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Mössbauer study of the Al-Fe decagonal phase

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Mössbauer spectroscopy has been used to get information about the atomic structure of the decagonal Al-Fe alloy. Mössbauer data distinctly support a structural model for the system which consists of a periodic stacking of two-dimensional Penrose lattices derived from the structure of the monoclinic $Al_{13}Fe_4$ phase. Results of earlier Mössbauer measurements on similar systems are also discussed.

Since the first discovery of a quasicrystalline phase in rapidly quenched Al-Mn alloys[1] considerable progress has been made in the field. Several different classes of systems have been discovered which can form quasicrystalline phases under suitable conditions.[2,3] Systems have been found in which quasicrystalline order may even represent a thermodynamically stable phase.[4] Besides the icosahedral phase possessing fivefold rotation symmetry, decagonal and dodecagonal phases possessing, respectively, tenfold and twelvefold rotation symmetries have also been discovered.[5,6] However, despite the extensive studies, both experimental as well as theoretical, the question of the atomic structure of these systems still remains unanswered.

In the Al-T (T=Mn,Cr,Fe) icosahedral phase, which is the most extensively studied system so far, most of the experimental data obtained using techniques sensitive to the local order in the system,[7-10] suggest that a Mackey's icosahedron[11] (MI) containing 12 T atoms and 42 Al atoms, is the basic structural unit. Based on such a structural unit, several models for the structure of icosahedral phase have been proposed, which differ from each other essentially in the way the MI's are connected to each other.[12-16] However, some recent studies create doubts about MI being the basic structural unit in these systems.[17-19] On the other hand, the structural studies on the decagonal Al-T phase are rather limited and their interpretations differ widely from each other; while some extended x-ray-absorption fine-structure spectroscopy (EXAFS) measurements suggest that MI is also the basic structural unit in the case of decagonal phase,[20] other Mössbauer and EXAFS studies give evidence against any such structural unit.[10,17] Two structural models have been proposed for the atomic structure of decagonal Al-T alloys.[21-23] Audier and Guyot[21] consider Mackey's icosahedron to be the basic structural unit of decagonal phase also, while Kumar *et al.*[22,23] have proposed a structural model which is derived from the structure of crystalline $Al_{13}Fe_4$.[24] It may be noted that the decagonal phase, being a two-dimensional quasicrystal, should have a simpler atomic structure as compared to the icosahedral phase, and thus should be easier to deal with. Several experiments suggest a close relationship between icosahedral and decagonal quasicrystalline structures,[25,26] and thus, understanding of the atomic structure in the decagonal phase should also be helpful in elucidating the structure of the icosahedral phase.

In the present work the decagonal Al-Fe phase has been studied using Mössbauer spectroscopy in order to obtain information about the atomic structure of this system. Specimens prepared by melt spinning of $Al_{84}Fe_{14}$ were kindly provided by Dr. T. Rajasekharan of Defense Metallurgical Research Laboratory, Hyderabad. TEM and x-ray-diffraction measurements revealed the specimen to consist of the decagonal phase dispersed in an Al matrix. Room-temperature Mössbauer spectra were measured with a ^{57}Co source in a Rh matrix using a Wissel-Mössbauer spectrometer. The spectrometer gave a linewidth of 0.22 mm/s for the inner lines of a thin α-Fe absorber.

The Mössbauer spectrum of the specimen shown in Fig. 1 suggests that the iron atoms exist at more than one nonequivalent site. Accordingly, the spectrum was fitted with two or more quadrupole doublets without putting any constraint on various parameters. Increasing the number of components beyond two did not result in any significant improvement in χ^2, suggesting that the Fe atoms exist in essentially two substantially different types of environments. The parameters obtained from the fit with two components are shown in Table I.

