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Structure of icosahedral Al-(M_{1-x}Fe$_x$) alloys (M = Cr, Mn, or Fe)

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Isomer shift and quadrupole splitting data from Mössbauer spectra of icosahedral Al-Fe alloys are interpreted in terms of local iron environment, Al-Fe distances, and local symmetry of the iron sites. A Mackay cluster is proposed that can fulfill these conditions.

Rapid solidification of Al alloyed with about 14 at.% Mn, Fe, or Cr may produce quasicrystals with the icosahedral point-group symmetry $m\bar{3}\bar{5}$.[1] A number of mathematical models have been presented for explaining the supposed incompatibility of fivefold rotational symmetry with long-range positional order.[2] The question "Where are the atoms?" put forward by Bak[3] is difficult to answer, because the presence of fivefold symmetry axes inhibits long-range periodicity. Thus diffraction techniques are of limited value for positioning the atoms. Experimental techniques, such as nuclear magnetic resonance (NMR),[4] extended x-ray-absorption fine structure (EXAFS),[5–7] and Mössbauer-effect (ME)[8–10] studies on icosahedral alloys containing Al, Mn, and Fe have produced additional information about the local structure around central Al, Mn, and Fe atoms. These investigations suggest that at least two distinct or possibly a wide distribution of Mn (or Fe) environments exist.

We report here on a ME study of a series of icosahedral Al-(M_{1-x}Fe$_x$) alloys, where M = Cr, Mn, or Fe. We will show that in particular the investigation of isomer shift (IS) and quadrupole splitting (QS) values measured for this series produces relevant information for the discussion of the local structure in icosahedral alloys.

Icosahedral alloys were prepared by using the melt spin techniques. Molten alloys of composition Al$_6$(M), Al$_5$(M), Al$_4$(M) (M = Cr, Mn, Fe), and Al$_6$($M_{0.7}$Fe$_{0.3}$) (M = Cr, Mn), and Al$_6$(Mn$_{0.3}$Fe$_{0.7}$) were rapidly quenched onto the outer surface of a rotating wheel. For each composition the effect of different circumferential disk speeds on the structure was studied. The fivefold symmetry was checked by angular dispensive x-ray diffraction (ADXD) and for some samples by transmission electron microscopy (TEM) and energy dispersive x-ray diffraction (EDXD).

In summarizing the investigation for icosahedral content of the ribbons produced, we found that for all Al-(M_{1-x}Fe$_x$), x = 0, 0.3, 0.7, and 1.0 the icosahedral phase can be prepared. However, this phase always coexists with fcc Al in the ribbons. In addition to these two phases, a third phase may be present for M = Mn. This is the decagonal T phase.[11] The existence of the decagonal phase may best be indicated by the presence of an ADXD peak at $q = 2.80$ Å^{-1}, because this is the most intense decagonal peak that does not overlap the icosahedral peaks.[12] For melts with $x = 0$, i.e., Al$_6$Mn, Al$_5$Mn, Al$_4$Mn, this peak is clearly visible although very weakly for the highest wheel speed of 45 m/s. This is in agreement with previous observations.[13,14] For melts with $x = 0.3$ and $x = 0.1$, the 2.80 Å^{-1} peak is generally not observed for wheel velocities larger than 30 m/s. However, even then, it is by no means certain that the decagonal phase is absent from the specimen because the main decagonal peak is much more intense than the peak at 2.80 Å^{-1}. The main decagonal peak consists of four overlapping peaks at q = 3.00, 3.02, 3.04, and 3.07 Å^{-1} (Ref. 12) that overlap the strong (110000) icosahedral peak located at 3.043 Å^{-1}. Therefore a decagonal contamination in icosahedral samples may only be observed as a broadening of the (110000) peak. Since broadening of icosahedral peaks may also be caused by frozen-in phason strain or random icosahedral packing,[15–17] the complete absence of the decagonal phase in icosahedral samples is difficult to verify from ADXD investigations.

The preparation of icosahedral Al-Fe alloys has been discussed elsewhere.[10] Also for these alloys the possibility exists that a decagonal phase coexists with the icosahedral phase and fcc Al.

For the case M = Cr no additional peaks or no line broadening is observed that may be associated with the presence of a third phase in the specimens.

We conclude that only for Al-(Cr$_{1-x}$Fe$_x$), $x = 0$ and $x = 0.3$ are we reasonably certain that just one quasicrystalline phase is present. For this reason we think that an investigation of the local structure in icosahedral specimens is more reliable for these samples than for the samples with M = Mn and Fe.

