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Quasicrystal structure of rapidly solidified Ti-Ni-based alloys

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Rapidly solidified $Ti_{56}Ni_{23}Fe_5Si_{16}$ has been prepared by quenching from the melt onto a single roller. X-ray diffraction measurements showed the alloy to be single phased with a pattern characteristic of the icosahedral structure. Diffraction peaks were indexed using scattering vectors described by a set of icosahedral basis vectors. The ratio of the quasilattice constant to the mean interatomic spacing for the corresponding crystalline alloy Ti_2Ni is 1.82. This is intermediate between the values for Al-Mn-Si type alloys, 1.65, and for Al-Zn-Mg type alloys, 2.00, and suggests a new type of icosahedral structure. The present diffraction intensities, along with a high Fe site symmetry previously reported from Mössbauer studies, suggests a decoration of Penrose rhombehedra with Fe and Ni at the vertices and Ti at the edges.

I. INTRODUCTION

Quasicrystalline structures were first observed in rapidly solidified Al–transition-metal (Al-T) alloys by Shechtman *et al.*[1] This report prompted extensive experimental and theoretical work on these and similar materials exhibiting bond orientational ordering but no translational ordering. Subsequent to the initial work on Al-T alloys, quasicrystalline ordering has also been reported in Al-T alloys,[2] Al-Zn-Mg,[3] Al-Cu-Li,[4] Pd-U-Si,[5] and Ti-Ni-V.[6] While the structure of Ti-Ni-based quasicrystals has typically been microquasicrystalline,[7] Chatterjee and O'Handley[8] have shown that the addition of Si to Ti-Ni promotes the growth of larger crystallites during solidification. Dunlap *et al.*[9] have shown that, given the proper quenching conditions, a single-phase Ti-Ni class alloy exhibiting icosahedral symmetry can be prepared and that, in this alloy, the Fe occupies a highly symmetric site. In the present work we report a detailed analysis of x-ray diffraction measurements of icosahedral $Ti_{56}Ni_{23}Fe_5Si_{16}$. A comparison with structural models of Al-Mn-Si and Al-Zn-Mg quasicrystals which are based on specific decorations of a three-dimensional Penrose lattice suggest a new type of icosahedral structure of the Ti-Ni class of alloys.

II. EXPERIMENTAL METHODS

Ribbons of $Ti_{55}Ni_{23}Fe_5Si_{16}$ were prepared by quenching from the melt under an atmosphere of He onto a single Cu roller. The surface velocity of the roller was 18 m/s and the melt was ejected through a 0.7-mm orifice by 70 kPa argon. Resulting ribbons were ~2 mm wide by 50 μm thick. X-ray diffraction measurements were performed at room temperature on a Siemens scanning powder diffractometer using Cu $K\alpha$ radiation.

III. RESULTS AND DISCUSSION

The x-ray diffraction pattern of $Ti_{56}Ni_{23}Fe_5Si_{16}$ is shown in Fig. 1. As discussed below, this pattern was found to agree well with that calculated for the icosahedral structure. An alloy quenched at a higher surface velocity (~65 m/s) showed diffuse x-ray diffraction peaks indicative of an amorphous or microquasicrystalline structure.

An analysis of the diffraction patterns of quasicrystals is generally performed in terms of a cut and projection from six dimensions.[10,11] As the six fivefold axes of the icosahedral structure are not orthogonal in three dimensions, it is necessary to construct the basis vector for this structure along the edges of a six-dimensional hypercube. The six three-dimensional axes are produced by a projection of the six basis vectors onto a three-dimensional hyperplane. The projection yields the six vectors: ϵ_1, $\epsilon_2, \ldots, \epsilon_6$ from which the scattering vectors are obtained. If the ϵ_i are taken to be unit vectors, orthogonality of the basis vectors in six dimensions implies[12]

$$\epsilon_i \cdot \epsilon_j = \begin{cases} 5^{1/2} & (i \neq j) \\ 1 & (i = j) \end{cases} . \tag{1}$$

