Coherent orientation relationship between an icosahedral phase and a cubic α phase in melt-spun Al-Si-Mn

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We report what we believe to be the first observation of definite coherent directional relationship between a cubic α phase and an icosahedral phase in rapidly quenched Al-Si-Mn. Electron-microscopic studies reveal that the set of three cubic orthogonal [001]-type directions are parallel, respectively, to three icosahedral twofold axes, and all cubic [111] directions are parallel to threefold icosahedral axes, while the fivefold icosahedral directions are very close to [530]-type cubic directions. Structural models of the quasicrystal as a disordered α phase are consistent with the present results.

There has been much recent interest in the structure of the newly-discovered icosahedral phase of Al-Mn,[1] Al-Mn-Si[2] and other alloys.[3] Most of the present work has been focused on theoretical and experimental determination of the diffraction patterns[4,5] and the local environments surrounding Mn atoms.[6–8,9] While mathematical models based on three-dimensional Penrose tilings reproduce the diffraction patterns quite accurately, little is known of the actual atomic positions which decorate the cells. From Mössbauer studies, Swartzendruder *et al.*[6] suggest two types of Mn sites in a quasicrystalline Al_6Mn; however, a more recent Mössbauer study by Eibschultz, Chen, and Hauser[7] concludes that the data are more consistent with a distribution of Mn sites, and the relatively broad electrical field gradient distributions at the Mn sites in icosahedral and amorphous Al_6Mn are very similar. Recent nuclear-magnetic-resonance (NMR) measurements[8] reached the same conclusion. Furthermore, the similarity of a number of properties and structural relaxation phenomena[10] to those of glassy metals suggests that the As-grown icosahedral $Al_{86}Mn_{14}$ consists of a highly disordered structure.

While x-ray diffraction could yield detailed information about the atomic structure of these phases, intensity measurements are presently limited by (1) small size of single crystals and (2) poor quality (strains, defects) of these crystals. One approach to deal with the atomic structure of the icosahedral phase is to correlate known structure to the icosahedral structure.[11] It is known that the three-dimensional Penrose tiling (3D PT) can be obtained by projection of a 6D cubic lattice to a 3D hyperplane at an incommensurate orientation. By tilting the projection hyperplane to a commensurate orientation, periodic packing of the same rhombohedra can be obtained. Thus the quasicrystalline structure can be considered as the limit of a sequence of periodic structures with ever larger unit cells. Elser and Henley[11] have demonstrated that the α-$(Al_{100}Si_{14}Mn_{24})$ can be decomposed into two different ways; a periodic packing of decorated three-dimensional Penrose rhombohedra, and a bcc packing of Mackay icosahedra.[12] In these approaches, the rhombohedral Penrose cells are decorated with Mn atoms at the vertices and Al atoms at the edges and faces. Alternatively, the Mackay icosahedra employed here are aggregates consisting of twelve Al atoms at the vertices of an icosahedron, surrounded by a mixture of Al and Mn atoms in such a way as to preserve the icosahedral symmetry. These icosahedra pack into a bcc array, with the spaces between them, filled with Al "glue" atoms. They suggest further that these icosahedra could be packed in a nonperiodic (or quasi-periodic) way, with the icosahedra remaining parallel. The resulting structure would still have sharp diffraction patterns. These two pictures of the α phase have immediate relevance to models for the icosahedral structures. In this communication, we report the first observation of a definite coherent directional relationship between a cubic α phase and an icosahedral phase in rapidly solidified Al-Si-Mn alloys. It will be shown that the set of three cubic orthogonal $\langle 100 \rangle$-type directions are parallel, respectively, to three icosahedral twofold axes, and all cubic $\langle 111 \rangle$-type directions are parallel to threefold icosahedral axes, while the fivefold icosahedral directions are very close to $\langle 530 \rangle$-type cubic directions. Theories of the quasicrystal as a disordered α phase are consistent with the present findings. These results would shed light on the atomic positions of the icosahedral Al-Si-Mn and its growth process.

$Al_{86-x}Si_xMn_{14}$ alloys were prepared by induction melting of high-purity Al, Si, and Mn in a boron nitride crucible in argon atmosphere. Thin ribbons, about 1 mm in width and and 30 μm in thickness were melt-spun on a copper wheel $\sim$20 cm in diameter rotating at 2000 rpm.

The solidification process was conducted in an enclosure filled with argon. For transmission electron microscopy (TEM) samples were obtained by ion thinning. The microscopy was performed using a JEOL 200 CX transmission electron microscope.

It was found that partial substitution of Al by Si destabilizes an icosahedral phase and stabilizes a cubic phase. X-ray and TEM examinations show that the binary $Al_{86}Mn_{14}$ alloy is nearly all icosahedral with a trace of fcc Al, in agreement with previous works,[1,2] while $Al_{80}Si_6Mn_{14}$ and $Al_{73}Si_{13}Mn_{14}$ samples consist of the icosahedral phase and a cubic phase. X-ray diffraction measurements show the lattice parameter of the cubic phase to be 12.63 Å. This is close to 12.68 Å found for α-$Al_{72.5}Si_{10.1}Mn_{17.4}$.[13] We calculated x-ray intensities using the atomic positions given for the α-Al-Si-Mn by Cooper and Robinson[13] and found that the intensities agree well enough, but not perfectly, with the diffraction data.

