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COMMENT

Comment on 'Atomic motions in the crystalline $Al_{50}Cu_{35}Ni_{15}$ alloy'

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Abstract
It was recently stated that fast atomic jumps observed in quasicrystals are a common feature in metallic alloys. We explain why this is not correct.

Recently Dahlborg *et al* [1] stated that fast atomic jumps are 'not a special property for quasicrystals'. To remove the ambiguities inherent to this assertion, we would like to point out the following:

(1) Although fast atomic jumps may indeed not be *unique* to quasicrystals, it is just not true to suggest that they would not be exceptional.
(2) In order to put things into the right perspective, we must add to this that we consider a discussion in terms of the qualifiers 'special' or 'not special' as completely inappropriate in view of the scientific motivation of our work [2, 3], which was to answer the question: what is a phason in a quasicrystal?

Following the logic of reference [1] it may seem contradictory that atomic jumps are not 'special' in a solid, while phasons in quasicrystals are. The solution of this apparent paradox lies in the fact that an essential piece of information is missing in its formulation, namely that the *sites* that are visited by the quickly jumping atoms in a quasicrystal are somewhat uncommon, while those in a classical alloy are indeed in no way unusual. As a matter of fact, the 'phason sites' in a quasicrystal are neither interstitialcies nor vacancies as in a regular solid, because it is impossible to have two sites that are linked by a phason jump occupied simultaneously by atoms [4]. These sites have therefore in some cases been dubbed 'half-vacancies' by Gähler and Roth [5] and they do not have a counterpart in periodic solids. The 'phason jumps' are expected on the basis of all relevant structural models [6] and there is no reason to question our attribution of the quasielastic signals observed in terms of such jumps. We think that this is the main point. We must further take issue with a large number of points in the paper by Dahlborg *et al* that are wrong, ambiguous or lack precision.

Information on the temperature dependence is lacking in that paper. Should the temperature dependence in their sample turn out to be conventional rather than exceptional as in quasicrystals (a property reflected in the introduction of the terminology 'assisted'), then

the whole of the apparent similarity between their results and those on quasicrystals would disappear, while this alleged similarity serves as the sole and unique rationale for the authors' claim that the fast atomic jumps would be a common feature in alloys. A similar observation applies to the $\boldsymbol{Q}$-dependence of the signal (see below).

What Dahlborg *et al* also fail to stress is that their sample is really exceptional and untypical, i.e. that it cannot be considered as representative for alloys in general by any standards, in that it is a B2 phase and as such may harbour up to an incredible level of 12% structural vacancies [7], which could play some rôle in the jumping process itself or its possible assistance scenario. It is not by finding one single (probably equally exceptional) case in another solid that one proves that fast jumps would be a common feature in alloys provided that the temperature was high enough. Such an unfounded extrapolation (based on a single observation) runs contrary to the entire body of existing data on self-diffusion in metals, which is vast.

In fact, Kaisermayr *et al* [8] have recently studied the (*documented* and simpler class) of *archetypal* binary B2 phases by means of quasielastic neutron scattering experiments on NiGa. This B2 phase does not exhibit ultrafast ($\Gamma \approx 500$ μeV) atomic jumps. Despite the fact that they are described as exhibiting record-setting fast diffusion, two other alloys investigated by Vogl's group [8], namely Ni_3Sb and $Ni_{53}Sb_{47}$, also fail to comply with the predictions made by Dahlborg *et al*. Dahlborg *et al* introduce here also a proviso that one must consider as *ad hoc*, by restricting some of their claims to ternary Al-based alloys. In relation to this, we may also mention a previously reported experiment on α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$, where close to the melting point there was a total absence of evidence for hopping on the timescales accessible to the T.O.F. (time-of-flight) spectrometer MIBEMOL ($\hbar\Gamma \in [50, 250]$ μeV). This information has now been completed by Mössbauer spectroscopy data from Brand [9] and co-workers whose measurements do not reproduce the strong and rather abrupt change of slope in the temperature dependence of the Lamb–Mössbauer factor that one observes in AlCuFe quasicrystals and approximants, and which marks the onset of phason hopping [3]. We mentioned in previous papers the cases of Hf and β-Ti which are considered as examples showing extremely fast self-diffusion in metals, but which actually show self-diffusion two orders of magnitude slower than what one observes in quasicrystals. Hence all experimental results available except those reported by Dahlborg *et al* contradict the viewpoint that ultrafast atomic hopping would be a common feature for non-quasicrystalline alloys. It is precisely because they are so exceedingly fast (combined with intrinsic limitations on the signal/background ratios accessible in the methods that he used) that the phason jumps eluded detection in the surveys of Janot [15, 16], who (at that time quite reasonably) considered that only the techniques of Mössbauer spectroscopy and neutron backscattering would be viable candidates for unearthing a first fingerprint of this kind of dynamics.