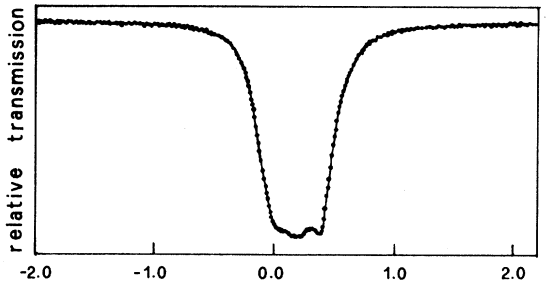

FIG. 1. Room-temperature Mössbauer spectrum of the decagonal Al-Fe alloy. Zero on the velocity scale corresponds to the centroid of the α-iron spectrum at room temperature.

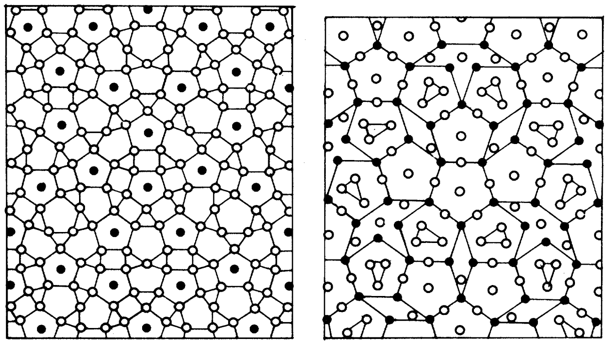
(a) (b)

FIG. 2. The 2DPL corresponding to the structure of the decagonal Al-Fe as suggested in Ref. 23. Open (filled) circles represent Al (Fe) atoms.

It may be noted that the Mössbauer spectrum of the decagonal Al-Fe alloy (Fig. 1) is qualitatively very similar to that of crystalline $Al_{13}Fe_{14}$.[27] This similarity between the two Mössbauer spectra suggests that the short-range structure of the decagonal phase should be closely related to that of the crystalline $Al_{13}Fe_4$ phase. $Al_{13}Fe_4$ is known to be a "near-quasicrystal Al-*T* Phase," the layered structure of which can be decomposed into rhombic tiles of a two-dimensional Penrose lattice.[28] TEM studies also have shown a close relation between the structures of Al-Fe decagonal phase and crystalline $Al_{13}Fe_4$.[29,30] On the other hand, some recent Mössbauer and EXAFS measurements suggest that MI is not the basic structural unit in decagonal alloys; Mössbauer measurements on decagonal $Al_7(Mn_{0.7}Fe_{0.3})_2$ in high magnetic field give a nonzero asymmetry parameter η, suggesting that Fe atoms are at sites with lower than axial symmetry, while in MI transition-metal atoms are located at sites with either axial fivefold or threefold symmetry for which η should be equal to zero.[17] EXAFS analysis of the decagonal $Al_{78}Mn_{22}$ alloy also does not give any evidence for MI being the structural unit.[10] Therefore, a structural model having some relationship to the crystalline $Al_{13}Fe_4$ structure such as the one proposed in Refs. 22 and 23 seems to be more appropriate for the decagonal Al-Fe alloys.

The model proposed by Kumar[23] contains two types of two-dimensional Penrose lattices (2DPL) shown in Fig. 2. The structure of the decagonal phase is generated by a periodic stacking of alternate layers of these 2DPL's. As far as the local environment of Fe atoms in this model is concerned, the following points may be noted: (i) All Fe atoms in the first 2DPL [Fig. 2(a)] have the same environment, while in the second 2DPL [Fig. 2(b)] one can find several Fe sites with slightly different environments. (ii) The symmetry around the Fe atoms in layer 1 is much higher than that around the Fe atoms in layer 2. (iii) The ratio of the number of Fe atoms in layer 1 to that in layer 2 is 1:2.

TABLE I. Parameters obtained from the best fit to the spectrum in Fig. 1. The isomer shift (IS), quadrupole splitting (QS), and the average linewidth Γ are in mm/s. Errors are ± 0.004 mm/s.

