Amorphous-to-Quasicrystalline Transformation in the Solid State

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$Al_{84}Mn_{16}$ multilayer films have been amorphized by room-temperature ion-beam irradiation. The amorphous phase was transformed into the quasicrystalline state through two routes: thermal and ion-beam-assisted thermal. The intensity of the quasicrystalline electron diffraction increases continuously with annealing between 270 and 350 °C. Ion irradiation of the amorphous phase produces a more complete set of icosahedral diffraction lines than thermal annealing.

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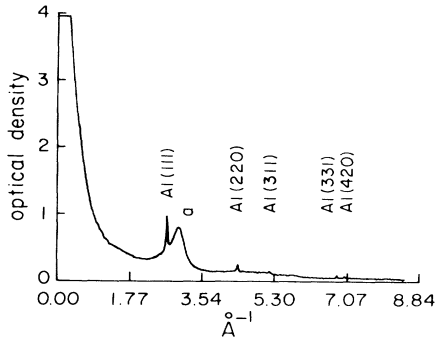
The quasicrystalline state of matter has received a large amount of study in the last year. The quasicrystalline state is characterized by long-range icosahedral order. This state was first reported by Shechtman *et al.*[1] and has since been the topic of many experimental studies.[2–7] In all these instances the quasicrystalline state was prepared by rapid quenching from the liquid state with use of melt spinning[1–7] or a scanning electron beam.[7]

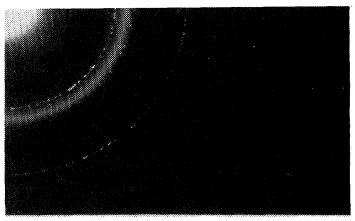
In this Letter we report the first observation of the formation of the quasicrystalline state by a solid-state polymorphic transformation from the amorphous phase by either thermal annealing or ion-beam irradiation. Although both processing techniques are capable of producing this transformation, only the ion-irradiation-induced transformation generates a nearly complete set of icosahedral powder diffraction lines. These transformations allowed us to probe the thermodynamic hierarchy of amorphous, quasicrystalline, and crystalline free energies. At 270 °C we confirm the expected thermodynamic hierarchy that the free energy of the amorphous phase is greater than the free energy of the quasicrystalline state, which in turn is greater than the free energy of the equilibrium crystalline phase. Our results for the amorphous-to-quasicrystalline transformation are consistent with a first- or second-order transformation. We propose a structural model for the amorphous-to-quasicrystalline transformation which can account for the kinetics in both thermal annealing and ion-beam mixing.

Multilayer Al-Mn films were deposited on NaCl substrates in a turbomolecular-assisted ion-pumped vacuum system by electron-beam evaporation. Rutherford-backscattering spectrometry determined that the films were 500 Å thick and had a composition of $Al_{84}Mn_{16}$. The films were floated off of the substrates onto transmission-electron-microscopy (TEM) grids and were amorphized by a room-temperature ion-beam irradiation of 8×10^{15} Xe^{++}/cm^2. The amorphous phase was then transformed to the quasicrystalline state by irradiation ($4\times10^{15}/cm^2$ Xe^{++}) at 150 °C. Irradiation experiments performed on coevaporated amorphous $Al_{80}Cr_{20}$ thin films have also produced similar results.[8] For all of the ion irradiations, the ion energy was 600 keV, the beam current was 0.025 $\mu A/cm^2$, and the vacuum in the implant chamber was less than 8×10^{-7} Torr. Ion ranges for 600-keV Xe are approximately 4 times the Al-Mn film thickness, thus making the incorporation of Xe unlikely. Thermal anneals were performed with use of both a turbomolecular-pumped vacuum furnace, with a pressure less than 4×10^{-8} Torr, and *in situ* annealing in the TEM.

