$^{57}$Fe Mössbauer-effect study of preferential site occupancy in quasicrystalline Al$_{86}$Cr$_{14-x}$Fe$_x$ alloys

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$^{57}$Fe Mössbauer-effect measurements are reported for rapidly quenched alloys in the series Al$_{86}$Cr$_{14-x}$Fe$_x$ (3 \( \leq x \leq 14 \)). These alloys have been shown to be quasicrystalline with the icosahedral structure. Mössbauer measurements show the existence of two distinct transition-metal sites. As Fe is substituted into Al$_{86}$Cr$_{14}$ in place of the Cr, the Mössbauer measurements show that the Fe preferentially occupies only one of the sites. These results are discussed in terms of structural models consisting of interconnected MacKay icosahedra.

I. INTRODUCTION

In recent years a number of rapidly quenched aluminum–transition-metal (Al-M) alloys have been shown to possess icosahedral symmetry (see, e.g., Ref. 1). The existence of these phases in Al-Fe alloys or Fe-substituted alloys of Al with other transition metals, leads to the possibility of performing $^{57}$Fe Mössbauer spectroscopy in order to gain insight into the local symmetry of the transition-metal atoms in the icosahedral structure. Some Mössbauer measurements have been reported during the past two years. In the present work we report $^{57}$Fe Mössbauer-effect measurements on the series of rapidly quenched alloys Al$_{86}$Cr$_{14-x}$Fe$_x$. These measurements complement our recent x-ray diffraction, electron diffraction, transmission electron microscopy, and thermal analysis study of these alloys.

II. EXPERIMENTAL METHODS

Rapidly solidified ribbons of Al$_{86}$Cr$_{14-x}$Fe$_x$ (x = 3, 6, 9, 12, 14) were prepared by the melt-spinning method. Details of the sample preparation have been reported previously (e.g., Ref. 3). Samples used here have been well characterized using various other experimental techniques. Previous x-ray diffraction, electron microscopy, and electron diffraction measurements on these alloys have shown them to consist of an aluminum matrix and quasicrystalline nodules. The quasicrystalline phase showed icosahedral symmetry; no evidence of a decagonal phase was found (see Ref. 8).

Room-temperature $^{57}$Fe Mössbauer-effect measurements were performed using a Wissel System II Mössbauer spectrometer. The source was Pd $^{57}$Co at room temperature and the system showed a linewidth for a thin $\alpha$-Fe absorber of 0.24 mm/s [full width at half maximum (FWHM)].

III. RESULTS

A typical Mössbauer spectrum for the alloys studied here is illustrated in Fig. 1. Parameters obtained from fits to two symmetric doublets are given in Table I.

The values of the isomer shift, as illustrated in Fig. 2, show a general trend towards more negative values as Cr is replaced by Fe. Lawther et al. have shown that the substitution of Fe for Cr in this series results in a relatively linear decrease in the interatomic spacing as a result of the difference in the atomic radii. As shown in Fig. 2, the isomer shifts obtained for the two doublets in a fit to a two-site model both show a monotonic decrease across the series of alloys. The figure shows that there is a considerable difference in the isomer shifts of the two sites obtained for the fit to two doublets, indicating a significant difference in the s-electron density for the two transition-metal sites.

Figure 3 indicates that the quadrupole splittings for a two-site model show very similar values and trends for the two sites. The measured quadrupole splittings for Al-Mn(Fe) (Ref. 3) are somewhat less than those of the
Al-Cr-Fe alloys with comparable 3d-4s electron concentration, indicating a slightly more symmetric average transition-metal environment in the former alloy.

Fitting to two symmetric doublets rather than a single doublet produced a significant decrease in $\chi^2$. This improvement was more significant for some alloys than for others. Similarly, the relative areas of the two fitted doublets is a function of composition, as shown in Table I. Neither fitting to three or more doublets (multiple sites), fitting to a distribution of splittings, or the inclusion of a singlet (to account for the possibility of isolated Fe impurities in the Al matrix) had a significant influence on $\chi^2$.

IV. DISCUSSION

The general similarity of the physical properties of icosahedral quasicrystals to those of certain crystalline materials has led to the prevalent opinion that the local structure of the icosahedral phase is very similar to that encountered in conventional crystal structures based on the MacKay icosahedron. On the basis of similarities between, e.g., $\alpha$-Al-Mn(Fe)-Si and icosahedral Al-M(Fe) alloys, along with an inspection of the TM sites in MacKay icosahedron-based crystalline materials, some insight into the identity of TM sites in quasicrystals can be gained. In $\alpha$-Al-Mn-Si, for example, the 54-atom MacKay icosahedron consists of an icosahedral cluster of 12 sp atoms (Al or Si) surrounded by an icosahedron of 12 Mn atoms at icosahedral vertices and 30 sp atoms at the bisection of icosahedral edges. Several models of the interconnection of MacKay icosahedra in a quasicrystal have been proposed. While it is not clear from a theoretical standpoint why more than a single distinct TM site should exist in MacKay icosahedron-based structures, there seems to be evidence, on the basis of NMR, Mössbauer effect, and magnetization moments, that multiple transition-metal sites exist in icosahedral quasicrystals. In some cases these results (e.g., Ref. 6) have been interpreted in terms of a two-site model and in other cases (e.g., Ref. 5) in terms of a distribution of sites. If such multiplicity of transition-metal sites exists then it is probable that the distinction lies in differences in the role of the sites in the bonding of adjacent icosahedra. In any case, there is no reason to believe a priori that the relative concentration of sites is related to the golden mean.

