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Mössbauer studies of $Al_{75}Cu_{15-x}Fe_xV_{10}$ icosahedral alloys

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^{57}Fe Mössbauer effect measurements have been performed at room temperature on the alloy series $Al_{75}Cu_{15-x}Fe_xV_{10}$ with $x = 0.15$ (amorphous and icosahedral phases), 3 and 6 (icosahedral phases). There is more disorder in the icosahedral phase of the $x = 0.15$ alloy than in its amorphous phase. The bimodal character of the distribution of quadrupole splittings becomes less pronounced with increasing x and disappears for $x \geq 6$. This is interpreted in terms of two classes of transition metal sites in Al-transition metal-based icosahedral alloys.

1. Introduction

Despite extensive theoretical and experimental effort, the problem of the exact microscopic structure of icosahedral alloys (IA) remains an open question. It is very difficult to distinguish between different competing structural models using only diffraction experiments since the differences in predictions of these models are often smaller than the actual resolution of the diffraction experiments. The local probes, such as NMR, EXAFS, or Mössbauer effect (ME), are therefore potentially useful in elucidating structural characteristics of IA.

It is expected that long-range quasiperiodic order and long-range orientational order, which are inherent to IA and other quasicrystals, should lead to novel physical properties found neither in crystalline nor in amorphous alloys. Recent experimental studies show that indeed such properties are observed in some IA [1]. In order to establish any possible unusual features in the physical properties of IA, it is useful to compare them to the properties of corresponding crystalline and/or amorphous alloys, preferably of the same composition [2].

Ternary alloys of the composition $Al_{75}Cu_{15}V_{10}$ can be produced in the amorphous phase, and then transformed into the icosahedral phase by annealing [3]. In this paper, we report the results of ^{57}Fe ME studies at room temperature of the icosahedral series $Al_{75}Cu_{15-x}Fe_xV_{10}$ for $x \leq 6$. Results of extensive X-ray diffraction (XRD), differential thermal analysis, magnetic susceptibility, and 4.2 K and room temperature ME studies for the compositions $0 \leq x \leq 15$ will be published elsewhere [4].

2. Experimental

Ingots of $Al_{75}Cu_{15-x}Fe_xV_{10}$ with $x = 0.15$, 3, and 6 were prepared by arc melting of high-purity elemental constituents in an argon atmosphere. For the composition $x = 0.15$, the iron metal used was enriched to 95% in the ^{57}Fe isotope. To ensure homogeneity of the ingots, they were remelted several times. They were next melt spun in a helium atmosphere by ejecting molten alloy through a 0.7 mm orifice in a quartz tube, with about 50 kPa overpressure of argon, onto the surface of a rotating copper wheel 15 cm in diameter. The tangential velocity of the wheel was 75 m/s for the $x = 0.15$ and 67 m/s for the $x = 3$ and 6 alloys. To obtain an icosahedral phase for the $x = 0.15$ composition, the amorphous ribbons were annealed in vacuum at 820 K for 300 s.

^{57}Fe ME measurements were performed at room temperature using a standard Mössbauer spectrometer operating in a triangular or a sine mode. The spectrometer was calibrated with a 12 μm Fe foil, and the spectra were folded. The surface densities of the Mössbauer absorbers corresponding to $x = 0.15$ (amorphous and icosahedral), 3, and 6 were, respectively, 51.0×10^{-3}, 51.3×10^{-3}, 40.4×10^{-3}, and 61.1×10^{-3} mg ^{57}Fe/cm^2; the absorbers can therefore be regarded as thin ones.

3. Results and discussion

The analysis of the XRD spectra shows [4] that the $x = 0.15$ sample produced by rapid quenching is in a single-phase amorphous state, and that the sample obtained from it by annealing is a single-phase icosahedral alloy. The samples $x = 3$ and 6 produced by rapid quenching are in a mostly single icosahedral phase [4].