Electron diffraction of the multilayer starting material which was subjected to the room-temperature irradiation indicates the presence of an amorphous phase plus crystalline Al. An electron-diffraction pattern from the amorphous phase is shown in Fig. 1. Visible is a broad band associated with the amorphous phase and several Al lines. Above this diffraction pattern is a microdensitometer scan which shows the structure more clearly. If the amorphous-plus-Al state is further irradiated at 150 °C, a new diffraction pattern is observed (Fig. 2). From a comparison of Figs. 1 and 2, it is clear that the amorphous phase has transformed into a new structure. A comparison of the Al diffraction lines in Figs. 1 and 2 reveals a roughly identical intensity distribution, indicating that the crystalline Al is not involved in the transformation. The reciprocal-lattice spacings (Q) corresponding to the diffraction lines in Fig. 2 were determined with use of the Al(111) reflection as a standard; these results are presented in Table I. The subset labeled Al in Table I is in excellent agreement with the published data for aluminum.[9] However, the remaining Q spacings do not correspond to any known equilibrium structures for the Al-Mn system. We therefore investigated the possibility that the remaining set was due to the crystalline state.[1–7,10]

Several papers[4,11,12] have suggested that the crystalline diffraction pattern may be indexed through the use of six vectors pointing to the vertices of an icosahedron. With use of the same six vectors as Bancel *et al.*[4] and with their choice of the line at 2.90 $Å^{-1}$ as the (100000) line, it is then possible to index all of the lines seen in the diffraction pattern as icosahedral lines. A comparison between line spacings calculated on the assumption that the (100000) line is the line at

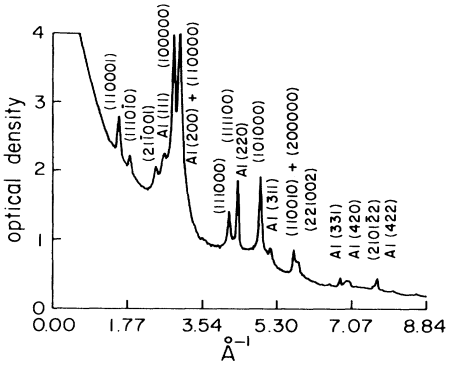


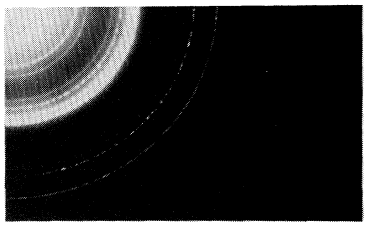


Ion beam mixing with
8×10^{15} Xe ions/cm^2 at RT:

Al-Mn ⟶ Amorphous + Al

FIG. 1. Electron diffraction pattern and microdensitometer trace of an Al-Mn multilayer thin film after a Xe irradiation at room temperature. Peak *a* corresponds to the amorphous diffraction signal.





Ion irradiation with 4×10^{15}
Xe ions/cm^2 at 150°C:

Amorphous + Al ⟶ Icosahedral + Al

FIG. 2. Electron diffraction pattern and microdensitometer trace of quasicrystalline state formed by Xe irradiation of the amorphous phase at 150 °C. Lines are labeled with their corresponding indexes (Table I).

2.90 Å^{-1} and the x-ray data of Bancel *et al.* is displayed in Table I. As can be seen, the agreement is excellent. Lines not appearing in Fig. 1 but appearing in Table I were obtained by overexposure of the diffraction pattern.

The thermal transformation of the amorphous-plus-Al state was examined *in situ* in a hot-stage TEM at a heating rate of approximately 17 °C/min. At 270 °C, the amorphous phase was observed to begin to transform into the quasicrystalline state. Some of the amorphous bands show a splitting into what later became sharp icosahedral diffraction lines. By 345 °C, the transformation is quite advanced, but is not as pronounced as in the ion-beam-irradiated sample. The changes in the diffraction patterns between 270 and 345 °C appeared continuous rather than abrupt. At 400 °C, a sudden transformation to the equilibrium structure took place but some of the quasicrystalline state was retained.

To examine the relative free energies involved in the transformation, we performed constant-temperature anneals in an external furnace. These show that a 3-h anneal at 200 °C had no effect on the amorphous state. When this sample was further annealed at 270 °C for 2.75 h, the diffuse diffraction band of the amorphous phase was observed to undergo the same splitting as observed in the *in situ* annealing. In addition to this splitting, sharp intensity spots were also observed superimposed on the new icosahedral lines. This was taken as evidence for the onset of crystallization to the equilibrium phase.

The ion-beam-irradiated sample was examined in both bright- and dark-field TEM. Dark-field imaging with use of the well-isolated (110001) and (111$\bar{0}$10) icosahedral diffraction lines showed a distribution of grain sizes extending from 100 to 270 Å which occupied a substantial portion of the sample. These grains possessed no obvious faceted structure.

