Quasicrystalline transformation by ion irradiation

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Amorphous Al-M films, where M = Cr, Mn, and Fe, were made by coevaporation and by room-temperature ion irradiation of multilayer films. The amorphous phase was transformed into the quasicrystalline state by ion-beam-assisted thermal anneals. All of the systems examined have essentially the same reciprocal-lattice spacings and fivefold diffraction patterns.

The quasicrystalline state of matter, first reported by Shechtman, Blech, Gratias, and Cahn[1] is characterized by long-range icosahedral order. The primary formation mechanism has been rapid quenching from the liquid by melt spinning[1-7] although scanned electron beams[7] have been used. Recently, ion-beam techniques have been used by several research groups to produce the quasicrystalline Al-Mn alloy.[8-11]

The quasicrystalline diffraction patterns have been calculated by several different methods[12-22] and predictions of these models have been compared with electron diffraction results by many authors[2,5,15-18,22] working solely in the Al-Mn system. At least six binary systems are known to transform into states that appear to have icosahedral symmetry.[3,4] Production of several different quasicrystalline systems by the same technique would help to define their similarities or differences in composition and structure and permit the testing of various models based upon differences in atomic scattering factors and structure.

This paper is the first report to compare the structure of several quasicrystalline systems formed by ion-beam techniques. We found that quasicrystals formed in the Al-Fe, Al-Cr, and Al-Mn systems have nearly the same reciprocal-lattice spacings, which implies that the real space structures are the same. They exhibit a systematic variation in the size of the unit reciprocal-lattice vector which scales with atomic number in accordance with several of the structural models.

Codeposited amorphous $Al_{80}Cr_{20}$ films were deposited on NaCl substrates in a cryopumped vacuum system using dual e-beam evaporation. The pressure during deposition was less than 5×10^{-8} torr. Multilayer $Al_{82}Fe_{18}$ and $Al_{84}Mn_{16}$ films were deposited on NaCl in a single e-gun vacuum system with a base pressure of less than 5×10^{-7}. The films were floated off of the substrates onto transmission-electron-microscopy (TEM) grids. The multilayer films were ion irradiated with 8×10^{15} Xe^{2+} ions/cm^2 at room temperature (RT) prior to the elevated temperature ion irradiations of 4×10^{15} Xe^{2+} ions/cm^2 which were carried out at 175 °C for the Al-Fe films, 150 °C for the Al-Mn films. The as-deposited Al-Cr films were ion irradiated at 200 °C. For all of the ion irradiations, the ion energy was 600 keV, the beam current was 0.026 μA/cm^2, and the pressure in the implant chamber was less than 8×10^{-7} torr. Ion ranges for 600 keV Xe are approximately four times the Al-transition metal film thickness thus making the incorporation of Xe unlikely.

Compositional analysis was performed by Rutherford backscattering spectrometry (RBS) of as-deposited samples and energy dispersive x-ray analysis (EDS) was performed on the transformed Al-Cr and Al-Mn samples. No oxygen was observable in the RBS spectra which indicates that the oxygen concentration in the samples is less than 2 at. %.

The compositions of the film are $Al_{80}Cr_{20}$, $Al_{82}Fe_{18}$, and $Al_{84}Mn_{16}$. EDS analysis of the Al-Cr ion irradiated films showed that the composition on the 100-Å scale is the same as on the micron scale.

Electron diffraction of the RT ion mixed multilayers or the codeposited starting material indicates the presence of an amorphous phase plus aluminum[8] except for the $Al_{80}Cr_{20}$ system, where no aluminum lines were observed.[10]

If the amorphous material is ion irradiated at elevated temperatures a new diffraction pattern is observed. A pattern from the Al-Fe system is shown in Fig. 1. The Al lines present in the Al-Fe and Al-Mn amorphous films did not appear to be affected by the ion irradiation. The reciprocal-lattice spacings (Q) corresponding to the diffraction lines for the three systems were determined by calibrating the TEM diffraction mode using a polycrystalline gold sample. All samples were examined during the same session with the objective focus unchanged. The samples were focused by z height adjustment assuring the most reliable calibration of the microscope.[23]

The ion-beam-irradiated sample was examined in both bright and dark field TEM. Dark field imaging using the well isolated (110001) and $(11101\bar{0})$ icosahedral diffraction lines showed a distribution of grain sizes extending from 100 to 270 Å that occupied a substantial portion of the sample. These grains possessed no obvious faceted structure.