The $Al_{80}Si_6Mn_{14}$ sample is nearly all icosahedral. The grain sizes vary from 300 Å to 1 μm. We could not find any α peaks in the x-ray data (see Fig. 1), although TEM studies show regions of α phase and fcc Al. The α phase tends to occur mostly by itself in isolated regions. The $Al_{73}Si_{13}Mn_{14}$ sample consists mostly of the α phase. The icosahedral regions are also present but consist of less than 5% of total volume. In both cases, where the two phases coexist, they show a definite crystallographic relationship which will be discussed in the following for the $Al_{73}Si_{13}Mn_{14}$, as an example.

A typical microstructure is shown in Fig. 2. It shows roundish icosahedral grains surrounded by rings of α phase. In this micrograph these rings are fairly narrow with respect to the central i grain. In some regions, the i grain is no longer apparent. In many situations, microstructures between these two extremes are found (see Fig. 4). In all cases the surrounding α phase has a very definite orientational relationship to the i phase. Figure 3(a) shows a higher magnification micrograph of the interface region between an α grain and an i grain. The micrograph was formed using a 20-μm objective aperture, which, when centered on the center spot, includes diffraction spots which arise from planes having spacings greater than 7 Å. The lattices fringes in Fig. 3(a) correspond to {110}-type cubic planes (spacing of 8.9 Å) and {100000}-type i planes[14] (average spacing of 9.2 Å). Figure 3(b) shows an overlapping twofold i pattern and a (001) α pattern. Figures 3(c) and 3(d) show the individual patterns for each phase. The ⟨001⟩-type cubic directions and the twofold-type icosahedral axes of the patterns coincide perfectly. More specifically, the 600-type cubic spots nearly coincide with the 221 001 (twofold-axis) -type icosahedral spots, with the 600 spots having about 2% smaller radius from the center spot in agreement with x-ray data (Fig. 1). The 530-type spots are also nearly coincident with the 211 111 (fivefold-axis) -type spots. In this orientation relationship the set of three cubic orthogonal directions, e.g., [100], [010], and [001], are parallel, respectively, to three icosahedral twofold axes. There are

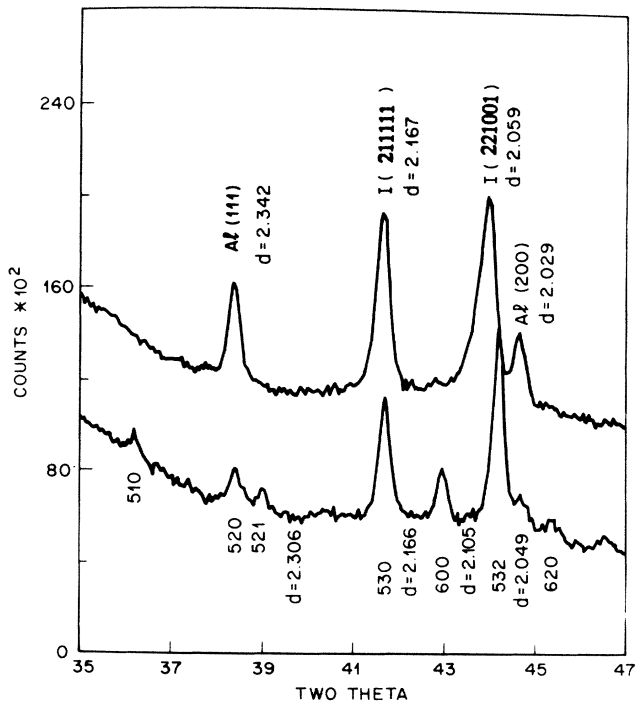


FIG. 1. X-ray diffraction data of As-spun $Al_{80}Si_6Mn_{14}$ (upper) and $Al_{73}Si_{13}Mn_{14}$ (lower). For clarity the data of the $Al_{80}Si_6Mn_{14}$ are shifted upward. Cu $K\alpha$ radiation was employed. Icosahedral indexes are labeled following Elser (Ref. 5). Interspacings (d) are also shown.

FIG. 2. A micrograph of As-spun $Al_{73}Si_{13}Mn_{14}$ alloy. Icosahedral grains are surrounded by rings of α-Al-Si-Mn grains.

