

Compressibility and stability of icosahedral Al-Mn up to 28 GPa

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The equation of state of icosahedral $\text{Al}_{86}\text{Mn}_{14}$ (*i*-Al-Mn) at room temperature has been determined up to ~ 28 GPa using diamond-anvil x-ray powder-diffraction techniques. The *i*-Al-Mn remained icosahedral over this pressure range; no phase transition was observed. The measured compression of the two strongest observed *i*-Al-Mn diffraction peaks (100000) and (110001), was isotropic within the measurement error: $d(110001)/d(100000) = 1.776 \pm 0.006$. The pressure-volume data were least-squares fit to a finite-strain equation of state to determine the zero-pressure bulk modulus, $K_0 = 117.6 \pm 16.8$ GPa, and its pressure derivative, $K'_0 = 6.0 \pm 2.4$.

I. INTRODUCTION

The explosion of interest in quasicrystals following the discovery of the icosahedral¹ and decagonal² phases in rapidly quenched Al-Mn has been summarized in numerous reviews,³⁻⁷ in two international conference proceedings^{8,9} and in several recent books.^{10,11} Most of the experimental and theoretical interest has focused on three fundamental issues: (1) What are the structures—where are the atoms? (2) How and why do the phases form—how do they nucleate and grow and what is the origin of their stability or metastability? (3) What are their physical properties—for example, what are the elastic, thermal, electronic, magnetic, and mechanical properties?

In this paper we present our experimental results on the compression of icosahedral $\text{Al}_{86}\text{Mn}_{14}$ (*i*-Al-Mn) under high pressure. This work involves primarily the second and the third issues. We addressed three questions in our experiment: Does *i*-Al-Mn exist, stably or metastably, at high pressure? Is the compression isotropic? How compressible is *i*-Al-Mn? We found that *i*-Al-Mn does not convert to the crystalline phase for pressures up to ~ 28 GPa, the compression is isotropic within the experimental error ($\pm 0.3\%$), and the zero-pressure bulk modulus, K_0 , is 117.6 ± 16.8 GPa, which is similar to the bulk modulus of silver. There are substantial differences between our results and previous work by other groups.^{12,13} We first briefly summarize these differences; a detailed comparison is presented in the Discussion section.

Although the high-temperature behavior of the icosahedral phases has been studied in detail (e.g., the thermal stability, heat of transformation, activation energy, specific heat, and relaxation have been measured¹⁴⁻¹⁷), there has been very limited experimental work on the behavior of icosahedral phases under pressure. There has, however, been considerable theoretical work on the general form of the elasticity¹⁸⁻²³ and very recently there has been an ambitious attempt to calculate

the actual values of the elastic constants using a density-functional formalism.^{24,25} This density-functional calculation of the bulk modulus, K_0 , for a hypothetical icosahedral phase of cobalt initially predicted a very large modulus, $K_0 = 395$ GPa (larger than that of tungsten) and the suggestion was made that the icosahedral phases might be very incompressible relative to the corresponding crystalline phases.²⁴ Subsequent improvements in the theory now indicate that the elastic moduli of quasicrystals might be significantly lower than the corresponding moduli for crystals, but additional improvements are needed before reliable values can be predicted.²⁵ In the only two previous high-pressure experiments on icosahedral materials, Parthasarathy *et al.*¹² reported irreversible pressure-induced crystallization of the icosahedral and decagonal phases of Al-Mn and Jaya *et al.*¹³ reported very large anisotropic compression of the icosahedral phase of Al-Fe (*i*-Al-Fe).