The generalized Bragg vector is constructed as

$$b\mathbf{Q}_\parallel = \tau \sum_{i=1}^{6} n_i \epsilon_i , \tag{2}$$

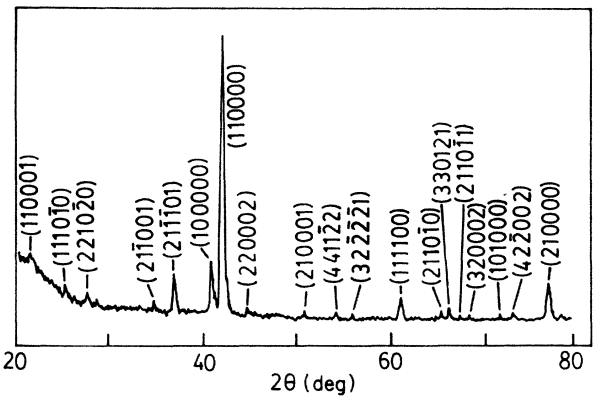

FIG. 1. Cu $K\alpha$ x-ray diffraction pattern of icosahedral $Ti_{56}Ni_{23}Fe_5Si_{16}$. Peaks are indexed as described in the text.

where b is a scale factor which depends on the interatomic spacing of the quasicrystal structure and the n_i are the six Miller indices of the reflection. In terms of Eq. (2) the q value of the $(n_1n_2n_3n_4n_5n_6)$ reflection is calculated to be

$$q = |\mathbf{Q}_\parallel| \ . \tag{3}$$

In the present analysis we have taken the six ϵ_i vectors to be a series of cyclic permutations of the form

$$\begin{aligned} &\epsilon_1 = \mu(1,\tau,0), \ \epsilon_2 = \mu(1,-\tau,0) \ , \\ &\epsilon_3 = \mu(0,1,\tau), \ \epsilon_4 = \mu(0,1,-\tau), \\ &\epsilon_5 = \mu(\tau,0,1), \ \epsilon_6 = \mu(-\tau,0,1) \ , \end{aligned} \tag{4}$$

where the golden ratio τ is given as $(1+\sqrt{5})/2 = 1.61803$. μ is given as $(1+\tau^2)^{1/2} = 0.52573$ and is required to fulfill the normalization conditions of Eq. (1).

Experimental results obtained from the present x-ray diffraction measurements along with calculated q values are given in Table I. Experimental values for icosahedral $Al_{86}Mn_{14}$ from Bancel *et al.*[10] are given for comparison. The scale factor b for $Ti_{56}Ni_{23}Fe_5Si_{16}$ was obtained by plotting measured q values as a function of calculated $b|\mathbf{Q}_\parallel|$ values for the same reflection. This is illustrated in Fig. 2. A least-squares fit to the data gives a value of $b = 1.119$ Å. The validity of the indexing scheme is indicated by the fact that the fit gives an intercept of 0.

Values of q were calculated for the $Al_{86}Mn_{14}$ structure in the same manner. Nearly all $Ti_{56}Ni_{23}Fe_5Si_{16}$ diffraction peaks corresponded to peaks in the $Al_{86}Mn_{14}$ structure. As we would anticipate for an alloy containing different elements, however, the relative peak intensities for the two systems are somewhat different. Four very weak peaks in the $T_{56}Ni_{23}Fe_5Si_{16}$ diffraction did not correspond to measurable $Al_{86}Mn_{14}$ peaks. These occur at q values of 3.725, 3.829, 4.433, and 4.608 Å^{-1}, and are readily indexed according to the scheme of Bancel *et al.*[10]