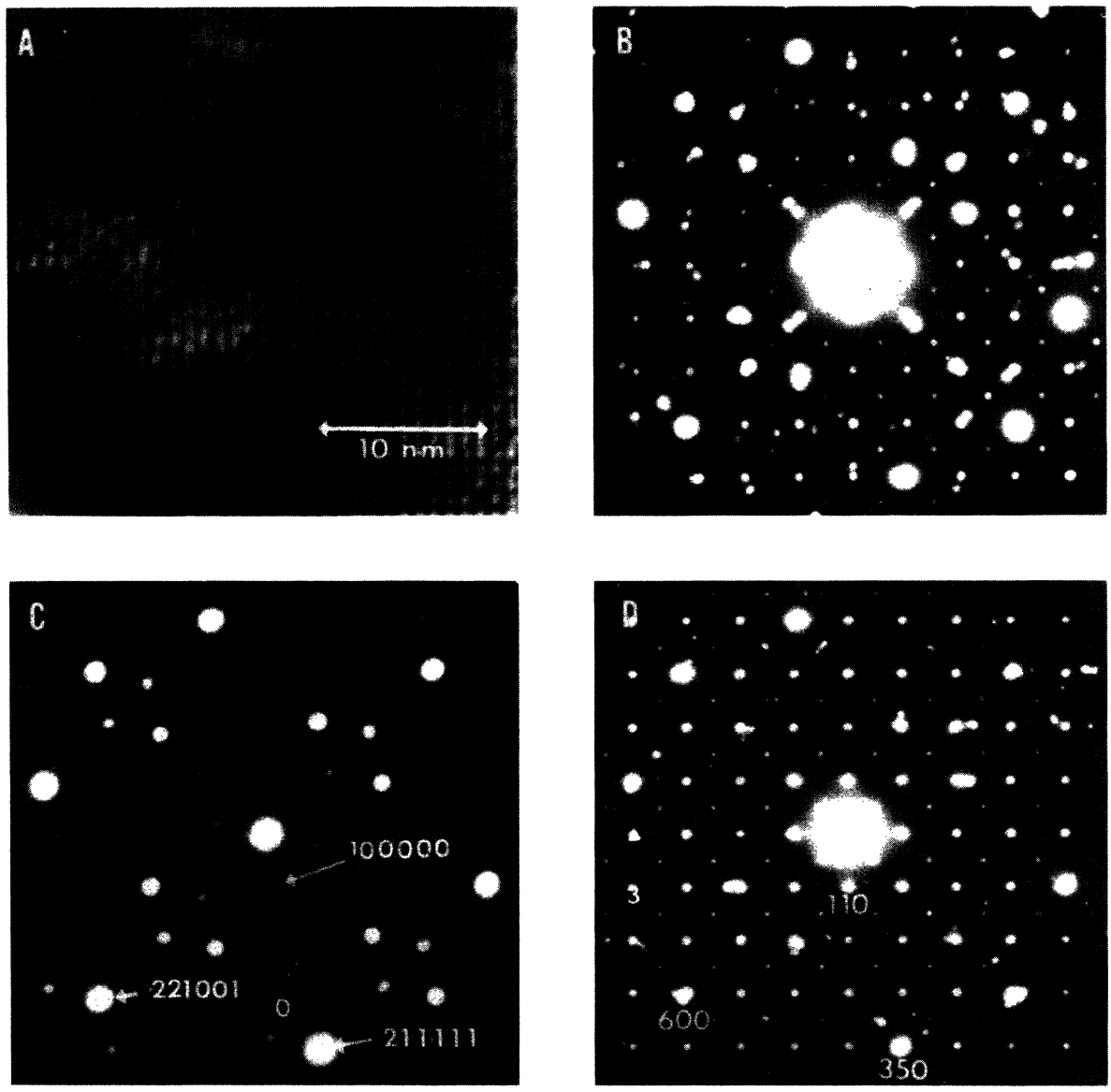


FIG. 3. *A*, A higher magnification micrograph of interface between α-Al-Si-Mn (on right) and *i*-Al-Si-Mn (on left), and corresponding diffraction patterns for *B*, interface; *C*, the icosahedral region (twofold zone axis); and *D*, α-region with $\langle 001 \rangle$ cubic zone axis.

five unique sets of orthogonal twofold axes in the icosahedral system giving five equivalent variants for the orientation relationship. The individual grains in the ring of α grains surrounding the *i* grain therefore can have five orientations relative to the center grain.

One consequence of the above orientation relationship is that all $\langle 111 \rangle$-type cubic directions coincide with threefold icosahedral directions. There are ten threefold icosahedral axes, or six more than the four $\langle 111 \rangle$-type cubic axes. These six other threefold axes lie parallel to irrational cubic directions which are about 0.1° from $\langle 13\,5\,0 \rangle$-type cubic directions. Figure 4 shows a threefold zone axis. The pattern is taken from an *i* grain and several adjacent α grains, each having a different variant of the orientation relationship. Two $\langle 111 \rangle$ cubic orientations are present with one pattern rotated 13.2° about the [111] axis with respect to the other. The 532-type spots of both [111] cubic patterns coincide closely with 221 001 (twofold-axis) -type spots in the threefold icosahedral pattern (also see Fig. 1). One of these coincidences of three spots is labeled. The other three variants are not as apparent, but have roughly $\langle 13\,5\,0 \rangle$-type zone axes with [001] type spots lying along any of the three twofold axes of the icosahedral pattern.