The positions of the six most intense icosahedral peaks in the ADXD diffractograms of the various alloys have been measured up to a value of $q = 5$ Å^{-1}. The q values of these peaks have been used to calculate the average reciprocal lattice constant q_0 that corresponds to the (100000) reflection. The linear increase of q_0 in Fig. 1(a) shows that the icosahedral structure contracts between Cr and Fe. Furthermore, the results in Fig. 1(a) show that Fe atoms are substituted for Cr and Mn atoms in the icosahedral Al-Cr and Al-Mn phases, respectively. Thus, the Fe atoms do not alloy with the Al atoms in a separate phase.

Figure 2 shows the ME spectrum of the icosahedral Al-(Cr$_{0.7}$Fe$_{0.3}$) alloy. It may be noted that this alloy is free of the decagonal phase and consequently the Mössbauer spectrum reflects the pure icosahedral phase. All icosahedral Al-(M_{1-x}Fe$_x$) samples produce a spectrum similar to the one shown in Fig. 2. This observation has some implications regarding the question of two or

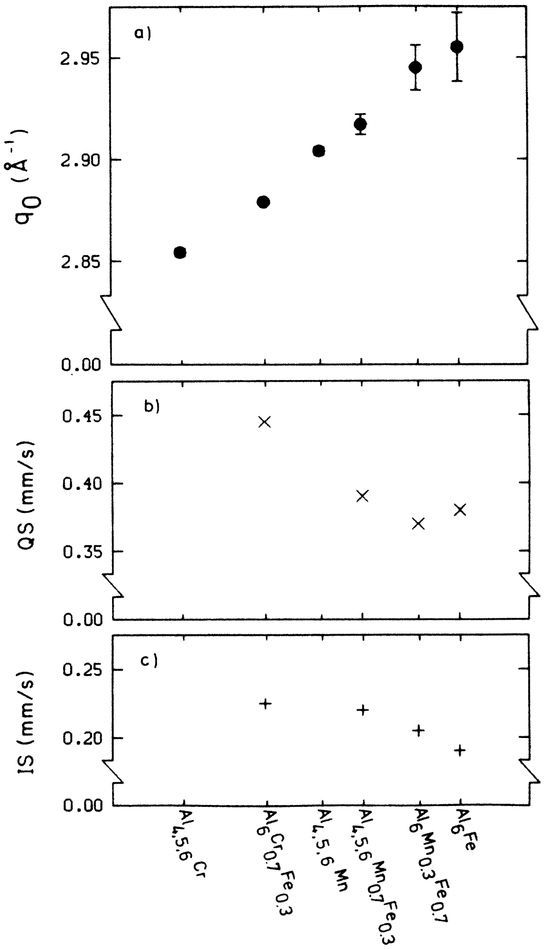

FIG. 1. (a) Reciprocal lattice constant, (b) quadrupole splitting values, and (c) isomer shift values, plotted vs the average number of 3*d* electrons in icosahedral alloys.

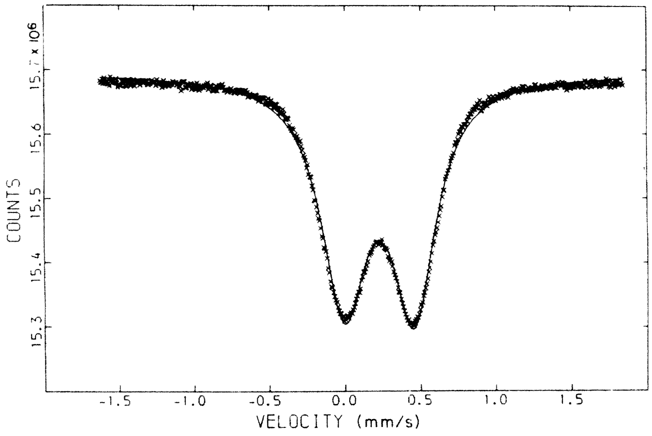

FIG. 2. Mössbauer spectrum of the icosahedral Al-($Cr_{0.3}Fe_{0.7}$) alloy.

more Mn sites in the icosahedral structure and a possible nonrandom substitution of these sites by Fe. A preferential occupation of a subset of Mn sites should show a large difference between the spectrum obtained for Al-($Mn_{0.7}Fe_{0.3}$) and Al-($Mn_{0.3}Fe_{0.7}$). Such a difference is not observed.

