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^{57}Fe Mössbauer study of icosahedral $Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and its 1/1 approximant

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Abstract

The icosahedral $Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ alloy and its 1/1 approximant of the same composition have been studied with ^{57}Fe Mössbauer spectroscopy (MS) in the temperature range 4.4–473.2 K. The average quadrupole splitting decreases with temperature as $T^{3/2}$ for both alloys and its value is significantly larger for the icosahedral alloy. The vibrations of the Fe atoms in both alloys are well described by a simple Debye model, with characteristic Mössbauer temperatures of 454(22) and 491(25) K for the icosahedral and approximant alloys. The local properties measured by zero-field ^{57}Fe Mössbauer spectroscopy are insensitive to the different nature of the long-range order, quasicrystalline vs. crystalline, in the investigated alloys.

Keywords: Icosahedral alloy; 1/1 approximant; Mössbauer spectroscopy; Debye temperature

1. Introduction

Quasicrystals (QCs) are a new form of the solid state which differs from the other two known forms, crystalline and amorphous, by possessing a new type of long-range translational order, *quasiperiodicity*, and a noncrystallographic orientational order associated with the classically forbidden symmetry axes. A central problem in condensed-matter physics is to determine whether quasiperiodicity leads to physical properties which are significantly different from those of crystalline and amorphous materials of the same/similar compositions.

The physical properties of QCs, and especially their electronic transport properties, are very unusual [1] and there has been a tendency to associate them with the quasiperiodic nature of these materials. However, it was found that equally unexpected electronic transport properties occur in the corresponding crystalline approximants to these QCs [2–4].

Physical properties of icosahedral (i) QCs in the Al–Cu–Fe system and of their approximants of the same compositions were also studied with ^{57}Fe MS and ^{27}Al and ^{65}Cu nuclear magnetic resonance (NMR) [5–8]. No changes in the various physical parameters measured by these techniques could be found between i-Al–Cu–Fe alloys and their approximants of the same compositions. It was concluded that local properties measured by ^{57}Fe MS and ^{27}Al and ^{65}Cu NMR are insensitive to the nature of the long-range order [5–8].

Recently Quivy et al. [9] reported that an i phase forms in the quaternary system Al–Si–Cu–Fe by liquid quenching. This phase transforms into the crystalline 1/1 approximant by annealing it at 923–953 K. Here we report on ^{57}Fe MS studies of i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and its 1/1 approximant. We demonstrate that there is a small, but significant, difference between the average values of the quadrupole splitting in these two alloys. However, other local physical properties are the same within the experimental error.

2. Experimental procedure

The i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ alloy and its 1/1 approximant were prepared as described elsewhere [10]. The X-ray diffraction study showed that the samples are single phase. The Rietveld analysis of the X-ray diffraction spectrum of the 1/1 approximant showed that this alloy has a cubic lattice [a=12.336(7) Å] with the space group $Pm\bar{3}$ [10].

^{57}Fe MS measurements were performed in the temperature range 4.4–473.2 K using a standard Mössbauer spectrometer operating in a sine mode. The spectrometer was calibrated with a 6.35 μm Fe foil [11], and the spectra were folded. Mössbauer absorbers were prepared by

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mixing the powdered alloys with powdered BN to ensure a uniform thickness of the absorbers and the random orientation of sample particles. This mixture was then put into a plastic sample holder for low- and room-temperature measurements and into a BN holder for high-temperature measurements. The surface densities of the Mössbauer absorbers corresponding to the i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ alloy and its 1/1 approximant were, respectively, 87×10^{-3} and 92×10^{-3} mg ^{57}Fe cm^{-2}. This corresponds to the effective thickness parameter [12] at room temperature of 1.89 and 2.06 (using the values of the absorber Debye–Waller factors of 0.8032 and 0.8276 determined below), respectively. As the resulting Mössbauer spectra are due to a multiple of elementary quadrupole doublets, the effective thickness parameter spreads over them and therefore the absorbers can be regarded as being thin [12].

