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Quasicrystalline Ti-Ni-Fe-Si: Mössbauer indications for high transition-metal-site symmetry

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Melt-spun $Ti_{56}Ni_{28-x}Fe_xSi_{16}$ shows the icosahedral phase recently reported for other rapidly quenched Ti-Ni-based alloys. ^{57}Fe Mössbauer measurements in this alloy yield a quadrupole splitting $\Delta \sim 0$. The value of Δ indicates a highly symmetric Fe site in the icosahedral structure. The relative intensities of the x-ray diffraction lines suggest a structure based on a three-dimensional Penrose tiling in which some of the transition-metal atoms occupy sites with icosahedral symmetry. This is the first experimental indication that a transition metal may occupy the icosahedral site in any quasicrystal.

The existence of quasicrystals with long-range orientational ordering but no long-range translational order was first reported for aluminum-transition metal alloys (Al-*M*) by Shechtman *et al.*[1] Since then the same or similar quasicrystalline structures have been reported in a variety of other alloy systems. These include Al-*M*-Si,[25] Al-*M*-Ru,[6] Al-Zn-Mg,[7] Al-Cu-Li,[8,9] Al-Zr-Cu-Mg,[10] and Pd-U-Si.[11] The Al-Mn-Si system is generally considered to be typical of the Al-based quasicrystals. These alloys show a local structure similar to that of crystalline α-(Al-Mn-Si),[12] which is a bcc assembly of Mackay clusters with the central icosahedral site vacant.[13] The icosahedral phase is also well described as a three-dimensional (3D) Penrose tiling.[6] In either structure model of quasicrystals [i.e., a derivative α-(Al-Mn-Si) or a 3D Penrose tiling], it is not clear if a Mn atom can sometimes be found in the central icosahedral site [vacant in α-(Al-Mn-Si) (Ref. 4)] or if there is a clustering of Mn at other sites in the structure. (Icosahedral site symmetry could lead to enhanced moments on transition metal atoms.[14]) ^{57}Fe Mössbauer-effect spectra of Fe-doped Al-*M* and Al-*M*-Si quasicrystals show a large (~ 0.4 mm/s) quadrupole splitting[12,15–17] indicating an Fe environment with local symmetry lower than would be expected for the central site. This in itself does not necessarily mean that other transition metals do not occupy the icosahedral site as there is some evidence of preferential site occupancy for Fe substituted into these structures.[12]

Kuo and co-workers[18,19] have recently reported a quasicrystalline phase exhibiting icosahedral symmetry in an alloy containing only transition metals; $Ti_{2-x}V_xNi$. Quasicrystals of Ti-Ni and Ti-Ni-V alloys contain crystallites which are much smaller than those of quasicrystalline Al-based alloys. Chatterjee and O'Handley[20] have recently shown that the addition of Si to Ti-Ni yields an icosahedral phase with crystallites of sufficient size to produce a sharp x-ray diffraction pattern. In the present work we use ^{57}Fe Mössbauer-effect spectroscopy to study the local environment of Fe substituted into quasicrystalline Ti-Ni-Si. In contrast to Mössbauer measurements[15–17] on all other quasicrystals we find no significant quadrupole splitting for Fe in icosahedral $Ti_{56}Ni_{28-x}Fe_xSi_{16}$. Crystalline $Ti_2Ni_{1-x}Fe_x$ and amorphous $Ti_{56}Ni_{28-x}Fe_xSi_{16}$ on the other hand show a splitting of $\Delta = 0.35-0.45$ mm/s.

Alloys of $Ti_{56}Ni_{28-x}Fe_xSi_{16}$ ($x = 2.5, 5, 7.5$) were prepared by rapid quenching from the melt onto the surface of a single Cu roller. The surface speed of the roller was 18 m/s. The melt was ejected by an over pressure of ~ 100 kPa of argon through a 0.7-mm orifice. Quenching was performed in an atmosphere of He. The resulting ribbons were ~ 2 mm wide and 0.05 mm thick. For comparison, we have studied $Ti_{56}Ni_{28-x}Fe_xSi_{16}$ alloys in the as-cast (slow-cooled) state as well as a crystalline alloy of $Ti_2Ni_{0.85}Fe_{0.15}$ prepared by arc melting. Finally, we have also investigated $Ti_{56}Ni_{28-x}Fe_xSi_{16}$ alloys in the amorphous state prepared by quenching at a higher rate (roller speed, 60 m/s). X-ray diffraction measurements were performed on a Siemens scanning diffractometer using Cu $K\alpha$ radiation. Room-temperature Mössbauer-effect measurements were made using a Wissel System II Mössbauer spectrometer and a *Pd* ^{57}Co source. This system showed a line width for α-Fe of 0.24 mm/s [full width at half maximum (FWHM)]. Fitting of the spectra was performed using a conventional nonlinear least-squares fit to combinations of Lorentzian lines.