Finally, in Fig. 5, a fivefold icosahedral axis is shown with overlapping patterns from several adjacent α grains. These grains are oriented with $\langle 035 \rangle$-type zone axes. Although some or all five of the orientation variants show up to greater or lesser degree, only the strongest cubic pattern is illustrated in the accompanying drawing. In this case $\langle 532 \rangle$-type and $\langle 600 \rangle$-type spots nearly coincide with the 221 001-type icosahedral spots.

We demonstrate here that there exists a very definite coherent orientational relationship between an *i* phase and

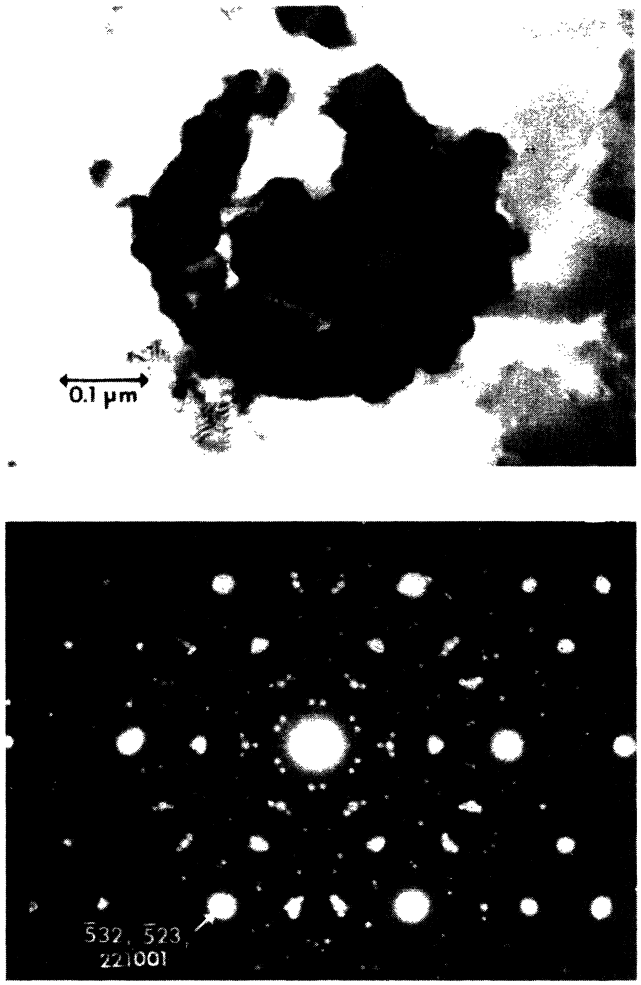
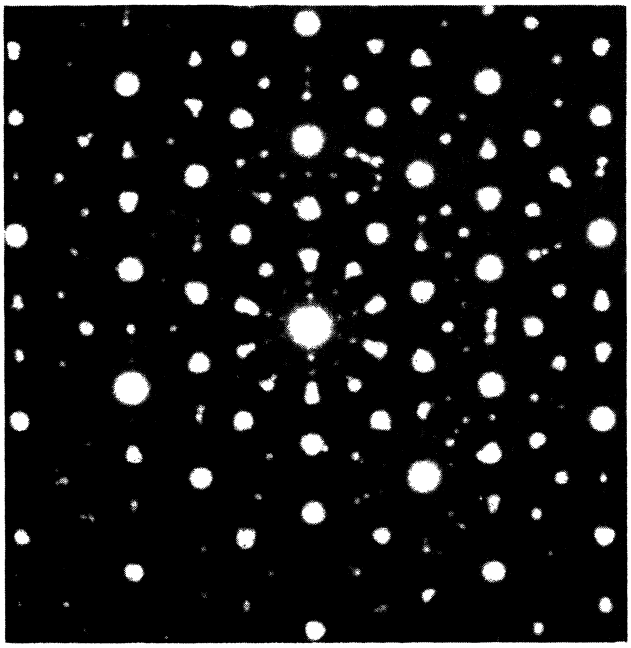


FIG. 4. A micrograph and diffraction pattern of an icosahedral grain with threefold zone axis surrounded by α-grains having $\langle 111 \rangle$ and $\langle 13\,5\,0 \rangle$ zone axes.

an α phase in rapidly solidified $Al_{73}Si_{13}Mn_{14}$. The same relationship is also found in $Al_{80}Si_6Mn_{14}$. The set of three cubic orthogonal $\langle 100 \rangle$-type directions are parallel, respectively, to three icosahedral twofold axes, and every cubic $\langle 111 \rangle$-type direction is parallel to a threefold icosahedral axis, while the fivefold icosahedral directions are very close to $\langle 530 \rangle$-type cubic directions. Aside from those which are parallel to the $\langle 001 \rangle$-type cubic directions, additional twofold icosahedral directions are very close, within 1°, to $\langle 532 \rangle$-type cubic directions. Furthermore, the brightest spots, e.g., $\langle 600 \rangle$, $\langle 530 \rangle$, and $\langle 532 \rangle$-type spots, in cubic patterns nearly coincide with spots in the corresponding icosahedral patterns. This suggests that the structure of the cubic phase is very closely related to the icosahedral structure.