**TABLE I.** Mössbauer parameters obtained at room temperature from a fit to two symmetric doublets for the Al$_{186}$Cr$_{14}$Fe$_{5}$ alloys. The isomer shift $\delta$, quadrupole splitting $\Delta$, and linewidths $\Gamma$ are given in mm/s. Errors are $\pm$0.005 mm/s. $A_i$ are the areas of the doublets. Isomer shifts are measured relative to $\alpha$-Fe. Values of $\chi^2$ for the fit to two doublets are normalized to 1.0 for a fit to a symmetric doublet for the same spectrum.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\delta_a$</th>
<th>$\delta_b$</th>
<th>$\Delta_a$</th>
<th>$\Delta_b$</th>
<th>$\Gamma_a$</th>
<th>$\Gamma_b$</th>
<th>$A_a / A_b$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.179</td>
<td>0.305</td>
<td>0.473</td>
<td>0.464</td>
<td>0.310</td>
<td>0.250</td>
<td>2.48</td>
<td>0.64</td>
</tr>
<tr>
<td>6</td>
<td>0.176</td>
<td>0.300</td>
<td>0.453</td>
<td>0.442</td>
<td>0.300</td>
<td>0.290</td>
<td>1.32</td>
<td>0.45</td>
</tr>
<tr>
<td>9</td>
<td>0.160</td>
<td>0.291</td>
<td>0.416</td>
<td>0.403</td>
<td>0.285</td>
<td>0.250</td>
<td>1.22</td>
<td>0.34</td>
</tr>
<tr>
<td>12</td>
<td>0.142</td>
<td>0.275</td>
<td>0.396</td>
<td>0.379</td>
<td>0.280</td>
<td>0.249</td>
<td>1.21</td>
<td>0.36</td>
</tr>
<tr>
<td>14</td>
<td>0.130</td>
<td>0.252</td>
<td>0.392</td>
<td>0.384</td>
<td>0.276</td>
<td>0.303</td>
<td>0.83</td>
<td>0.21</td>
</tr>
</tbody>
</table>
The results of the Mössbauer measurements presented in Table I clearly indicate differences in the microscopic Fe environment between Fe-rich alloys and Cr-rich alloys. The alloys with large \( x \) (Fe rich) show a clear distinction between two inequivalent Fe sites, while alloys with small \( x \) do not show this well-defined duality. This conclusion is based on the following observations: (1) A two-doublet fit to alloys with large \( x \) shows a significantly smaller \( \chi^2 \) than a fit involving only one doublet. This is not true for alloys with small \( x \); (2) the relative areas for the two doublets obtained from a fit to two sites are comparable for the Fe-rich alloys but one doublet has a significantly greater area than the other for the Cr-rich alloys.

Since a fit to two doublets involves a larger number of fitting parameters than a fit to only one doublet, it is, in general, to be expected that the former will yield a lower \( \chi^2 \). Choosing one fit as physically more valid than another on the basis of \( \chi^2 \) is a matter of weighing the improvement in the fit against the increase in the number of free parameters. On the basis of present results, the evidence for two or more Fe sites on Al\(_{86}\)Fe\(_{14}\) seems convincing while for Al\(_{86}\)Cr\(_{11}\)Fe\(_3\) the situation is considerably less certain.

The fitted area ratios shown in Table I are consistent with the above discussion; Fe-rich alloys show two doublets of comparable area while the Al\(_{86}\)Cr\(_{11}\)Fe\(_3\) alloy, in particular, shows that one doublet is clearly dominant.

Eibschütz et al.\(^5\) have demonstrated that it is difficult, on the basis of \( \chi^2 \) analysis of Mössbauer spectra, to distinguish between the existence of two sites in these alloys and a distribution of sites. The present comparison of fitted values for one or two doublets for alloys with different \( x \) indicates a much stronger case for two or more Fe sites in Al-Cr than in Al-Fe. The linewidths observed for the two-site fits are, in general, close to the spectrometer linewidth, but do show some slight broadening. On the grounds of our \( \chi^2 \) analysis and the observed linewidths, the model of Eibschütz et al.\(^5\) of two distinct classes of sites, each with a distribution of splittings, seems reasonable.

Two interpretations of these results are possible: (1) As Fe is substituted into Al-Cr there is a preference for the Fe to fill one type of transition-metal site before the other. (2) Al-Fe alloys show a distinction between different types of transition-metal sites while Al-Cr alloys do not show this distinction.

We prefer the former explanation. There is no reason \( a \) \( p r i o r i \) to think that there should be any intrinsic differences in structure between Al-Cr and Al-Fe. If disorder is responsible for the broadened x-ray peaks in Al-Fe (see, e.g., Refs. 7 and 8) then we would expect the site distinction to be lost in this alloy and not in Al-Cr. We feel, therefore, that there is fairly convincing evidence of preferential site occupancy for Fe in icosahedral Al-Cr alloys and that this preferred site has a considerably less positive isomer shift.

Following the development of Dunlap et al.,\(^4\) some distinction between these two sites on the basis of isomer shifts can be made. The present measurements, along with previous measurements on Fe in crystalline alloys, are given in Table II.

There are two possibilities concerning the dual nature of the transition-metal sites in icosahedral alloys: (1) the distinction arises because of differences in the sites within a MacKay cluster, or (2) the distinction arises because of differences in the sites in terms of their roles in the interconnection of clusters. In the first case \( \langle r \rangle \) for site \( b \) is similar to that for \( \langle r \rangle \) in Al\(_2\)Fe, indicating that these sites may represent Fe on MacKay cluster vertices while site \( a \) may represent Fe on cluster edges. We feel, however, that the second alternative is probably more realistic, with site \( a \) representing vertex Fe with neighboring Al from adjacent clusters, and site \( b \) representing Fe which is not adjacent to atoms in neighboring icosahedra.

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