	IS	QS	Γ	Relative area
Doublet 1	0.220	0.122	0.228	1.0
Doublet 2	0.227	0.431	0.263	1.9

From Table I one finds that in the decagonal Al-Fe phase the Fe atoms exist in two types of environments. A substantial difference between the quadrupole splitting of the two doublets suggests that the two sites have very different local symmetries. Furthermore, the area of the second doublet, which has larger quadrupole splitting, is about twice that of the first doublet, indicating that the number of Fe atoms located in the less symmetric environment is twice the number of atoms located in the more symmetric environment. This experimentally determined local environment of iron atoms agrees very well with the prediction of the 2DPL model, if one associates the first doublet with the iron atoms located in the first 2DPL and the second doublet with those located in the second 2DPL. Furthermore, it may be noted that the linewidth of the first doublet is very close to the instrumental linewidth of 0.22 mm/s. This indicates that all the atoms corresponding to this doublet have a very similar environment. In contrast to this, the second doublet has much broader lines, indicating that the corresponding atoms have a distribution of environment. Again, this observation agrees very well with the predictions of the above model, according to which all the Fe atoms in the first 2DPL have identical environments while Fe atoms in the second 2DPL exist at several sites with small differences in their environments. Thus, the present Mössbauer data strongly supports the 2DPL model for the structure of the decagonal Al-Fe alloys.

Koopmans, Schurer, and van der Woude have reported the Mössbauer measurements on $Al_7(Mn_{0.7}Fe_{0.3})_2$ decagonal alloy.[31] They also found two nonequivalent sites for iron atoms with their quadrupole splitting values being respectively $\Delta_1 = 0.22$ mm/s and $\Delta_2 = 0.55$ mm/s; isomer shifts being respectively $\delta_1 = 0.20$ mm/s and $\delta_2 = 0.19$ mm/s; and the area ratio of the two doublets being 1.5:1. These parameters are considerably different from those for the Al-Fe decagonal phase listed in Table I. Particularly, the area ratio of the two doublets is reversed; while in the Al-Fe alloy the doublet with smaller quadrupole splitting has a smaller area, in Al-Mn-Fe alloy this doublet has a larger area. This may mean that the two alloys have very different atomic structure. However, it may be noted that in an EXAFS study of the Al-Mn-Fe decagonal phase,[32] the radial distribution of atoms around Mn was found to be broader than that around Fe atoms. This difference in the two radial distributions has been interpreted as being due to the preferential occupation of one of the transition-metal sites by the iron atoms. In a recent Mössbauer study of the $Al_{86}(CrFe)_{14}$ icosahedral phase alloy it was also found that Fe atoms do not substitute Cr atoms randomly.[33] Thus, the large difference observed in the relative populations of the two types of sites in Al-Fe and Al-Mn-Fe decagonal alloys is more likely to be due to a preferential occupation of one of the transition-metal sites by the iron atoms. A higher relative area of the first doublet (with smaller quadrupole splitting) in the case of the Al-Mn-Fe alloy would mean that iron atoms preferentially occupy the site with higher symmetry, i.e., the first 2DPL in Fig. 2. Further comparison of Mössbauer parameters of decagonal Al-Fe and Al-Mn-Fe alloys show that in the Al-Mn-Fe system, the isomer-shift values of both the Mössbauer components are lower while their quadrupole splittings are higher as compared to the corresponding parameters in the Al-Fe system. A smaller isomer shift in the Al-Mn-Fe specimen may be attributed to an increase in the s-electron density due to the presence of Mn atoms. A larger quadrupole splitting of the two doublets in the Al-Mn-Fe system may suggest that the presence of two types of transition-metal atoms cause some distortion in the structure of the decagonal phase.

It may be noted that on the basis of neutron-diffraction data Janot and Dubois[19] have developed an atomistic model for the icosahedral phase by decorating a 3DPL, which is very different from the models based on Mackey's icosahedron. In view of the close relationship between the structures of icosahedral and decagonal phases,[25,26] the success of a 2DPL model for the structure of the decagonal phase lends support to the models for the icosahedral phase based on the decoration of 3DPL.[14,19]

Thus, one may conclude the following: (i) The structure of the Al-T decagonal phase can be described as a periodic stacking of alternate layers of two types of 2DPL derived from the structure of crystalline $Al_{13}Fe_{14}$. (ii) In a decagonal Al-Mn-Fe alloy, the iron atoms do not occupy the transition-metal sites randomly, rather, they have a tendency to preferentially occupy the sites with higher local symmetry.

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