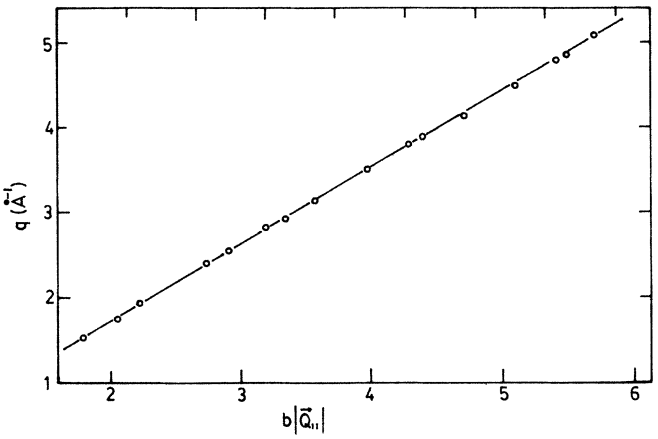

FIG. 2. Experimentally determined q values for icosahedral $Ti_{56}Ni_{23}Fe_5Si_{16}$ plotted as a function of calculated $b|\mathbf{Q}_\parallel|$ values.

TABLE I. X-ray diffraction peaks observed in icosahedral $Ti_{56}Ni_{23}Fe_5Si_6$. Experimental values of the parameters for $Al_{86}Mn_{14}$ from Bancel *et al.* (Ref. 10) are given for comparison. The peak width Δ is given as the half width at half maximum.

	$Al_{86}Mn_{14}$				$Ti_{56}Ni_{23}Fe_5Si_{16}$			
Reflection	q (Å^{-1})	Intensity	Δ (Å^{-1})	q_{calc} (Å^{-1})	q (Å^{-1})	Intensity	Δ (Å^{-1})	q_{calc} (Å^{-1})
(110001)	1.632	22	0.018	1.628	1.53	3	0.02	1.580
(111010)	1.876	8	0.014	1.880	1.792	3.6	0.013	1.825
(221020)	2.000			1.998	1.956	1.2	0.01	1.942
(311111)	2.20	1.5		2.208				
(211001)	2.49	3		2.486	2.446	3.9	0.009	2.415
(211101)	2.64			2.659	2.589	13.5	0.01	2.582
(100000)	2.896	100	0.009	2.893	2.861	19.7	0.013	2.809
(110000)	3.043	78	0.022	3.043	2.947	100	0.012	2.953
(220002)	3.24	1		3.253	3.133	1	0.02	3.162
(111101)	3.44			3.450				
(210001)	3.576	1.5	0.04	3.576	3.513	1		3.472
(320011)	3.63							
(421122)					3.729	1.5		3.717
(220001)	3.92	0.5		3.929				
(322221)					3.829	1.5	0.02	3.831
(221010)	4.04			4.059				
(111000)	4.200	11	0.21	4.198				
(111100)	4.307	3	0.02	4.302	4.178	8.3	0.018	4.177
(211010)	4.60	0.5		4.599	4.433	3.1	0.02	4.466
(330121)					4.483	3.9	0.015	4.471
(211011)	4.70	0.5		4.694	4.544	1	0.02	4.558
(320002)					4.608	2	0.02	4.606
(101000)	4.928	20	0.021	4.921	4.798	1	0.02	4.779
(422002)	4.99	0.5		4.969	4.805	2.2	0.02	4.830
(210000)	5.23			5.269	5.102	12.6	0.017	5.092

as (441122), (322221), (330121), and (320002), respectively. As seen in Table I as well as in Fig. 2, there is some scatter in the experimentally determined peak location compared with those which have been calculated on the basis of the scale factor b. Typically, line positions agree within about one FWHM of the sharpest lines. This is the case for both our data and those of Bancel *et al.*[10] This is also the case in similar measurements of other Al-T quasicrystals.[13] While Yamane, Kimura, Shibuya, and Takeuchi[13] consider that these discrepancies fall within the expected experimental error, it is possible that they represent quasicrystalline anisotropies related to the strains which Bancel *et al.*[10] have suggested are responsible for the preferential line broadening observed in Al-based quasicrystals.