Dahlborg *et al* state that positron annihilation experiments provide evidence for the existence of 'large' concentrations of thermal vacancies in quasicrystals, but do not cite more reliable results from Mössbauer spectroscopy [10] which contradict [4] these claims and suggest instead that these concentrations are not so high. Also, the fact that the diffusion constants in quasicrystals are rather low [11] corroborates the idea that thermal vacancies are not so abundant, independently of whatever might be the ultimate verdict on the importance of the Kalugin–Katz diffusion model [12] for self-diffusion in quasicrystals.

As Dahlborg *et al* argue that the fast jumps will occur whenever the vacancy concentration becomes high enough at elevated temperatures, one would be inclined to understand that the jumps are thermal-vacancy mediated, but the authors also claim that the jumping atoms are located on interstitialcies. If we nevertheless try to make sense of this, perhaps we should invoke a scenario of jumps between interstitialcies assisted by the passage of thermal vacancies in their neighbourhood. There is nothing against such an idea, but one could reasonably start

pondering such considerations only after having established that the temperature behaviour is of the 'assisted' type.

Dahlborg *et al* claim that the structure factor of the elastic scattering signal proves the existence of atomic jumps at 570 °C but that the relevant quasielastic intensity is not detected, probably as it cannot be observed under the prevailing conditions of experimental resolution. This is just wrong. If the signal is too narrow it will be integrated into the resolution-broadened 'elastic peak'. The structure factor of the effective sum of the elastic and quasielastic signals within this resolution-broadened 'elastic peak' will then (see equations (4) and (5)) be a constant (apart from the Debye–Waller factor), just as though there were no jumps at all. If the quasielastic signal is broad enough but too weak, then again the 'elastic' signal should have a constant structure factor, owing to the very same sum rule as we just invoked. To conclude this argument, let us point out that it would be far-fetched to suggest that the signal at 570 °C could be missed because it is too wide and therefore leads to a flat contribution, since (1) it cannot be upheld seriously that a jump process would be so fast that its detection would remain elusive under the experimental conditions used on MIBEMOL, and especially since (2) at higher temperatures, where it should *a priori* be even faster, it did not go undetected. Once this point has been made, we must come to the following conclusion: if the elastic intensity at 570 °C is modulated in the absence of quasielastic intensity, then the elastic intensity at 920 °C cannot be used to draw conclusions about the quasielastic intensities—as is done in figure 8 of the paper by Dahlborg *et al*, where they are based on a misinterpretation of an elastic signal that is due to *static* short-range order [13]. A whole chain of conclusions on the geometry of the jumps has been built on this analysis.

Recent additional results indicate that the atomic jumps in AlMnPd are correlated [14]. There are no analogous results available for the B2 phase (see above). The very unusual character of these correlations in QC further emphasizes that a comparison between B2 phases and QCs is partial when it uniquely focuses on a similarity of the jump rates. In this context, we should mention that the statement by Dahlborg *et al* that we would have observed correlations in AlCuFe is erroneous. It is based on a misunderstanding of the paper cited [14], where figure 2 was only illustrating one possible example of an assistance scenario among many other alternative possibilities discussed in the same paper. There is nothing in the AlCuFe data that enables us to decide whether there are correlations between jumps or not. We must further point out that if correlations of the type illustrated in that figure were present in AlCuFe, then they could not produce the collective effects uncovered in AlMnPd, which require a much more unusual mechanism.

Dahlborg *et al* state that their claims that fast atomic jumps are a common feature in alloys at high temperatures are confirmed by results of Mehrer's group, but on consulting the papers cited, the reader will notice that there is no experimental evidence of this type at all in these references [11].

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