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Short Communication

Evidence for Atomic Hopping of Fe in Perfectly Icosahedral AlFeCu Quasicrystals by ^{57}Fe Mössbauer Spectroscopy

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Abstract. — By ^{57}Fe Mössbauer spectroscopy in a special experimental set-up we have shown the existence of Fe atomic jumps in $\text{Al}_{62}\text{Fe}_{25.5}\text{Cu}_{12.5}$ perfect icosahedral quasicrystals. The (preliminary) results indicate that at 790 °C 20% of the Fe atoms are jumping at a time scale corresponding to 4 μeV .

1. Introduction

In quasicrystals there are two kinds of dynamics, *viz.* conventional phonons and so-called phasons ⁽¹⁾. In quasicrystals these “phasons” are not dynamical modes but atomic jumps. Their study is important for the understanding of many basic issues in quasicrystallography, e.g., stability (within the context of the random tiling model [2]), phase transitions (for which phasons could be a driving mechanism), a novel type of diffusion process (as anticipated by Kalugin and Katz [3]), and even structural studies. Despite this importance, experimental evidence for their existence has remained scarce. This is predominantly due to the difficulty of the experiments.

Previously, we [1] have performed studies by time-of-flight inelastic neutron scattering on AlFeCu quasicrystals revealing the existence of a Lorentzian quasi-elastic signal that could be interpreted in terms of atomic jumps. The temperature and Q -dependence of the signal were reported and it has been shown by isotopic substitution that the observed signal was entirely due to Cu motion. The results of reference [1] raised several questions, which will be discussed

⁽¹⁾ The terminology “phasons” was adopted due to an analogy with incommensurate systems, which are just like quasicrystals described by a method of cut and projection in a high-dimensional superspace. But in reality, this analogy is very misleading (as has been discussed in the past [1]) and the world-wide established adoption of the terminology “phasons” has to be considered as rather unfortunate.

in a separate paper [4]. One of them is why Fe jumps were not observed in these and other experiments [5].

2. Experimental Procedures and Results

In the present communication we settle this question by reporting ^{57}Fe 14.41 keV γ -ray Mössbauer spectroscopy results on atomic jumps in perfectly icosahedral $\text{Al}_{62}\text{Fe}_{25.5}\text{Cu}_{12.5}$. The standard Mössbauer approach as used in reference [5] has two serious drawbacks, *viz.* the energy resolution (which is too good) and the poor signal/noise ratio, which is inherent in a transmission experiment. The problem of the energy resolution can be tackled by using high Doppler velocities. We used 161 mm/s in our experiments. But this, in turn, raises the question of the velocity calibration, as the usual technique based on a measurement of the well-known hyperfine splitting in Fe can no longer be adopted due to the small energy range that is spanned by these lines. In fact, at such high transducer speeds the six lines merge into one single central line. The calibration problem was solved by using a laser interferometer as described in reference [6]. The origin of the poor S/N ratio can be understood as follows. Let the average number of counts per channel in the far off-resonance region be $\mathcal{N}$. Assume the maximum absorption at the elastic peak position amounts to a fraction f , i.e., the depth of the elastic line is $f\mathcal{N}$. Even if, e.g., 20% of the Fe atoms are jumping, the depth $cf\mathcal{N}$ of the quasielastic line will be only of the order $c = 0.01$ or less, if this line is very broad. The number $cf\mathcal{N}$ has to be detected against the background of the off-resonant counting statistics $\sqrt{\mathcal{N}}$, i.e., one needs $cf\mathcal{N} > \sqrt{\mathcal{N}}$ or $\mathcal{N} > (\frac{1}{cf})^2$. This calculation suggests to try to improve the contrast by using thicker samples. However, routinely the sample thickness is already optimised so as to take into account competitive interactions (such as Rayleigh scattering and photo-electric effect) and background counts due to Compton events within the detection window of the (Kr gas-proportional) counter, from higher energy γ -rays, *viz.* 85% 122 keV and 11% 136.5 keV γ -rays from the ^{57}Co ϵ -decay. This compromise is normally calculated such that the shape of the elastic line is not distorted due to self-shielding effects and that one can use samples with natural Fe. This analysis shows that we can gain in contrast by a factor of $2085 = (1/a)^2$ (with $a = 0.0219$ the natural abundance of ^{57}Fe) in the far off-resonance region by using 100% ^{57}Fe -enriched samples. For sure, this will jeopardise completely the elastic line shape, but this is of no concern if one wants to detect any possible quasi-elastic signal.