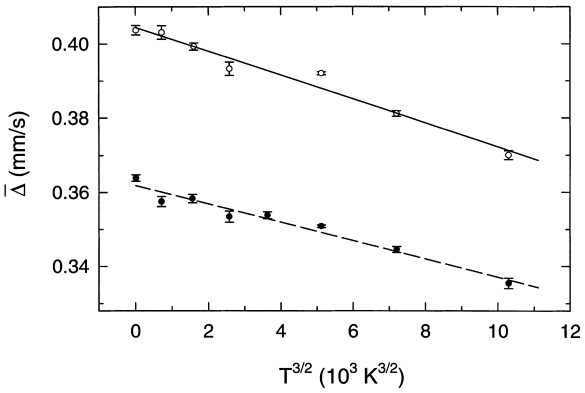

Fig. 2. Temperature dependence of the average quadrupole splitting of i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ (open circles) and its 1/1 approximant (closed circles). The solid and broken lines are the fits to the equation $\bar{\Delta}(T) = \bar{\Delta}(0) - BT^{3/2}$, as explained in the text.

3. Results and discussion

Mössbauer spectra of the i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ alloy and its 1/1 approximant (Fig. 1(a) and (b)), similar to the spectra of other nonmagnetic i alloys [13], consist of a broadened asymmetric doublet which results from the distribution of the quadrupole splittings, $P(\Delta)$. These spectra were fitted with the constrained version [14] of the Hesse–Rübartsch method [15]. A slight asymmetry of the spectra was accounted for by assuming a linear relation between the centre shift δ, and Δ of the elementary doublets [13]. Satisfactory fits, as judged by the values of χ^2 and by the residuals (Fig. 1(a) and (b)), were obtained for the distributions $P(\Delta)$ shown in Fig. 1(c). The presence of wide distributions $P(\Delta)$ for both alloys indicates the presence of quasi-continuous distributions of local environments in the studied alloys.

The distribution $P(\Delta)$ is directly related to the local atomic structure [13]. There is a small, but significant, difference between $P(\Delta)$ corresponding to i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and its 1/1 approximant (Fig. 1(c)). This shows that, as expected, the local atomic structure of these two alloys is slightly different. In principle, the experimentally determined distribution $P(\Delta)$ could be used to narrow down the possible structural models for the i-Al–Si–Cu–Fe system. This would require band-structure calculations of the electric-field-gradient tensor for a given structural model, which is challenging [16,17].

The distributions $P(\Delta)$ similar to those in Fig. 1(c) were determined from the fits of the spectra of i-$Al_{55}Si_7Cu_{25.5}$-$Fe_{12.5}$ and its 1/1 approximant measured at other temperatures. The temperature dependence of the average value of the quadrupole splitting $\bar{\Delta}$ could be fitted (Fig. 2) to the equation $\bar{\Delta}(T) = \bar{\Delta}(0) - BT^{3/2}$, where $\bar{\Delta}(0)$ is the value of $\bar{\Delta}$ at 0 K and B is a constant. Such a temperature dependence has been observed in many noncubic metallic alloys

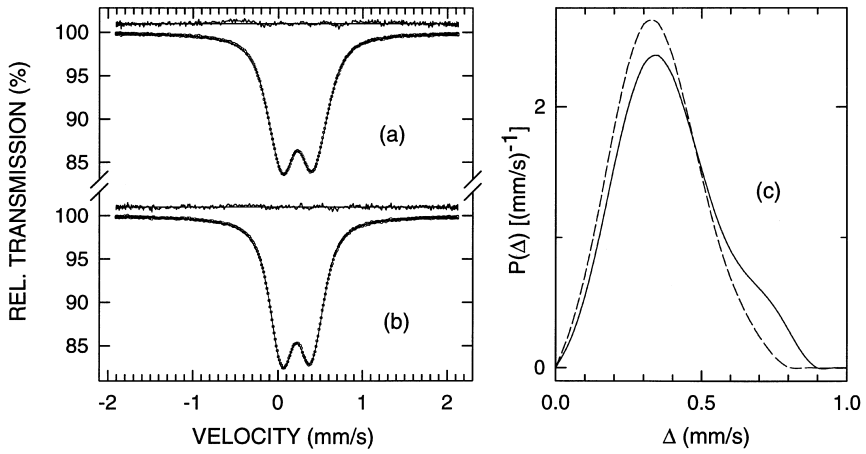

Fig. 1. ^{57}Fe Mössbauer spectra measured at 297.2 K of (a) i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and (b) its 1/1 approximant fitted (solid line) with the distribution $P(\Delta)$ shown in (c) (solid and broken lines, respectively). The residuals, multiplied by a factor of three, are shown above each spectrum.