A possible description of the amorphous-to-quasicrystalline transformation is that of the icosahedral ordering. The icosahedral units will move into registry producing a volume of material with long-range icosahedral order. This ordering could occur by either a nucleation and growth mechanism or a continuous transformation. Both of these models would cause the gradual sharpening of the diffraction lines observed in our experiments.

If the amorphous-to-crystalline transformation is a

TABLE I. Icosahedral indices and measured Q spacings of the quasicrystalline state formed by Xe irradiation at 150 °C.

Index	Observed Q (Å^{-1})	Calculated[a]	Observed[b] x-ray
$I(2200\bar{1}1)$	1.17	1.16	1.16
$I(110001)$	1.63	1.63	1.632
$I(1110\bar{1}0)$	1.88	1.88	1.876
$I(21\bar{1}001)$	2.49	2.49	2.49
Al(111)	2.69		
$I(100000)$	2.90	2.89	2.896
$I(110000)$	3.04	3.05	3.043
Al(200)	3.10		
$I(220002)$	3.26	3.26	3.24
$I(210001)$	3.57	3.57	3.576
$I(111000)$	4.21	4.20	4.20
$I(111100)$	4.31	4.31	4.307
Al(220)	4.40		
$I(2110\bar{1}0)$	4.63	4.60	4.60
$I(101000)$	4.95	4.93	4.928
Al(311)	5.18		
$I(210000)$	5.19	5.19	5.23
$I(121000)$	5.28	5.27	
Al(222)	5.40		
$I(110010)$	5.75	5.71	5.708
$I(221002)$	5.82	5.83	5.83
$I(1210\bar{2}2)$	5.91	5.91	
Al(400)	6.12		
$I(211000)$	6.53	6.54	6.53
$I(111222)$	6.60	6.58	
Al(331)	6.82		
Al(420)	6.97		
$I(\bar{2}01122)$	7.03	7.06	
Al(422)	7.65		
$I(\bar{1}1\bar{2}111)$	7.70	7.78	
Al(511,333)	8.08		

[a]On the basis of the line at 2.90 Å^{-1} being the (100000) and with use of the Al lines to determine the camera constant.

[b]Reference 4.

nucleation and growth process, we believe that precursor nuclei already exist in the amorphous material. There is both theoretical and experimental evidence to support this argument. Sachdev and Nelson[13] successfully calculated the x-ray diffraction structure of vapor-deposited amorphous cobalt using a model containing icosahadral short-range order. Since recent experiments suggest that the quench rate during vapor deposition is faster than that during irradiation,[14] we believe that the ion-irradiated amorphous Al-Mn structure will also contain icosahedral short-range order similar to metallic glasses[13,15-17] and amorphous metals.[14]

The production of a large volume of material with long-range icosahedral order requires atomic motion. Clearly it is energetically unfavorable to rotate whole icosahedral groups. Elser[18] has proposed a three-dimensional Penrose tiling constructed of two distorted rhombuses which exhibits icosahedral symmetry. In this model, growth of the icosahedral grain would require only the motion of a few atoms contained in the necessary rhombus. This will be energetically more favorable.

The degree of the transformation to the quasicrystalline state will depend upon steric and compositional hindrances. In thermal annealing, these will be the limiting factors determining the size of the icosahedral grains. Removal of all the hindrances will require long-range diffusion which should result in crystallization prior to the completion of the transformation. This explains both the incomplete nature of the thermal transformation and the continual sharpening of the electron diffraction lines as a function of annealing temperature.

Landau-Ginzburg calculations indicate that the quasicrystalline-to-liquid transition is first order.[11,12,19] Evidence from the melt-quenching experiments[1-7] indicates a first-order nucleation-and-growth mechanism. The solid-state formation of the quasicrystalline state may also be the result of a first-order transformation. Our thermal-annealing studies are consistent with a continuous transformation between the amorphous and quasicrystalline state. This is in sharp contrast to the sudden crystallization transformation observed between the quasicrystalline and equilibrium state. If we are correct in assuming that icosahedral short-range order exists in our amorphous phase, then many subcritical quasicrystalline nuclei may be present before the onset of annealing. As the sample is heated, nucleation will readily occur and be followed by grain growth which will result in the observed sharpening of the icosahedral diffraction signals. The gradualness of this transformation can then be attributed to high nucleation rate and grain growth as opposed to a higher-order continuous transformation. Since particle irradiation has shown itself to be quite effective in inducing grain growth, our irradiation results can also be explained by such a model.[20]