The structural model of the icosahedral phase as a distorted α phase is consistent with present results. In any periodic packing of icosahedral rhombohedra, each twofold or threefold symmetry axis of the unit cell will be oriented with a twofold or threefold axis of the icosahedral basis vectors. If we consider the α-Al-Si-Mn as a bcc array of (54-atom) Mackay icosahedra, the cubic $\langle 530 \rangle$-type axes would nearly coincide with the



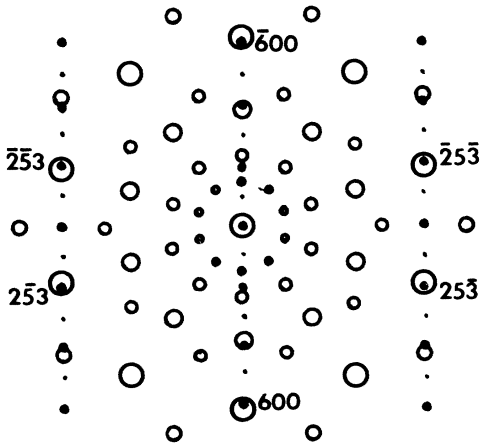


FIG. 5. Fivefold icosahedral pattern with overlapping $\langle 035 \rangle$-type cubic patterns. One of the five cubic patterns (●) is drawn with the icosahedral pattern (○).

icosahedral $\{100\,000\}$ (fivefold) -type axes. The angles between these axes and the twofold zone axes are 59.09° $[=\tan^{-1}(5/3)]$ and 58.28° $[=\tan^{-1}\tau$, where $\tau=(1+\sqrt{5})2]$, respectively. these correlations are indeed observed experimentally. Elser and Henley[11] have decomposed the α phase into Penrose rhombohedra, and shown that the crystal structure can be regarded as a periodic analog of a Penrose tiling. From the x-ray data for the icosahedral phase shown in Fig. 1, we calculate the rhombohedral edge length $a_R=13.308/|g_{211\,111}|=4.59$ Å (see, e.g., Elser[5]). Here $|g_{211\,111}|=2\pi/d_{211\,111}=2.899$ Å^{-1}. On the other hand, the lattice constant of the α phase is $a=12.63$ Å, where $a=a_R(4+8/\sqrt{5})^{1/2}$.[11] It gives $a_R=4.59$ Å, in complete agreement with the

model. Accordingly, the local structure of α and the icosahedral phase is similar though it need not be identical. Recent extended x-ray-absorptions fine-structure data have revealed close resemblance in the first coordination surrounding Mn atoms between an i-$Al_{74}Si_6Mn_{20}$ and α-$Al_{100}Si_{14}Mn_{24}$.[9]

The α-Al-Si-Mn phase is almost body-centered belonging to the $Pm\,3$ space group.[13] There are two types of manganese atom, Mn(1) and Mn(2). Mn(1) atoms have ten Al neighbors at an average distance of 2.63 Å and Mn(2) atoms have nine Al neighbors. There are two large holes in the structure, one at the origin, and the other at the center of the unit cell, and each are surrounded by 12 Al atoms. It is significant to note that the 12 Al atoms are positioned at the vertices of an icosahedron surrounding the vacant site, and Mn atoms on the second shell of the icosahedra. This in contrast to the naive belief that smaller Mn atoms would occupy the center of icosahedra surrounded by larger Al atoms.[15] Apparently, besides atomic sizes factors such as electronegativity, charge transfer, etc., determine the atomic structure of these alloys.

Microstructures shown in Figs. 2 and 4 indicate that the icosahedral phase nucleates and grows, then transforms to the α phase. It appears that the icosahedral phase rejects excess Al and Si as it is growing, causing the α phase to become more stable and precipitate coherently around the periphery of the icosahedral grain. The most striking feature is the definite coherent orientational relationship between the central i grain and the surrounding α precipitates. If we regard the α phase as a periodic bcc packing of $(Al,Si)_{42}Mn_{12}$ Mackay icosahedra and the icosahedral structure as a disordered packing together of these icosahedra in a noncrystalline (or quasiperiodic) way (with the icosahedra still parallel), we can imagine the transformation from the i phase to the α phase as being simply the consequence of a slight modification in packing sequence, from quasiperiodic to periodic, of the icosahedra. The possible existence of such icosahedral clusters has been proposed.[11] In alloy systems, the interatomic interactions play a significant role as it has been shown that short-range order resembling that in corresponding intermetallic phases exists in alloy glasses.[16] During a rapid solidification the α phase is suppressed and the i phase nucleates when there is not enough time for the periodic packing of the icosahedral clusters. As the i phase grows, the rate of growth decreases. When there is sufficient time for the clusters to form a periodical array, the i phase transforms into the α phase with definite directional relationships. The nucleation barrier of an α phase would be very small.