By comparison, the indexing scheme proposed by Elser[12] can be obtained from the one used here by appropriate application of the inflation and deflation operators to the Miller indices $(n_1n_2n_3n_4n_5n_6)$.[12] It is also found that the scale factor obtained by the present method b is related to the quasilattice constant a given by Elser[12] as

$$a=\sqrt{5}(1+\tau^2)^{1/2}b \ . \tag{5}$$

Thus for $Ti_{56}Ni_{23}Fe_5Si_{16}$ we obtain $a=4.761$ Å, in comparison with the value of 4.60 Å reported for $Al_{86}Mn_{14}$.[10]

The parameter a is described[14] in terms of the model comprised of a three-dimensional Penrose tiling (3D PT) as the rhombohedra edge length. The value of a can be compared with the rhombohedral cell length in related crystalline materials. Some crystalline early-late transition-metal alloys are known to form the $C15$ Laves phase. This phase can be modeled in terms of prolate rhombohedra which are only slightly different from those of the 3D PT (vertex angle $\alpha=60°$ for the Laves phase, and $\alpha=63.4°$ for the 3D PT). A typical example of the $C15$ phase in an early-late transition-metal system, $TaCo_2$, in fact, shows a rhombohedral cell length which is also 4.76 Å.

Henley and Elser[14] have described two distinct icosahedral structures: the Al-Mn-Si type[15] and the Al-Zn-Mg type.[14] Microscopically these are both modeled as 3D PT, comprised of packings of prolate and oblate rhombohedra but they differ in the atomic decoration of the rhombohedra. Emperically, the two types of structures can be distinguished on the basis of the quasilattice parameter and its relationship to the average interatomic spacing in an analogous crystalline alloy d. Parameters for the categorization of various icosahedral structures are given in Table II. Henley and Elser[14] have suggested that those alloys with values of, and near, 2.0 are of the (Al,Zn)-Mg icosahedral structure, while those with, and near, 1.65 are of the Al-Mn-Si icosahedral structure. Values shown in Table II for Pd-U-Si and for Ti-Ni-Fe-Si are intermediate between the values for (Al, Zn)-Mg and Al-Mn-Si. Henley and Elser[14] have suggested that Pd-U-Si is of the Al-Mn-Si type and, in fact, its value of $a/d=1.77$ is somewhat closer to 1.65 than 2.0. For Ni-Ti-Si the structure cannot be distinguished on the basis of a/d.

Some insight can be gained into the decoration of icosahedral Ti-Ni-Fe-Si on the basis of recently reported Mössbauer effect measurements and x-ray diffraction line intensities. Dunlap, McHenry, and O'Handley[9] have shown that the Fe quadrupole splitting as measured by ^{57}Fe Mössbauer spectroscopy is essentially zero. This is in sharp contrast to Fe sites in icosahedral Al–transition-metal alloys where the quadrupole splitting $\Delta\sim0.4$ mm/s. This indicates a much more highly symmetric transition-metal site in Ti-Ni-Fe-Si than in Al-based quasicrystals.

A notable feature of the present x-ray diffraction pattern is the relatively low intensity of the (100000) peak. Calculations of structure factors for icosahedral phases based on different decorations of prolate and oblate rhombohedra have been reported by Ishihara and Shingu.[20] The relationship of these two rhombohedral cells is shown in Fig. 3. Ishihara and Shingu[20] have considered models of quasicrystals constructed from rhombohedra with atoms at vertics, vertices and edges, or vertices and faces. In these calculations, only when atoms are present at vertices and at edges is the intensity of the (100000) peak significantly lower than that of the (110000) peak. It is difficult to determine uniquely atomic positions in the Ti-Ni-Fe-Si structure. However, in terms of our x-ray measurements and previous Mössbauer measurements, it is reasonable to assume a decoration where Ni and Fe atoms are placed on the rhombohedral vertices and Ti and Si atoms are placed on the rhombohedral edges.

TABLE II. Quasilattice parameters and corresponding average crystalline interatomic spacing in some icosahedral alloys. d is the average interatomic spacing of the crystalline structure.