Ion-beam irradiation affects the amorphous-to-quasicrystalline transformation in several ways. The irradiating ion deposits kinetic energy in the sample creating highly defective regions. This radiation damage will tend to remove steric and compositional hindrances by displacement of the atoms from their previous sites. We suggest that bordering icosahedral grains will tend to grow into the defective region, resulting in larger grain sizes. This hypothesis is supported by recent 1-MeV electron-irradiation damage studies,[21] which have shown that the quasicrystalline material can be amorphized and tends to regrow from adjacent undamaged quasicrystalline regions. Thus grain impingement should be the limiting factor in determining

the final grain size.

For higher-temperature ion irradiations, we expect that icosahedral nuclei forming in the defective region will compete with the bordering icosahedral grains producing a finer-grained structure. This will result in less complete transformation and less intense icosahedral diffraction signals. A 200 °C ion irradiation shows a lower degree of transformation as predicted by the model.[8]

In summary, we have observed that thin multilayer Al-Mn films with overall composition $Al_{84}Mn_{16}$ can be ion-beam mixed at room-temperature to form an amorphous alloy. This alloy can then be transformed into the quasicrystalline state by a solid-state reaction either by ion irradiation at 150 °C or by thermal annealing at 345 °C. The intensity of the icosahedral diffraction signals increases continuously with annealing temperature. The irradiation-induced transformation was much more complete compared to the thermal transformation and results in the appearance of a greater number of and sharper icosahedral diffraction lines. The expected free-energy hierarchy has been confirmed. The amorphous-to-quasicrystalline transformation may be successfully described as an icosahedral-ordering transition. We were able to account for the kinetics of the thermal and ion-beam-irradiation transformations.

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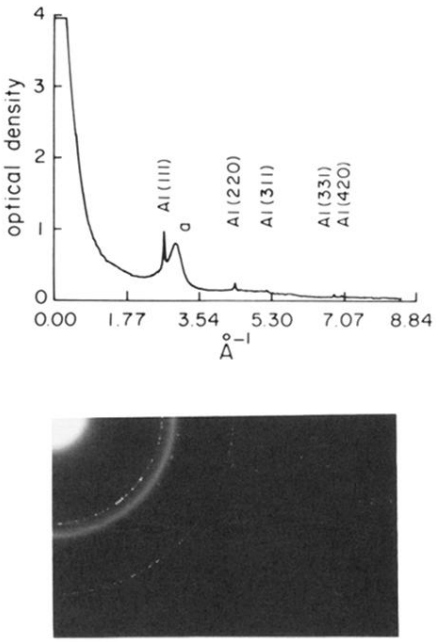

FIG. 1. Electron diffraction pattern and microdensitometer trace of an Al-Mn multilayer thin film after a Xe irradiation at room temperature. Peak *a* corresponds to the amorphous diffraction signal.

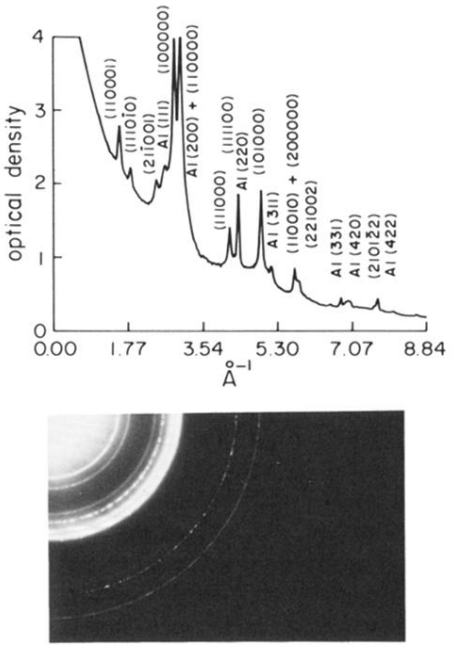

FIG. 2. Electron diffraction pattern and microdensitometer trace of quasicrystalline state formed by Xe irradiation of the amorphous phase at 150 °C. Lines are labeled with their corresponding indexes (Table I).