[18–20]. The values of $\bar{\Delta}(0)$, B determined from the fits for i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and its 1/1 approximant are, respectively, 0.4044(13) mm s^{-1}, 7.97(61)$\times 10^{-6}$ K$^{-3/2}$ mm s^{-1} and 0.3619(8) mm s^{-1}, 6.86(53)$\times 10^{-6}$ K$^{-3/2}$ mm s^{-1}. It can be concluded that although the temperature dependence of $\bar{\Delta}$ in i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and its 1/1 approximant is the same within the experimental error, the values of $\bar{\Delta}$ are significantly different.

The average centre shift at temperature T, $\bar{\delta}(T)$, determined from the fits of the spectra of i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and its 1/1 approximant (Fig. 1) is given by $\bar{\delta}(T) = \delta_I + \delta_{SOD}(T)$, where δ_I is the intrinsic isomer shift and $\delta_{SOD}(T)$ is the second-order Doppler shift which depends on lattice vibrations of the Fe atoms [12]. The second-order Doppler shift is insensitive to the details of the real vibrational spectrum. Nevertheless, it is often possible to extract information about the vibrations of the Fe atoms in structurally related compounds. In terms of the Debye approximation for the lattice vibrations, $\delta_{SOD}(T)$ is expressed by the characteristic Mössbauer temperature Θ_M [21,22]. The characteristic Mössbauer temperature Θ_M is distinct from the Debye temperature determined from specific heat measurements, which is based on a different weight of the phonon frequency distribution [22]. By fitting the experimental data $\bar{\delta}(T)$ to the expression $\bar{\delta}(T) = \delta_I + \delta_{SOD}(T)$ (Fig. 3), the quantities δ_I and Θ_M can be determined. They are 0.3277(28) mm s^{-1}, 454(22) K and 0.3283(33) mm s^{-1}, 491(26) K, respectively, for i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and its 1/1 approximant. The corresponding values of the Debye–Waller factors for these two alloys at room temperature (297.2 K) are 0.8032(35) and 0.8276(31).

The values of δ_I are the same within the experimental error for i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and its 1/1 approximant. As δ_I is the measure of the s electron density at the nucleus [12], the same values of δ_I indicate that electronic properties of i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and its 1/1 approximant are very similar. It is surprising that the temperature dependence $\bar{\delta}(T)$ (Fig. 3) can be well accounted for within the frame of a simple Debye model of lattice vibrations of the Fe atoms.

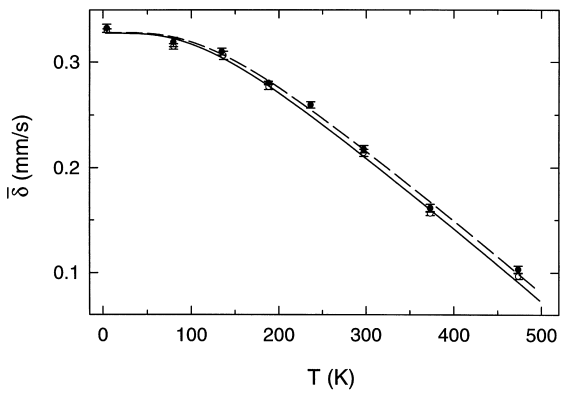

Fig. 3. Temperature dependence of the average centre shift of i-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ (open circles) and its 1/1 approximant (closed circles). The solid and broken lines are the fits to the equation $\bar{\delta}(T) = \delta_I + \delta_{SOD}(T)$, as explained in the text.

4. Conclusions

Local properties of the icosahedral $Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ alloy and its 1/1 approximant of the same composition have been studied with ^{57}Fe MS. A small, but significant, change has been found in the value of the average quadrupole splitting for these two alloys. This indicates a different local atomic structure in these alloys. The temperature dependence of the average quadrupole splitting follows the $T^{3/2}$ dependence characteristic for metallic alloys. The lattice vibrations of the Fe atoms in both alloys are well described by a Debye model with the characteristic Mössbauer temperatures of 454(22) and 491(25) K. No unusual properties which could be associated with the quasiperiodic nature of the icosahedral $Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ alloy have been found.

Acknowledgements

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