Icosahedral structure		Corresponding crystal structure			
Alloy	(Å)	Composition	Structure	(Å)	a/d
Al-Mn-Si	4.60[a]	$Al_{72.5}Mn_{17.4}Si_{10.1}$ (α-Al-Mn-Si)	bcc	2.79[b]	1.65
Al-Zn-Mg	5.14[c]	$(Al\text{-}Zn)_{49}Mg_{32}$	bcc	2.57[d]	2.00
Pd-U-Si	5.134[e]	Pd_3U	hex.	2.9[f]	1.77
Ti-Ni-Fe-Si	4.76[g]	Ti_2Ni	fcc	2.61[h]	1.82

[a] References 12 and 14.
[b] Reference 16.
[c] Reference 14.
[d] Reference 17.
[e] References 5 and 14.
[f] Reference 18.
[g] This work.
[h] Reference 19.

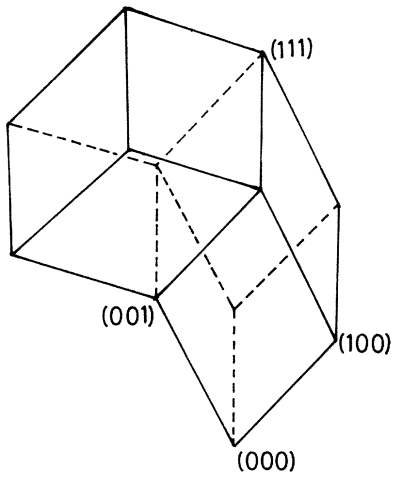

FIG. 3. Relationship of the prolate and oblate rhombohedra in the 3D PT model of icosahedral structures.

The decoration is consistent with the calculated x-ray line intensities and the symmetric Fe environment observed by Mössbauer investigations presently underway on icosahedral Ti-Ni-Fe-Si alloys with higher Fe concentrations will indicate if, for higher concentrations, the Fe occupies other less symmetric sites as well.

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[1]D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[2]R. A. Dunlap and K. Dini, J. Mater. Res. **1**, 415 (1986).

[3]R. Ramachandra Rao and G. Sastry, Pramana **25**, L225 (1985).

[4]P. Sainfort, B. Dubost, and A. Dubus, C. R. Acad. Sci. **301**, 689 (1985).

[5]S. J. Poon, A. J. Drehman, and K. R. Lawless, Phys. Rev. Lett. **55**, 2324 (1985).

[6]Z. Zhang, H. Q. Ye, and K. H. Kuo, Philos. Mag. A **2**, L49 (1985).

[7]L. Bendersky, Mater. Sci. Eng. (to be published).

[8]R. Chatterjee and R. C. O'Handley (unpublished).

[9]R. A. Dunlap, M. E. McHenry, and R. C. O'Handley (unpublished).

[10]P. A. Bancel, P. A. Heiney, P. W. Stephens, A. I. Goldman, and P. M. Horn, Phys. Rev. Lett. **54**, 2422 (1985).

[11]J. W. Cahn, D. Schechtman, and D. Gratias, J. Mater. Res. **1**, 13 (1986).

[12]V. Elser, Phys. Rev. B **32**, 4892 (1985).

[13]H. Yamane, K. Kimura, T. Shibuya, and S. Takeuchi, Institute of Solid State Physics, University of Tokyo, Technical Report Ser. A. No. 1848, 1987 (unpublished).

[14]C. L. Henley and V. Elser, Philos. Mag. B **53**, L59 (1986).

[15]V. Elser and C. L. Henley, Phys. Rev. Lett. **55**, 2883 (1985).

[16]M. Cooper and K. Robinson, Acta. Crystallogr. **20**, 614 (1966).

[17]G. Bergman, J. L. T. Waugh, and L. Pauling, Acta. Crystallogr. **12**, 909 (1959).

[18]T. J. Heal and G. I. Williams, Acta. Crystallogr. **8**, 495 (1955).

[19]G. A. Yurko, J. W. Burton, and J. G. Parr, Acta. Crystallogr. **12**, 909 (1959).

[20]K. N. Ishihara and P. A. Shingu, J. Phys. Soc. Jpn. Lett. **55**, 1795 (1986).