Quasicrystalline diffraction patterns may be indexed through the use of six vectors pointing to the vertices of an icosahedron. Using the same six vectors as Bancel *et al.*[4] and taking the line at or near 2.88 Å^{-1} as the (100000) line, it is then possible to index all of the lines in all three systems as icosahedral diffraction lines. The indices corresponding to the diffraction lines are shown in Table I and labeled on the microdensitometer plot of Fig. 1. This demonstrates that the amorphous Al-M material has transformed to the quasicrystalline state.

The presence of the proper powder diffraction lines is not the only evidence for the existence of the quasicrystal-
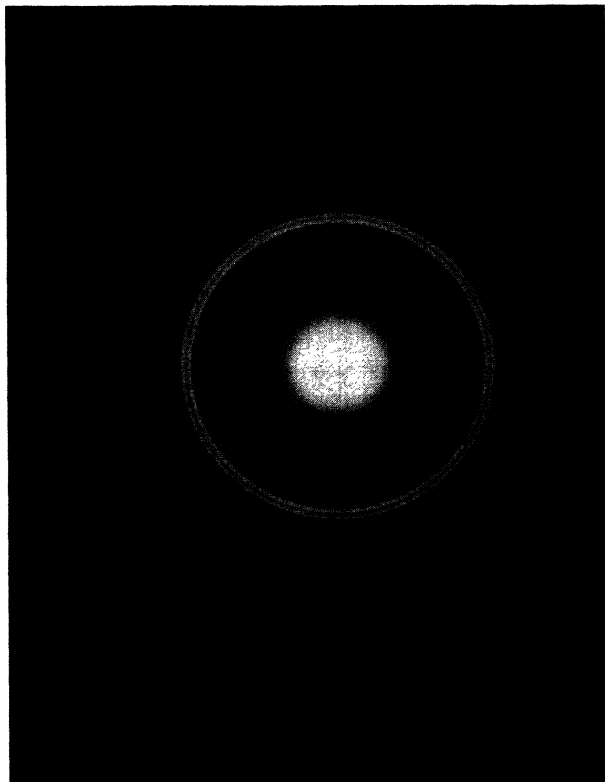
FIG. 1. Electron diffraction pattern of $Al_{82}Fe_{18}$ after ion irradiation at 175 °C with 4×10^{15} Xe^{2+} ions.

FIG. 2. Fivefold diffraction pattern from the $Al_{82}Fe_{18}$ system.

line state. Microdiffraction was used to examine the Al-Cr and Al-Fe systems and fivefold (as well as twofold and threefold) patterns characteristic of the icosahedral symmetry were found. Figure 2 is a fivefold diffraction pattern from a single grain in the Al-Fe system. Thus the material in these systems possess both the proper diffraction
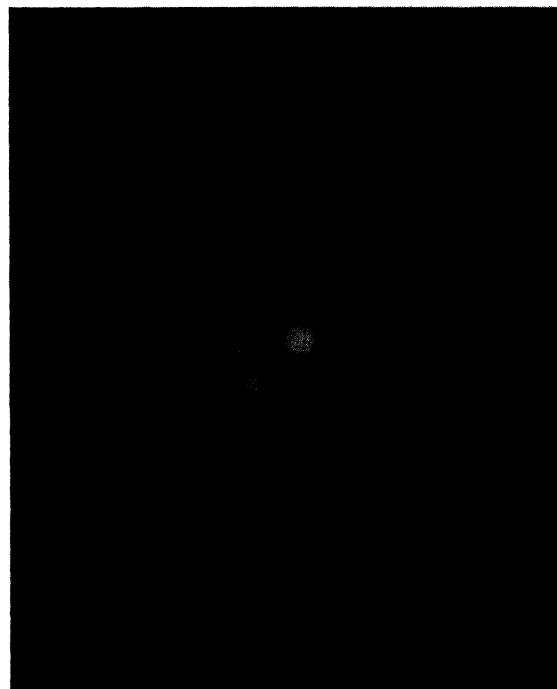
patterns and the line spacings to be quasicrystalline material.