The remainder of this paper is organized as follows. First, the essential features of the high pressure x-ray diffraction measurements and the resulting pressure-volume data are described in Sec. II. Then in Sec. III, the data analysis procedure and the resulting equation of state parameters are presented. The results are discussed and compared with previous work in Sec. IV. The conclusions are summarized in Sec. V.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The experiments reported here were conducted using x-ray powder diffraction from *i*-Al-Mn samples in a super-pressure diamond anvil cell (DAC).²⁶ To obtain quasihydrostatic pressures an alcohol mixture (methanol : ethanol = 4 : 1) was used as the pressure medium.²⁷ The pressure was determined from the wavelength shift of the ruby R_1 fluorescence line.²⁸ Multiple ruby chips were arranged on the surface of the sample to provide a direct measure of the pressure distribution; this was especially important above the freezing point, ~ 10.5 GPa, of the pressure medium,²⁷ where the effective pressure was cal-

culated as the areal average of the measured pressures. The ruby pressure determination was doublechecked by determining the compression of the coexisting fcc-Al surrounding the icosahedral grains. The measured compression of the fcc-Al agreed with the known equation of state of Al indicating that the effective pressure was being determined accurately. The x-ray powder diffraction measurements required ~ 24 hour exposures with Kodak DEF-392 film using Mo $K\alpha$ radiation from a conventional fine focus tube operated at 900 W (45 KV, 20 mA). The radius of the Debye camera was 50 mm. The camera-to-sample distance was determined at each pressure using KCl as an external standard on the outside surface of the exiting diamond anvil. The film reading uncertainty and the sample-to-camera distance error produced a total error of about 0.2% in the d spacings (note however that the ratio of two d spacings is determined to about 0.3%).

The sample was prepared by melt spinning at the National Bureau of Standards; the melt composition was 27 wt. % Mn. The sample, pressure medium and ruby chips were arranged in an ~ 80 μm diameter hole in the precompressed ~ 70 μm thick inconel gasket. At zero pressure (prior to the compression) six diffraction peaks from *i*-Al-Mn, three fcc-Al peaks and two broad diffraction lines from the inconel gasket were observed. The observed peak positions are shown in Table I. The measured *i*-Al-Mn peak positions for these small DAC samples agree very well with the positions reported by Bancel *et al.*²⁹ As the pressure was increased, the weaker peaks could not be reliably determined. In addition, one of the strong icosahedral peaks, (110000), and the Al(200) peak could not be reliably determined because of overlap with the broad diffraction from the inconel gasket. The *i*-Al-Mn results reported here are for the two strongest observed icosahedral peaks, (100000) and (110001) and the fcc-Al results are for the Al(111) peak.

Icosahedral Al-Mn and fcc-Al diffraction data were collected between 0 GPa and 28.5 GPa. Above 28.5 GPa the gasket diffraction started to overlap with the (100000) line and the experiments were stopped. Data was taken both as the pressure was increased and as the pressure

TABLE I. The ten observed diffraction lines for the *i*-Al-Mn sample in the DAC. The six observed icosahedral lines, Q_{obs} , are in good agreement with the corresponding diffraction lines, Q^* , and the relative intensities, I , reported by Bancel *et al.* (Ref. 29). The three fcc-Al lines and the two broad inconel gasket lines are also shown.

Q_{obs} (\AA^{-1})	Q^* (\AA^{-1})	Reflection	I
1.637	1.632	(110001) (32 $\bar{1}$ 1 $\bar{1}$ 2)	22
1.870	1.876	(1110 $\bar{1}$ 0)	8
2.700		Al(111)	
2.911	2.896	(100000) (32 $\bar{1}$ 002)	100
3.035	3.043	(110000) (gasket)	78
3.105		Al(200)	
3.509		(gasket)	
4.204	4.200	(111000) (3300 $\bar{1}$ 1)	11
4.401		Al(220)	
4.927	4.928	(101000)	20