We note that the substitution of Al with a small amount of Si (≤ 13 at. %) tends to suppress the formation of the icosahedral phase as it stabilizes the α-Al-Si-Mn. Further increase in Si content, in turn, destabilizes the α phase, and the As-spun $Al_{86-x}Si_x\ Mn_{14}$ with $20 \leq x \leq 50$ is found to be glassy. The large composition range over which these alloys can be vitrified by melt quenching is surprising, given the phase diagrams of the system involved. For instance, the Al-Mn system shows no eutectics at all, only peritectics, while the Al-Si system has a shallow eutectic. It is likely that the icosahedral short-range order resembling that in α and icosahedral phases exists in the glassy alloys. It thus may be possible to model the glasses as a dense packing of the (54-atom) Mackay icosahedra (MI) with the remaining space filled with "glue". The large MI cluster, containing 54 atoms, would facilitate the glass formation. Structure studies of these glassy alloys should prove useful.

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[1]D. Schectman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984); P. A. Bancel, P. A. Heiney, P. W. Stephens, A. I. Goldman, and P. M. Horn, Phys. Rev. Lett. **54**, 2422 (1985).

[2]C. H. Chen and H. S. Chen, Phys. Rev. B. **33**, 2814 (1986).

[3]For example, the icosahedral phase has been found in a rapidly solidified $Mg_{32}(Al,Zn)_{49}$ [P. Ramachandrarao and G. V. S. Sastry, Pramana **25**, L225 (1985)] and in the transformation of glassy PdUSi [S. J. Poon, A. J. Drehman, and K. R. Lawless, Phys. Rev. Lett. **55**, 2324 (1985)].

[4]See, e.g., D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984); N. D. Mermin and S. M. Troian, *ibid.* **54**, 1524 (1985); P. Bak, *ibid.* **54**, 1517 (1985); D. R. Nelson and S. Sachdev, Phys. Rev. B **32**, 689 (1985).

[5]See, e.g., P. Kramer and R. Neri, Acta Crystallogr. Sect. A **40**, 580 (1984); M. Duneau and A. Katz, Phys. Rev. Lett. **54**, 2688 (1985); V. Elser, Phys. Rev. B **32**, 4892 (1985).

[6]L. J. Swartzendruder, D. Shechtman, L. Bendersky, and J. W. Cahn, Phys. Rev. B **32**, 1383 (1985).

[7]M. Eibschutz, H. S. Chen, and J. J. Hauser, Phys. Rev. Lett. **56**, 169 (1986).

[8]W. W. Warren, H. S. Chen, and J. J. Hauser, Phys. Rev. B **32**, 7614 (1985).

[9]M. A. Marcus, H. S. Chen, G. P. Espinosa, and C. L. Tsai (unpublished).

[10]See, e.g., H. S. Chen, C. H. Chen, A. Inoue, and J. T. Krause, Phys. Rev. B **32**, 1940 (1985); H. S. Chen and C. H. Chen, *ibid.* **33**, 668 (1986).

[11]V. Elser and C. L. Henley, Phys. Rev. Lett. **55**, 2883 (1985); P. Guyot and M. Audier, Philos. Mag. B **52**, L15 (1985).

[12]A. L. Macky, Acta Cryst. **15**, 916 (1962).

[13]M. Copper and K. Robinson, Acta Crystalogr. **20**, 614 (1966).

[14]We use the icosahedral indexing scheme of V. Elser, Phys. Rev. B **32**, 4892 (1985). The basis vectors $\mathbf{e}^i$ line up with the six fivefold symmetry axes of the icosahedron, with $\mathbf{e}^1$ a polar vector surrounded in cyclic order by $\mathbf{e}^2, \ldots, \mathbf{e}^6$.

[15]K. Hiraga, M. Hirabayashi, A. Inoue, and T. Masumoto, Sci. Rep. RITU. **32A**, 309 (1985); D. Schechtman and I. A. Blech, Met. Trans. **16A**, 1005 (1985).

[16]H. S. Chen, Rep. Prog. Phys. **43**, 353 (1980).