The Mössbauer spectra of the studied samples (figs. 1 and 2) show a doublet structure with broad lines characteristic for amorphous alloys and IA, which indicates the existence of the distribution $P(\Delta)$ of the quadrupole splittings Δ. While the spectra of the $x = 3$ and 6 samples are very similar (fig. 2), those of the amorphous and icosahedral samples $x = 0.15$ (fig. 1) differ significantly.

The Mössbauer spectra were analyzed using a constrained version [6] of the Hesse–Rübartsch method [7] and assuming a linear relationship $\delta = \delta_0 + a\Delta$ between the isomer shift δ (relative to α-Fe) and Δ, where δ_0 and a are fitted parameters. The linewidth Γ of component doublets of the distribution $P(\Delta)$ was also fitted since the commonly used procedure of fixing it to an a priori chosen value may lead to spurious features in $P(\Delta)$ [5]. The values of relevant parameters obtained from the fit are given in table 1 and the derived $P(\Delta)$ are presented in fig. 3.

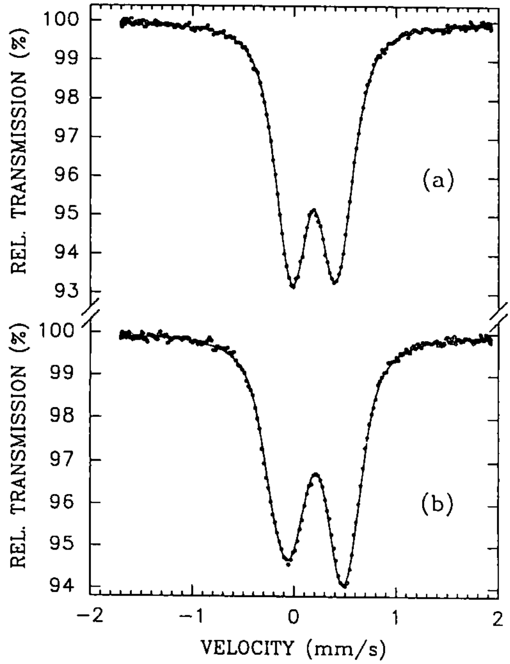

Fig. 1. ^{57}Fe Mössbauer spectra of amorphous (a) and icosahedral (b) $Al_{75}Cu_{14.85}Fe_{0.15}V_{10}$ alloys. The solid line is a least-squares fit, as explained in the text.

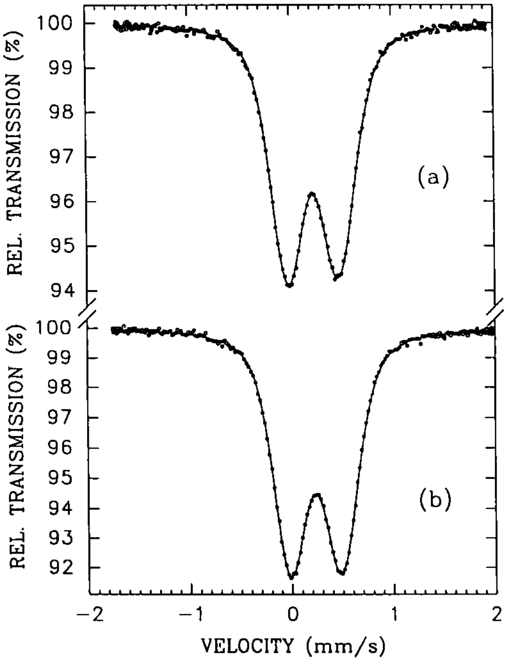

Fig. 2. ^{57}Fe Mössbauer spectra of icosahedral $Al_{75}Cu_{12}Fe_3V_{10}$ (a) and $Al_{75}Cu_9Fe_6V_{10}$ (b) alloys. The solid line is a least-squares fit, as explained in the text.