The spectra can be fitted with an asymmetric doublet. The ratio between the depths of the low-velocity and high-velocity peak is $D1/D2=0.97(1)$ for all spectra. A least-squares fit with more than one doublet significantly improves the quality of the fit. However, in this paper we want to discuss the average values of the isomer shift and the average values of the quadrupole splitting measured for the series of alloys. It should be noted that the values of δ_{IS} and Δ_{QS} measured for a particular icosahedral alloy do not depend on the quenching rate, i.e., the wheel velocity that was used. The values shown in Figs. 1(b) and 1(c) are the result of averaging δ_{IS} or Δ_{QS} values of a particular alloy for up to three different quenching rates. Furthermore, the δ_{IS} and Δ_{QS} values of icosahedral alloys obtained by melt spinning $Al_6(Mn_{0.7}Fe_{0.3})$, $Al_5(Mn_{0.7}Fe_{0.3})$, and $Al_4(Mn_{0.7}Fe_3)$ are all the same.

Mössbauer spectra give additional information about local electron densities and symmetries. The relevant parameters for these Al-($M_{1-x}Fe_x$) alloys are the isomer shift and the quadrupole splitting. In the Miedema-van der Woude model,[18] the chemical contribution to δ_{IS} of an ^{57}Fe nucleus that is completely surrounded by Al in a strain-free structure is calculated from

$$\delta_{IS}^{max}=P'(\phi_{Fe}^{*}-\phi_{Al}^{*})+Q'(n_{ws}^{Fe}-n_{ws}^{Al}) \ . \tag{1}$$

If Fe atoms have Fe nearest neighbors, the δ_{IS} changes according to

$$\delta_{IS}=(1-x_s)\delta_{IS}^{max}+\delta_{IS}^{vol} \ . \tag{2}$$

The surface concentration around a central Fe atom is given by

$$x_s=\frac{xV_{Fe}^{2/3}}{(1-x)V_{Al}^{2/3}+xV_{Fe}^{2/3}} \ , \tag{2a}$$

where x is the iron concentration (at. %). The molar volumes, the work functions ϕ^*, and the electron densities n_{ws} in the Wigner-Seitz cell are shown in Table I. $P'=-0.66$ and $Q'=0.26$ are obtained from a large number of crystalline and amorphous iron alloys.

The volume term in (2) is, again for the case of an Fe atom, surrounded by Al atoms given by

$$\delta_{IS}^{vol}=\frac{0.615B_{Al}}{0.615B_{Al}+B_{Fe}}(V_{Al}-V_{Fe})\frac{\partial(\delta_{IS})}{\partial V} \ .$$

The bulk moduli B are shown in Table I, $\partial(\delta_{IS})/\partial V=0.19$

TABLE I. Parameters for calculation of the isomer shift. One density unit (d.u.) corresponds with approximately 4.7 ± 10^{22} electrons/cm^3.

	ϕ^* (V)	n_{ws} (d.u.)	V_m (cm^3)	B (10^{11} N/m^2)
Al	4.20	2.69	9.9	0.72
Fe	4.93	5.55	7.1	1.684
Mn	4.45	4.17	7.4	0.60
Cr	4.65	5.18	7.1	1.90

mm/cm^3 is obtained from the pressure dependence of δ_{IS} in α iron.[19]

According to Eq. (1) the δ_{IS} values for an Fe atom in a strain-free Al structure is expected to be 0.26 mm/s. This value is only slightly larger than the values measured for crystalline $\mathrm{Al_6Fe}$ ($\delta_{\mathrm{IS}}=0.22$ mm/s) (Ref. 20) and $\mathrm{Al_{13}Fe_4}$ ($\delta_{\mathrm{IS}}=0.20$) (Ref. 21) where Fe atoms are completely surrounded by 9 to 11 Al atoms in strain-free environments as may expected for intermetallic compounds. The calculated value is also close to the icosahedral values shown in Fig. 1(b).

According to (2) and (2a), δ_{IS} decreases if Al atoms are replaced by Fe, Cr, or Mn atoms. For instance, for an Fe atom completely surrounded by ten Al atoms, a replacement of one Al by such a transition-metal (TM) atom would decrease the δ_{IS} by about 0.03 mm/s.

However, the δ_{IS} values for icosahedral $\mathrm{Al_6(Mn_{0.7}Fe_{0.3})}$, $\mathrm{Al_5(Mn_{0.7}Fe_{0.3})}$, and $\mathrm{Al_4(Mn_{0.7}Fe_{0.3})}$ are all the same within 0.005 mm/s and these values also agree with the δ_{IS} values of intermetallic compounds. Furthermore, for each composition of Al-($M_{1-x}\mathrm{Fe}_x$) that produced an icosahedral phase, the δ_{IS} value did not depend on the quenching rate. From these results we conclude that in icosahedral alloys just as in crystalline alloys the Fe atoms are completely surrounded by Al atoms. A random substitution of Al by TM atoms does not take place.