was decreased. No hysteresis in the position of the diffraction lines versus the direction of the pressure change was observed. The measured scattering angles (2θ 's) were converted to d spacings for the three selected peaks: the two icosahedral peaks, $d(100000)$ and $d(110001)$, and the fcc-Al peak, $d(111)$. To obtain the volume versus pressure, $V(p)$, the relationship between the d spacings and the volume is required. For systems with such high symmetry (icosahedral and cubic) the compression is predicted to be isotropic and $V(p)$ will be proportional to $[d(p)]^3$. To see whether *i*-Al-Mn compressed isotropically as expected, we calculated the ratio of our measured d spacings, $d(110001)/d(100000)$, versus pressure. As shown in Fig. 1, the observed ratio (1.776 ± 0.006) is isotropic within the measurement error of $\pm 0.3\%$. Since the observed *i*-Al-Mn compression versus pressure was isotropic, the volume ratio, $V/V_0 \equiv V(p)/V(p=0)$, was calculated by averaging the two volume ratios, $[d(p)/d(0)]^3$, for $d(100000)$ and $d(110001)$. For the fcc-Al the volume ratio was calculated from $d(111)$. The resulting pressure-volume data for *i*-Al-Mn and for fcc-Al are shown in Fig. 2. The volume compressions at the highest applied pressure, 28.5 GPa, are $\sim 14\%$ for *i*-Al-Mn and $\sim 20\%$ for fcc-Al.

III. DATA ANALYSIS

To determine the equation of state from the measured pressure-volume data, we assumed that the Eulerian finite-strain equation of state, which is widely accepted as an appropriate formulation for large compressions in isotropic or cubic materials, can also be used for *i*-Al-Mn (Ref. 30). In this equation of state, the strain parameter, f , which is a function of the measured volume ratio,

$$f = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right],$$

and the normalized pressure, F , which is a function of the

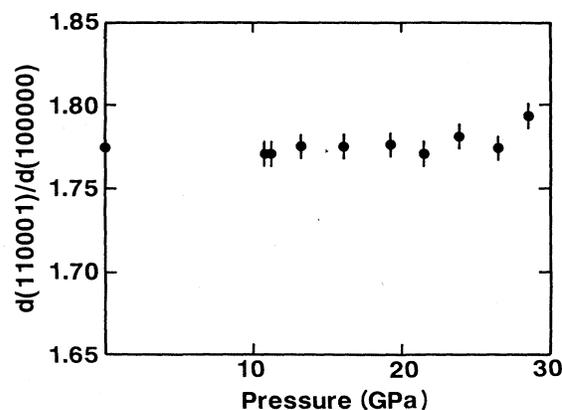


FIG. 1. Plot of the ratio of the measured d spacings, $d(110001)/d(100000)$, for icosahedral Al-Mn. The observed ratio (1.776 ± 0.006) is constant within the experimental error of $\pm 0.3\%$ indicating that the linear compressions of these two reflections are isotropic.

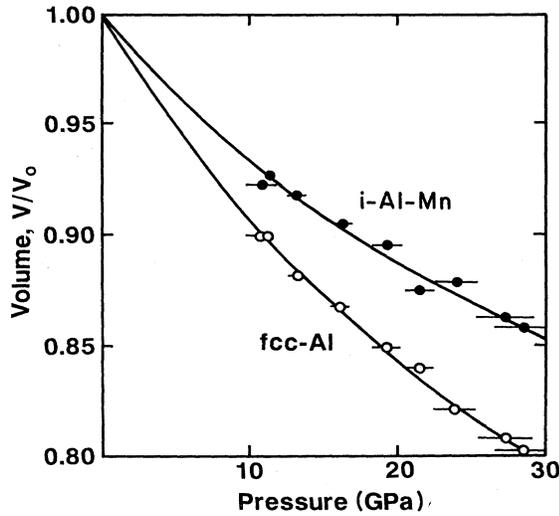


FIG. 2. The measured pressure-volume data for icosahedral Al-Mn and for the coexisting fcc-Al in the sample. The solid lines are the corresponding fits to the finite-strain equation of state. The resulting bulk moduli, K_0 , and pressure derivatives, K'_0 , are $K_0 = 117.6 \pm 16.8$ GPa and $K'_0 = 6.0 \pm 2.4$ for icosahedral Al-Mn and $K_0 = 85.2 \pm 8.8$ GPa and $K'_0 = 3.8 \pm 1.2$ for fcc-Al.