A comparison of the quasicrystalline lines for all three systems presented in Table I shows that the reciprocal-lattice spacings of the ion irradiated transformed material are nearly the same. All three sets of data are related to the calculated data and experimental Al-Mn x-ray data by a single scale factor for each system.

The differences between neighboring columns of diffraction lines of the three systems are about 1–2%. The exper-

TABLE I. Icosahedral phase diffraction lines in the Al-Fe, Al-Mn, and Al-Cr systems. The units are $Å^{-1}$. The indexing is the same as used by Bancel et al. (Ref 4). Uncertainty in the last decimal place is given in parentheses.

Index	Calculated Q	Al-Cr Q	Al-Mn Q	Al-Fe Q	Al-Mn x ray[a]
220011	1.163	1.15(1)	1.15(1)		1.16
110001	1.630	1.61(1)	1.62(1)	1.65(1)	1.632
111010̄	1.882	1.84(1)	1.89(1)	1.91(1)	1.876
311̄1̄11	2.212		2.26(1)		2.20
211001	2.490			2.52(1)	2.49
211̄1̄01	2.662	2.62(2)	2.68(2)	2.70(2)	2.64
100000	2.896	2.84(2)	2.89(2)	2.93(2)	2.896
110000	3.045	3.00(2)	3.04(2)	3.08(2)	3.043
220002	3.260	3.20(2)	3.24(2)		3.24
111101	3.454	3.35(2)		3.50(2)	3.44
210001	3.580	3.51(2)	3.55(2)	3.60(2)	3.576
111000	4.202	4.13(2)	4.19(2)	4.26(2)	4.13
111100	4.306	4.21(3)	4.28(3)	4.37(3)	4.20
101000	4.927	4.84(3)	4.90(3)	5.00(3)	4.84
110001	5.715	5.59(3)	5.69(3)	5.78(3)	5.708
200000	5.792	5.66(3)	5.77(3)	5.80(3)	5.79

[a]See Ref. 4.

imental resolution of 0.6% is sufficient to show that there is a systematic behavior between the three systems. This conclusion is confirmed by the x-ray data of Dunlap and Dini[24] for melt spun ribbons. The Bancel *et al.* scheme for indexing the diffraction patterns is characterized by a parameter Q^* which will be a material property. Q^* was extracted for each system in the following manner. For each diffraction line, Q is divided by the magnitude of the sum of the $q_i s$. Q^* is found by taking the mean. The values are Al-Cr, 1.494 ± 0.004; Al-Mn, 1.520 ± 0.004; and Al-Fe, 1.540 ± 0.004. Thus the Al-Cr system should have the largest lattice constant of the three systems studied while Al-Fe will have the smallest.

Two models which are consistent with the diffraction data also predict the atomic positions of the Al and Mn in the Al-Mn quasicrystalline structure.[19,20] They show that the quasicrystal consists of empty Al icosahedra contained inside of Mn icosahedra. These units are connected by octahedral groups. Each of these models can be broken down into obtuse and acute rhombohedra which will form a three-dimensional Penrose tiling. The length of the rhombohedra edge is the scale determining length in the diffraction calculations. In these models, Mn bonds only with Mn and Al bonds only with Al. The size of the rhombohedral edge will depend indirectly on the length of the bond of each constituent atom. If another transition metal is substituted for Mn, the rhombohedral edge should scale with its bond length.