With these improved S/N and velocity conditions we have performed Mössbauer scans at temperatures T of 786 °C, 720 °C, 660 °C, and 20 °C. Further details on the experimental set-up and the general principles of the use of Mössbauer spectroscopy to study self-diffusion in metals and metallic alloys have been reported elsewhere [7]. The wavevector modulus Q corresponds to $7.28 \text{ \AA}^{-1}$. The thickness of the sample was typically 15.3 mg/cm^2 (this figure corresponds to the whole sample, not only iron). It was encapsulated in a thin BeO container. The ^{57}Fe enrichment in the sample used was 95.2%. The sample was not taken from the powders that were sed previously for studies of atomic hopping [1] and for structure determinations [8] by neutron scattering techniques, but they were prepared using the same experimental procedures. Heating the sample beyond 750 °C has two effects, *viz.* it undergoes substantial sintering and there is a gradual formation of β -phase unless the container is made from alumina (which was not feasible in the present experiment). However, it has been checked that the transformation does not affect the jump behaviour, in the sense that the quasi-elastic signal is not dependent on the thermal history of the sample. A similar conclusion had been reached in time-of-flight neutron scattering experiments on the rhombohedral $\rightarrow$ icosahedral transition in $\text{Al}_{62.5}\text{Cu}_{26.5}\text{Fe}_{11}$ [9]. This result is easily understood if one realises that the

Fig. 1. — Low transducer speed Mössbauer spectrum of a non-isotopically enriched sample. The fit with two Lorentzians is not appropriate to describe the quadrupole splitting, as discussed in the text.

Fig. 2. — Residuals of the fit of the elastic line for the Mössbauer data from the 660 °C run. The levels of 0.5% of the total off-resonant intensity above and under the base line are shown. The off-resonance counts are scattered symmetrically around the base line.

jumps are observed on a local scale and that in the related phases the short-range order is identical. Nevertheless, in view of our concern about the quality of the data, the samples have been refreshed regularly after a heating above 750 °C. The Mössbauer spectra have been fitted in two steps. First, the central line is fitted with a shape that allows for two Lorentzian

Fig. 3. — a) Residuals of the fit of the elastic line for the Mössbauer data from the 780 °C run. A systematic deviation from the baseline is observed that can be fitted with a Lorentzian shape of roughly $4 \mu\text{eV}$ width and 20% of the elastic intensity; b) Fit of the total intensity with three Lorentzians. The levels of 0.5% of the total off-resonant intensity above and under the base line are shown in both parts.

contributions (in order to take into account the effects of quadrupole splitting). In principle, such an analysis is not correct, as has been described by Stadnik and Stroink [10] (and shown in Fig. 1) for a normal low velocity run on a sample made with natural Fe. Mössbauer results

were reported on samples *of the same origin* and fitted in the same way in [11]) ⁽²⁾. In the present deteriorated experimental conditions for the elastic line shape, this procedure, which also takes the respective isomer shifts into account, works perfectly at 660 °C, resulting in a fit as shown in Figure 2.

At high temperatures though, the residuals clearly reveal a systematic deviation, evidencing the existence of a third component. A spectrum at 786 °C is shown in Figure 3. This effect cannot be an artifact of the fit (as has been checked by trying extreme values for the parameters) as it is too broad, and disappears on lowering the temperature. It is reproducible and showed also up in lower velocity runs at 100 mm/s and 150 mm/s. Some low and high temperature runs were done under *strictly identical conditions*, i.e., without touching the experimental set-up during and in between the data acquisitions. By fixing the parameters of the central lines the shape of the broad quasielastic (Lorentzian) signal can be determined.

3. Discussion

The quality of these preliminary data is not sufficient to draw quantitative conclusions from such fits. The elastic line intensity is strongly affected by self-shielding effects. On the other hand the baseline intensity has to be corrected for non-resonant counts. A detailed investigation will require a different experimental set-up with a fresh source and enhanced geometry to optimise the counting rates by a factor of 10. But it can be stated already now that the results of [5] on the Debye-Waller factor can probably be explained in terms of phason jumps without having to refer to speculations about cluster vibrations. Our data show that our previous interpretation of the quasi-elastic neutron scattering spectra in terms of atomic hopping is correct; no other physical explanation can properly account for such vastly different time scales in the Fe and Cu dynamics. A neutron scattering experiment with a resolution of 1–2 μeV using ($^{65}\text{Cu}/^{\text{nat}}\text{Cu}$) isotopic substitutions should be able to show that this signal is purely due to iron jumps [13]. Similar neutron scattering experiments on AlPdMn powders and single crystals should be very interesting [13].

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