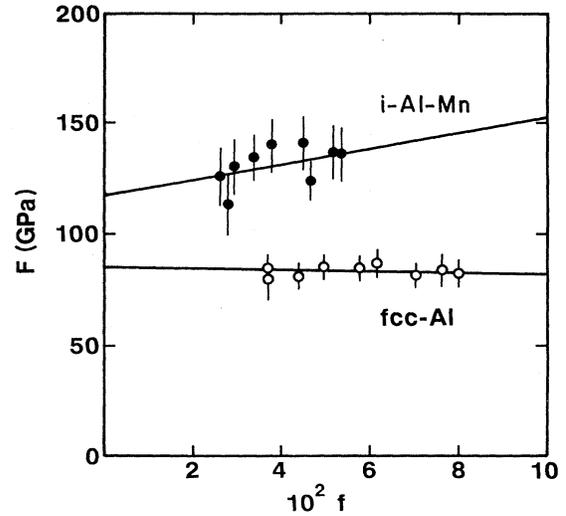


FIG. 3. Plot of the normalized pressure, F , vs the strain parameter, f , for icosahedral Al-Mn and fcc-Al. The solid lines indicate the fits to the linear equation: $F = a_0 + a_1 f$. The $F(f=0)$ intercepts are equal to the corresponding best fit bulk moduli, K_0 , and the slope is related to K_0 and K'_0 by $a_1 = \frac{3}{2}(K'_0 - 4)K_0$.

measured pressure and volume ratio,

$$F(f) = p [3f(1+2f)^{5/2}]^{-1},$$

are related by the polynomial expansion,

$$F(f) = a_0 + a_1 f + a_2 f^2 + \dots,$$

where a_0, a_1, a_2, \dots , are the parameters to be obtained by least-squares fitting. These parameters are related to the bulk modulus, K_0 , and its pressure derivatives, K'_0, K''_0, \dots , by

$$a_0 = K_0,$$

$$a_1 = \frac{3}{2}(K'_0 - 4)K_0,$$

$$a_2 = \frac{K_0}{6} [9K_0 K''_0 + 9(K'_0)^2 - 63K'_0 + 143].$$

This equation of state has the very convenient feature of transforming the nonlinear pressure-volume equation into a simple polynomial relationship between the normalized pressure, F , and the strain parameter, f . In addition, because both the pressure and the volume errors in the measurements are included in the calculated errors in the normalized pressures, the least-squares fitting produces the correct errors in the resulting bulk modulus and its pressure derivatives.

The normalized pressure versus strain parameter plots for *i*-Al-Mn and fcc-Al are shown in Fig. 3. This plot shows that the data is only accurate enough to obtain the first two coefficients, a_0 and a_1 . The solid lines indicate the corresponding linear least-squares fits to $F(f) = a_0 + a_1 f$. This first-order linear f - F equation corresponds to the Birch-Murnaghan equation of state³⁰

$$p = \frac{3}{2}K_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \times \left[1 + \frac{3}{4}(K'_0 - 4) \left(\frac{V_0}{V} \right)^{2/3} \right],$$

when the pressure is expressed in terms of the volume ratio.

The fcc-Al equation of state is clearly determined much better than *i*-Al-Mn equation of state, because the volume compression of the fcc-Al is much larger than that of *i*-Al-Mn. The resulting bulk moduli, K_0 and pressure derivatives, K'_0 , are $K_0 = 117.6 \pm 16.8$ GPa and $K'_0 = 6.0 \pm 2.4$ for *i*-Al-Mn and $K_0 = 85.2 \pm 8.8$ GPa and $K'_0 = 3.8 \pm 1.2$ for fcc-Al. Because the K_0 and K'_0 determined for fcc-Al are in good agreement with the known equation of state for Al (Ref. 31), the pressure on the fcc-Al must be essentially equal to the pressure on the ruby chips. The K_0 and K'_0 for *i*-Al-Mn are consistent with the known bulk moduli of Al and Mn and are similar to Al-Mn alloys.^{31,32}