X-ray diffraction measurements showed arc melted $Ti_2Ni_{0.85}Fe_{0.15}$ to be of the $Fd3m$ structure expected for Ti_2Ni.[21] This structure consists of pairs of Ni-centered interpenetrating icosahedra which share a common five-membered ring. Two of the ring atoms are Ni, the remaining are Ti. As-cast $Ti_{56}Ni_{28-x}Fe_xSi_{16}$ alloys showed a mixture of Ti_5Si_3 and NiTi phases. Presumably the Fe substitutes for Ni in NiTi which is of the bcc structure.

The x-ray pattern of rapidly quenched (18 m/s) $Ti_{56}Ni_{28-x}Fe_xSi_{16}$ alloys can be indexed to the icosa-

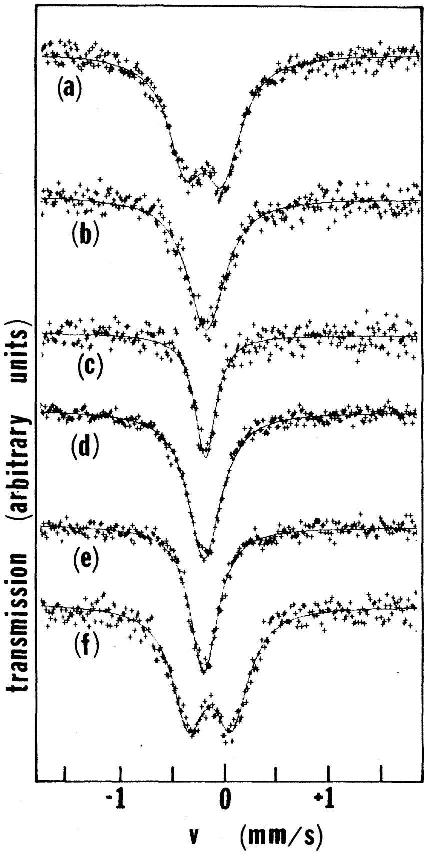

FIG. 1. ^{57}Fe Mössbauer-effect spectra obtained at room temperature for (a) crystalline $Ti_2Ni_{0.85}Fe_{0.15}$, (b) crystalline $Ti_{56}Ni_{25.5}Fe_{2.5}Si_{16}$, (c) icosahedral $Ti_{56}Ni_{25.5}Fe_{2.5}Si_{16}$, (d) icosahedral $Ti_{56}Ni_{23}Fe_5Si_{16}$, (e) icosahedral $Ti_{56}Ni_{20.5}Fe_{7.5}Si_{16}$, and (f) amorphous $Ti_{56}Ni_{25.5}Fe_{2.5}Si_{16}$. The solid lines represent computer fits to two doublets for (a) and to one singlet for (b)–(e) and one doublet for (f).

hedral structure using the scheme of Bancel *et al.*[22] A detailed analysis of the x-ray pattern of this phase is reported elsewhere.[23] While Chatterjee and O'Handley[20] have found the presence of crystalline Ti_2Ni in addition to the quasicrystalline phase in rapidly quenched $Ti_{56}Ni_{28}Si_{16}$, the related Fe-containing quasicrystal shows no diffraction lines from this crystalline phase and suggest that the presence of Fe helps to stabilize the icosahedral structure. The icosahedral Ti-Ni structure shows diffraction peaks with smaller q values than those of Al-Mn indicating an average interatomic spacing which is about 3% larger in the former alloy. This is consistent with interatomic spacings based on the elemental components of these alloys.

Room-temperature ^{57}Fe Mössbauer-effect spectra of crystalline $Ti_2Ni_{0.85}Fe_{0.15}$ and $Ti_{56}Ni_{25.5}Fe_{2.5}Si_{16}$ and also quasicrystalline $Ti_{56}Ni_{25.5}Fe_{2.5}Si_{16}$ and amorphous $Ti_{56}Ni_{25.5}Fe_{2.5}Si_{16}$ are shown in Fig. 1.

The spectrum of crystalline $Ti_2Ni_{0.85}Fe_{0.15}$ shows an asymmetric doublet and was therefore fit to two quadrupole split patterns. Results of parameters obtained from this fit are given in Table I. Fitting this spectrum to more complex combinations of doublets and singlets did not improve χ^2 and, as well, yielded physically unrealistic values for some of the fitting parameters (e.g., linewidth). The Fe site duality may be due to the existence of two distinct Ni environments in Ti_2Ni. However, of more importance for our present purpose is the large quadrupole splitting determined for both of these sites. The spectrum of crystalline Ti-Ni-Fe-Si (see Fig. 1) showed a singlet and these fitted parameters are also shown in Table I. Because of the structure of NiTi (i.e., bcc) the observed zero quadrupole splitting is expected. The line broadening presumably results from the presence of disorder.

The Mössbauer spectra of icosahedral Ti_{56}-Ni_{28-x}-Fe_x-Si_{16} ($x < 7.5$) also show singlets as illustrated in Fig. 1. We have fit these spectra to various combinations of singlets and doublets. On the basis of χ^2 we find no evidence that more than a single type of Fe site exists for any icosahedral alloys with $x < 7.5$.