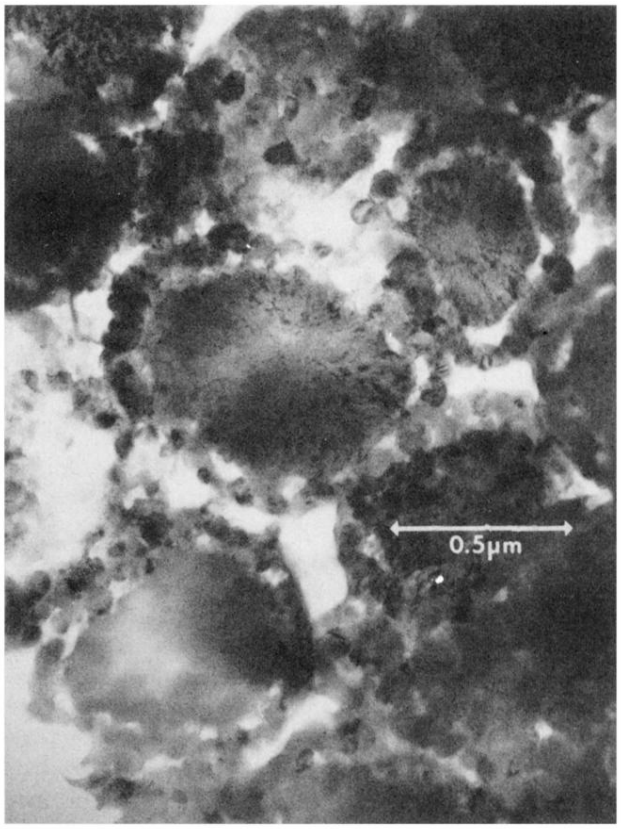


FIG. 2. A micrograph of As-spun $Al_{73}Si_{13}Mn_{14}$ alloy. Icosahedral grains are surrounded by rings of α-Al-Si-Mn grains.

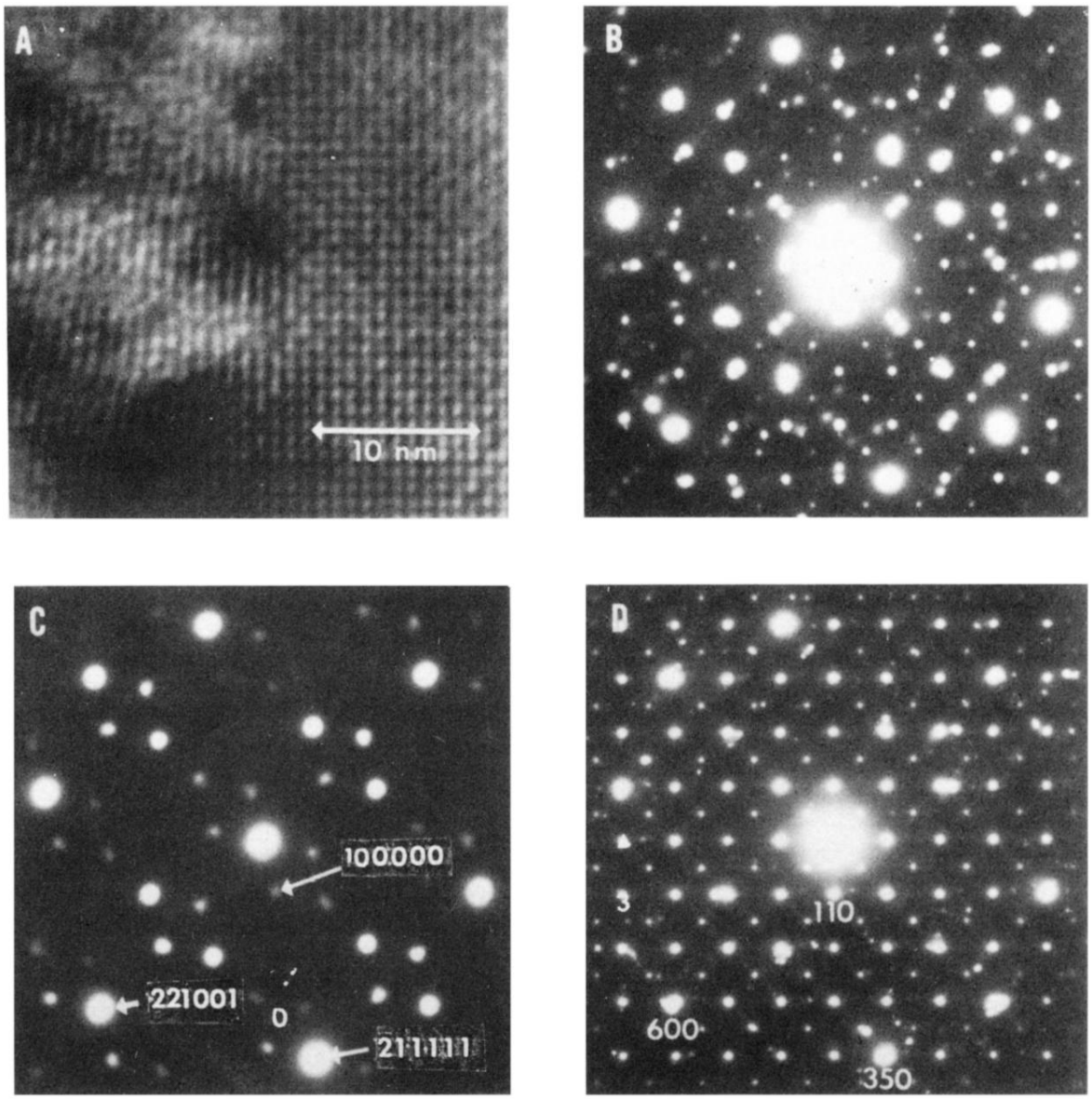


FIG. 3. *A*, A higher magnification micrograph of interface between α-Al-Si-Mn (on right) and *i*-Al-Si-Mn (on left), and corresponding diffraction patterns for *B*, interface; *C*, the icosahedral region (twofold zone axis); and *D*, α-region with $\langle 001 \rangle$ cubic zone axis.

