order to elucidate it, new experiments are needed that will span the total temperature range and not just probe the asymptotic ranges at high T (neutrons) and low T (ultrasound and NMR).

Our last point concerns the similarity of the experimentally detected atomic motions in d-AlNiCo and B$_2$-based τ phase of AlCuNi. From the theoretical considerations, a clear difference between the two cases is expected. In d-AlNiCo, the microscopic model of atomic jumps involves motion over the very open structure of "half-vacancy pipes" (this name and the related "columnar vacancies" were introduced by Yan *et al.*,[10,11] wherefrom also our notation of "vacant sites" used in I). These empty sites may be termed *phason sites*, but there is nothing quasicrystal-specific with these sites, as a very similar structural situation (too closely spaced sites to be occupied simultaneously) was found also in con-

ventional solids (e.g., $SrTiO_3$). The AlCuNi, on the other hand, is a ''vacancy-ordered'' material, where a large number (up to several at. %) of lattice sites are vacant due to stability reasons. The structure is again very open for jumping and the usual vacancy diffusion is expected to be the main atomic jump channel. These two very different materials were chosen for comparison on purpose, with the aim to compare a pure QC material (with nominally *no* vacancies in the usual sense) with a material where we *know* there is a large concentration of vacancies. This comparison was triggered also by the recent high-T neutron measurements,[12] which reported very similar activation energies for atomic jumps for the same two samples (for the d-AlNiCo Coddens and Steurer[13] report $E_a = 0.553$ eV, whereas for the AlCuNi $E_a = 0.60$ eV was reported by Dahlborg *et al.*[12]), where these values are also very close to both the activation energy of atomic migration (0.61 eV) and the activation enthalpy for single-vacancy formation (0.67 eV) in pure aluminum. Due to proximity of these values, caution should be taken when discriminating different atomic jump mechanisms from the experimental data. Though theoretical expectations give a clear hint that the jump physics of the two investigated samples should be fundamentally different, experiments do not give a clear distinction. We do not share the opinion

raised in the Comment that this similarity of E_a values is just a numerical coincidence; it is more likely that these figures are associated with similar atomic transfer processes.

As the NMR data (see Fig. 3 of I) show the same similarity in the atomic motion between the d-AlNiCo and AlCuNi (in this case in the low-T regime), and since NMR finds these motions to be of low-E_a and diffusive, this gives basis for our conclusion in I that ''though the detected atomic motions in d-AlNiCo are compatible with phason jumps, they are *not* QC specific.'' Again we use the cautious statement ''compatible with phason jumps'' and not the direct statement ''phason jumps.'' The experimental similarity between the d-AlNiCo and AlCuNi data makes us believe that the observed motion is a feature of close-packed structures—either periodic of quasiperiodic—that contain structural vacancies. By ''structural vacancies'' we mean unoccupied lattice sites of any origin, either due to usual vacancies or due to too closely spaced atomic sites that cannot be occupied simultaneously.

We hope that this discussion will catalyze future work on the atomic dynamics in QC's, which should lead towards a more complete understanding of this interesting phenomenon.

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