Finally, the Mössbauer spectrum of amorphous Ti-Ni-Fe-Si is shown in Fig. 1. As is typical for paramagnetic amorphous alloys, this spectrum showed a quadrupole split doublet with broadened lines. The relatively small asymmetry observed here indicates little or no correlation between the quadrupole splitting and the isomer shift distributions. A doublet was used to fit the spectrum to obtain mean isomer shift and quadrupole splitting values. These are given in Table I.

In order to compare our Mössbauer data with those on another well-known quasicrystalline material, the mea-

TABLE I. Room-temperature ^{57}Fe Mossbauer-effect parameters of Ti-Ni-Fe-Si alloys studied in the present work. Results from Al-Mn(Fe) from Ref. 14 are given for comparison. The isomer shift δ is measured relative to α-Fe. The error in δ, the quadrupole splitting Δ, and the linewidth (FWHM) Γ are ±0.005 mm/s. A_1/A_2 is the ratio of the areas of the two components. Reasons for the patterns which have been fit are described in the text.

		Site 1			Site 2			
Alloy	Structure	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	A_1/A_2
$Ti_2N_{0.85}Fe_{0.15}$	$Fd3_M$	−0.171	0.350	0.388	−0.240	0.531	0.441	5.7
$Ti_{56}Ni_{25.5}Fe_{2.5}Si_{16}$	bcc (NiTi)	−0.159		0.45				
$Ti_{56}Ni_{25.5}Fe_{2.5}Si_{16}$	icosahedral	−0.180		0.254				
$Ti_{56}Ni_{23}Fe_5Si_{16}$	icosahedral	−0.167		0.388				
$Ti_{56}Ni_{20.5}Fe_{7.5}Si_{16}$	icosahedral	−0.175		0.346				
$Ti_{56}Ni_{25.5}Fe_{2.5}Si_{16}$	amorphous	−0.105	0.456	0.43				
$Al_{85.3}Mn_{12.5}Fe_{2.2}$	icosahedral	+0.150	0.298	0.289	+0.141	0.550	0.272	1.6

sured Mössbauer parameters for a two-doublet fit to a room-temperature ^{57}Fe spectrum of icosahedral Al-Mn(Fe) as reported by Swartzendruber *et al.*[15] are given in Table I. No Mossbauer data are available for other major icosahedral classes.

The small quadrupole splitting (effectively zero) in icosahedral Ti-Ni-Si indicates an Fe environment of cubic or higher symmetry. As the present x-ray measurements indicate an essentially single-phase icosahedral structure, it appears that the Fe occupies the central icosahedral site ($\Delta \sim 0$) since all other sites are of lower than cubic symmetry.

It is interesting to note the large difference in Δ between crystalline Ti_2Ni and icosahedral Ti-Ni-Si. This is in contrast to the situation in crystalline and icosahedral Al-Mn-Si,[17] where the Mössbauer spectra show a large average quadrupole splitting and no evidence of a site with zero or small splitting for either structure. While the local structure of icosahedral Al-Mn-Si is believed to be closely related to cubic α-(Al-Mn-Si), the present results for the Ti-based alloys illustrate that the local structure of the icosahedral alloy is very different from that found in crystalline Ti_2Ni.

The linewidth of the singlet in the $x = 2.5$ quasicrystalline sample is essentially equal to the intrinsic line width while for the $x = 5$ samples it is considerably larger than the natural linewidth of the spectrometer. However, this latter value of Γ is comparable with that observed for quasicrystalline Al-Mn alloys when fitting their quadrupole split spectra to two broadened Lorentzians (~ 0.36 mm/s).[17] The anomalous linewidth for icosahedral AlMn has been interpreted in terms of a distribution of Fe environments. Because of the probable existence of disorder in all quasicrystalline materials, it is not unexpected that broadened Mössbauer lines are observed. The present results show that any quadrupole distribution giving rise to the broadened Mössbauer lines in the Ti-Ni-Fe-Si $x = 5$ and 7.5 has a peak at or near zero. We feel on the basis of the present analysis that an upper limit on the mean value of Δ of ~ 0.05 mm/s is reasonable.

The number of different transition metal sites in icosahedral Al-*M* alloys has been the subject of several recent investigations (Refs. 4, 12, 15, and 17). Although the results presented here for icosahedral Ti-Ni-Si do not indicate the existence of more than one type of Fe site, this cannot be taken as conclusive evidence that more than one type of Ni site does not exist. Dunlap *et al.*[12] and Eibschutz *et al.*[24] have suggested that, although more than one type of TM site exists in icosahedral Al-*M* alloys, Fe preferentially substitutes for only one of these. Details of studies of site occupancy for higher Fe concentrations in Ti-Ni-based quasicrystals will be presented elsewhere.[25]

The present Mössbauer measurements indicate a high-symmetry site for Fe in icosahedral Ti-Ni-Fe-Si in alloys. The x-ray line intensities have been analyzed in detail by Dunlap *et al.*[23] On the basis of calculated icosahedral diffraction patterns,[26,27] Dunlap *et al.*[23] have proposed a structure of this alloy based on a three-dimensional Penrose tiling of oblate and prolate rhombohedra where at least some of the transition metal sites have local icosahedral symmetry. The present measurements are consistent with this interpretation and are the first reported indication of a highly symmetric transition-metal site in a quasicrystalline structure.

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