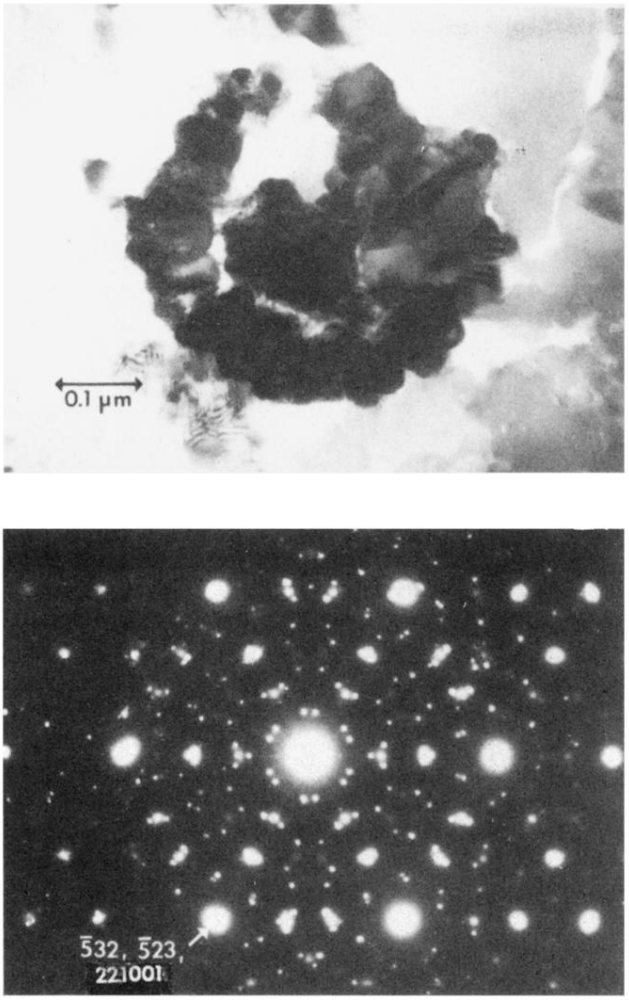
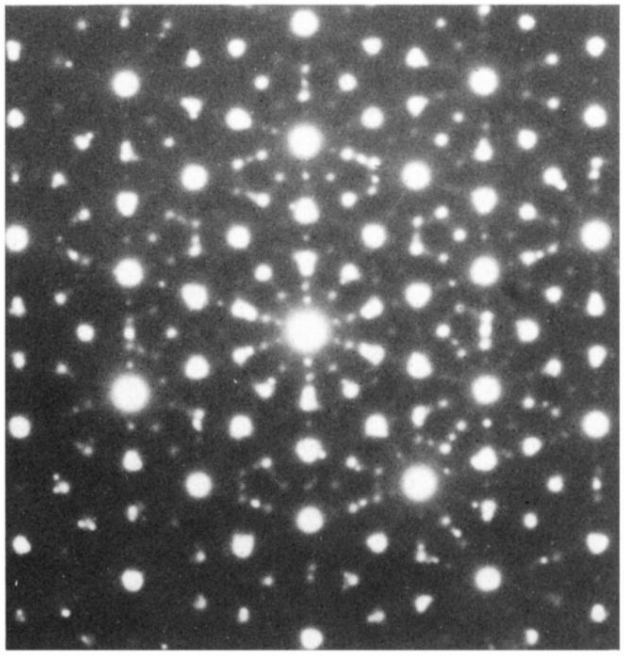
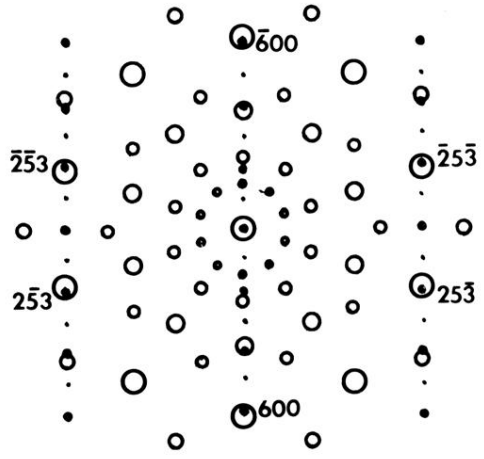


FIG. 4. A micrograph and diffraction pattern of an icosahedral grain with threefold zone axis surrounded by α-grains having $\langle 111 \rangle$ and $\langle 13\,5\,0 \rangle$ zone axes.





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