Moving along the periodic table from Cr to Fe has the effect of increasing the number of electrons, causing the atomic radius to be decreasing from Cr to Fe. Thus when we substitute a different element for Mn, the quasicrystalline system will be affected. There are several radii (covalent, atomic, metallic, or ligancy 12) that could be used to estimate this effect. We choose the ligancy 12 radius because this most closely matches the radius expected for icosahedral structures[25] but the fit is equally good using any of the other radii. Cr is approximately 0.6% larger than Mn and thus the Al-Mn Q^* should be about 0.6% larger than the Al-Cr Q^*. The actual value is approximately 2%. Similarly the Al-Fe Q^* should be about 0.6% larger than that of Al-Mn. The actual ratio is approximately 1%. Thus the sign and order of magnitude of this simple argument are in agreement with the data. This argument should apply directly to all first row transition metals alloying with aluminum. This conclusion is supported by the data of Dunlap and Dini.[26]

The observation that some of the lines are absent in some of the quasicrystalline systems is an indication that the atomic scattering factor is playing a role in quasicrystalline diffraction. This may prove to be useful in determining the location of atoms in the quasicrystalline structure.

In summary, we have observed that amorphous thin films in the Al-Mn, Al-Fe, and Al-Cr systems can be transformed into the quasicrystalline state by a solid state reaction using ion irradiation at elevated temperatures. All three systems have roughly equal reciprocal-lattice spacings and the models of Guyot and Audier[20] and Henley and Elser[19] can be used to understand qualitatively the differences between the three systems which scale with atomic number.

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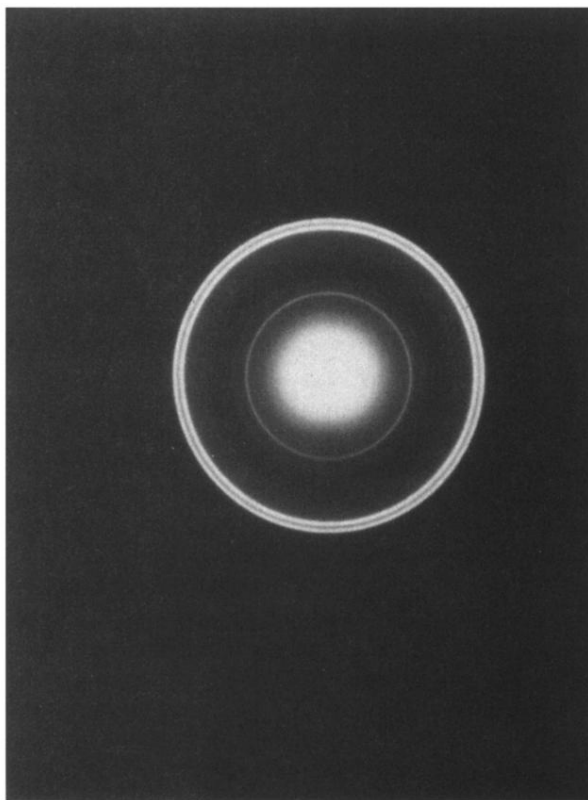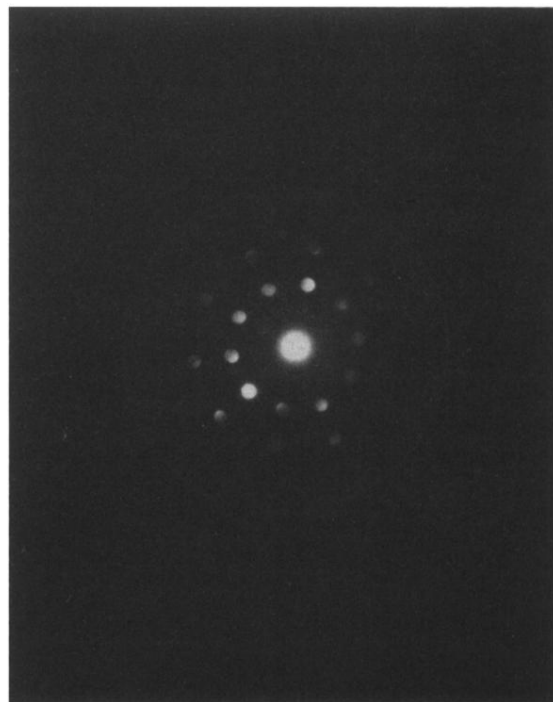FIG. 1. Electron diffraction pattern of $Al_{82}Fe_{18}$ after ion irradiation at $175\,°C$ with 4×10^{15} Xe^{2+} ions.

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