The δ_{IS} values decrease slightly between $M=\mathrm{Cr}$ and $M=\mathrm{Fe}$ [Fig. 1(c)]. This can be related to the increase in the reciprocal lattice constant [(Fig. 1(a)]. As a result of the contraction of the lattice the s-electron density at the ^{57}Fe nucleus apparently increases. This results in a lowering of the δ_{IS} magnitude.

All the Mössbauer spectra of the iron containing quasicrystals show a quadrupole splitting of about 0.4 mm/s, indicating that the iron atoms are mainly in sites with a lower-than-cubic symmetry. For example, the center of an icosahedron is too symmetric and at least the majority of iron atoms have to be accommodated in other sites.

In summary, three requirements for the sites of the iron atoms can be formulated: (a) iron atoms completely surrounded by Al atoms, (b) Fe-Al distances as in intermetallic compounds, and (c) lower than cubic symmetry. These three requirements plus the general requirement of icosahedral symmetry may be fulfilled by a cluster proposed by Mackay[22] that has icosahedral symmetry. In order to investigate this, we have built Mackay clusters that consist of Al and MM spheres. The radius of the MM sphere is taken about 10% smaller than the Al spheres (Table I). We have selected 2.45 Å as the shortest distance between Al atoms. This value is the shortest Al-Al distance found in Fe-Al[23,24] and Mn-Al[25] alloys. Table II shows the Fe-Al distances of Fe atoms up to the fourth shell in the most dense cluster that was built. These distances can be compared with those in crystalline $\mathrm{FeAl_6}$ where the Fe atoms are surrounded by 10 Al atoms occupying 10 of the 12 vertices in a distorted icosahedron. In this structure the Fe-Al distances spread from 2.445 to 2.616 Å. with an average of 2.55 Å.[24] From this comparison we conclude that an Fe atom in a Mackay cluster is expected to produce a δ_{IS} magnitude slightly lower but close to that in crystalline $\mathrm{FeAl_6}$ since the average Fe-Al distance in the cluster is slightly less. Table II also shows that the Fe atoms in the first three shells will experience different electric field gradients (EFG). As a result, the Δ_{QS} values will be different for these positions. It is expected that Fe atoms in additional fourth, fifth, etc. shells will all produce different EFG's. In other words, the Mackay cluster produces a distribution of Δ_{QS} values.

As shown in Fig. 1(b), Δ_{QS} increases slightly between $M=\mathrm{Fe}$ and $M=\mathrm{Cr}$. This is consistent with an expansion of the Mackay cluster as indicated in Fig. 1(a), because the expansion would increase the asymmetry in the Fe-Al distances shown in Table II.

The expansion can be understood from the ϕ^* values shown in Table I. Since $\phi^*_{\mathrm{Al}}-\phi^*_{\mathrm{Fe}}>\phi^*_{\mathrm{Al}}-\phi^*_{\mathrm{Cr}}$, more charge transfer takes place from Al to Fe than from Al to Cr. This causes the volumes of Fe and Al to become more equal. As a result a more compact and symmetrical packing of Al and Fe compared to Al and Cr is expected.

In conclusion, the choice of 3d transition elements and the quenching rate determines which of the quasicrystalline phases precipitate during rapid solidification. For Al-($\mathrm{Mn}_{1-x}\mathrm{Fe}_x$) ($x=0,0.3,0.7,1$) alloys both the icosahedral and the decagonal phase are produced during

TABLE II. Fe-Al distances between Fe and Al spheres at vertex (v), edge (e), or face (f) positions in the first four sheels of a Mackay cluster.

	Neighbor	No. of neighbors	Distance (Å)
Fe_{2v}	Al_{1v}	1	2.338
	Al_{2e}	5	2.458
	Al_{3v}	1	2.725
	Al_{3e}	5	2.338
			Average Fe-Al distance 2.42 Å
Fe_{3f}	Al_{2e}	3	2.358
	Al_{3e}	6	2.608
	Al_{4f}	3	2.411
			Average Fe-Al distance 2.50 Å

the quenching process except possibly for very fast quenching rates. The presence of Cr apparently favors the icosahedral structure to such an extent that a second quasicrystalline phase is not found in Al-($Cr_{1-x}Fe_x$) ($x=0,0.3$). For this reason Al alloyed with Cr is more suitable as an icosahedral model alloy for many experimental techniques than Al-Mn. Our ME study of a series of icosahedral alloys shows that in the icosahedral phase the Fe atoms are situated in strain-free Al nearest-neighbor structures that do not have cubic symmetry. Such a local structure can be constructed in a Mackay cluster that consist of two unequal spheres.

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