Table 1

Parameters determined from the fits of the spectra in figs. 1 and 2. The meaning of parameters is described in the text and χ^2 is defined in the usual way [8].

x	$\bar{\Delta}$ (mm/s)	δ_0 (mm/s)	$a \times 10^3$	$\bar{\delta}$ (mm/s)	Γ (mm/s)	χ^2
0.15 [a)]	0.449(1)	0.190(2)	6.2(1.0)	0.192(3)	0.222(1)	1.048
0.15 [i)]	0.572(3)	0.242(2)	- 65.8(1.5)	0.205(3)	0.261(1)	1.768
3	0.510(20)	0.216(2)	12.4(1.5)	0.222(3)	0.213(1)	1.057
6	0.508(13)	0.232(2)	5.2(1.2)	0.235(3)	0.230(1)	1.299

[a)] Amorphous phase.

[i)] Icosahedral phase.

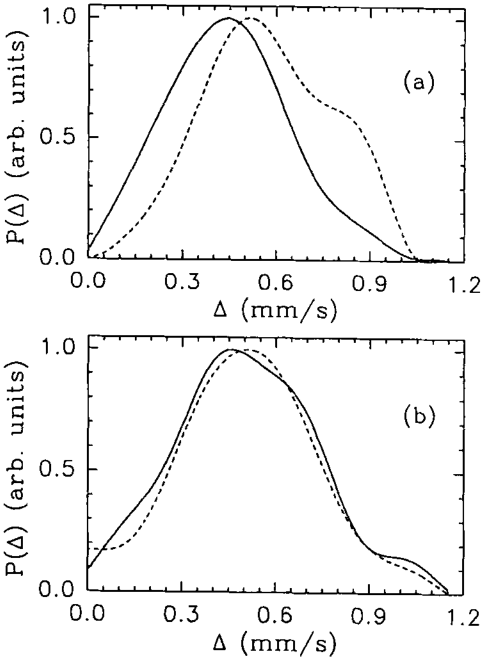

Fig. 3. The distribution function $P(\Delta)$ corresponding to the fits in figs. 1 and 2 of (a) amorphous (solid line) and icosahedral (broken line) $Al_{75}Cu_{14.85}Fe_{0.15}V_{10}$ alloys, and icosahedral (b) $Al_{75}Cu_{12}Fe_3V_{10}$ (solid line) and $Al_{75}Cu_9Fe_6V_{10}$ (broken line) alloys.

Although disorder is an intrinsic property of IA, as evidenced by the presence of $P(\Delta)$ even in the high-quality thermodynamically stable Al–Cu–Fe IA with no phason strain [8–10], one would expect to find for a given alloy larger values of

$\bar{\Delta}$ and broader $P(\Delta)$ for its amorphous phase than for its icosahedral phase. This has indeed been observed experimentally [9-11]. The reverse is observed for the $x = 0.15$ sample (table 1 and fig. 3(a)). This is a puzzling result which requires further study.

It is evident from the $P(\Delta)$ shape for the icosahedral $x = 0.15$ alloy (fig. 3(a)) that it has a bimodal structure, which becomes less pronounced for the $x = 3$ alloy and disappears for the composition $x \geq 6$ (fig. 3 and ref. [4]). One can tentatively explain this behaviour using the notion of two separate *classes* (not to be confused with two distinct sites [4,5,8]) of transition metal (TM) sites in Al-TM-based IA [12], and taking into account some recent experimental support [12,13] for the possibility that *very small* amounts of Fe atoms substitute randomly for TM atoms, i.e. they enter into both classes of sites, whereas for larger Fe concentrations, they preferentially enter only one class of sites. The bimodal character of the $P(\Delta)$ shape for the icosahedral $x = 0.15$ alloy is also consistent with the EXAFS studies of icosahedral $Al_{82}Cu_7V_{11}$ [14], which demonstrates the presence of the asymmetrical Cu-Al radial distribution function.

Acknowledgements

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