Since the *i*-Al-Mn is embedded in fcc-Al which has a different bulk modulus, the effective pressure on the *i*-Al-Mn and on the fcc-Al are different.³³ For a high modulus material embedded in a lower modulus material, the pressure on the high modulus material will be higher. This is called pressure intensification and can generate serious errors in the determination of the equation of state for a phase in a composite material. The pressure intensification factor, η , which is the ratio of the pressure on the *i*-Al-Mn, $p(i)$, to the pressure on the fcc-Al, $p(\text{Al})$, is given by

$$\eta \equiv \frac{p(i)}{p(\text{Al})} = \left[\frac{3K(\text{Al}) + 4G(\text{Al})}{3K(i) + 4G(\text{Al})} \right] \left[\frac{K(i)}{K(\text{Al})} \right],$$

where η depends on the bulk moduli of *i*-Al-Mn and Al and on the shear modulus, G , of Al. For our moduli, η is about 1.1 over the pressure range studied, indicating that the effective pressure on the *i*-Al-Mn was at most about 10% higher than the value measured using the ruby standard. The systematic error associated with the pressure intensification therefore corresponds to about a 10% increase in the bulk modulus for *i*-Al-Mn. This difference is comparable to the random error in the measured modulus, $\pm 14\%$.

The pressure-volume equation of state curves for *i*-Al-Mn and fcc-Al corresponding to the K_0 and K'_0 values determined from the linear $F(f)$ analysis are indicated by the solid lines in Fig. 2. There is good agreement with the pressure-volume data. Silver has very similar elastic parameters to *i*-Al-Mn: $K_0 = 103$ GPa and $K'_0 = 6.1$ (Refs. 31 and 34). The corresponding equation of state line for silver in Fig. 2 would be indistinguishable from the *i*-Al-Mn line.

IV. DISCUSSION

A. Thermodynamic stability

At room temperature and atmospheric pressure, *i*-Al-Mn is metastable; the stable phase is the orthorhombic crystalline Al_6Mn (*c*-Al-Mn) phase. The reported heat of transformation for the *i*-Al-Mn to *c*-Al-Mn transition is about 2.34 kJ/mol with the main transformation occurring between 700 and 800 K (Refs. 14 and 15). The kinetics of the thermally induced conversion from *i*-Al-Mn to *c*-Al-Mn follow an Avrami form, $x = 1 - \exp(-bt^n)$ with $n \sim 2$, suggesting diffusion limited kinetics.¹⁵ The reported activation energy is 222 kJ/mol which is comparable to the self-diffusion energy in crystalline transition metals.

Our results show that *i*-Al-Mn can remain without any phase transitions up to ~ 28 GPa. Pressure can affect the stability or metastability of the icosahedral phase in three ways:

(1) If the *i*-Al-Mn phase remains metastable at high pressure and if diffusion limited transformation kinetics are dominant, the applied pressure will enhance the metastability of the icosahedral phase by decreasing the diffusion coefficients.³⁵⁻³⁷

(2) The *i*-Al-Mn phase may become stable relative to *c*-Al-Mn at high pressure. The free energy difference, ΔG , between *i*-Al-Mn and *c*-Al-Mn is given by,³⁸

$$\Delta G(p, T) = U_c + pV_c - TS_c \\ -(U_i + pV_i - TS_i) \equiv \Delta U + p\Delta V - T\Delta S.$$

At room temperature and atmospheric pressure, the metastable *i*-Al-Mn phase is about 1% less dense than the stable *c*-Al-Mn phase.^{14,15} Consequently, an applied hydrostatic pressure will initially make the *i*-Al-Mn phase less stable relative to the *c*-Al-Mn phase since $\Delta V(0, T) > 0$. However, at sufficiently high pressure,⁵ if

the compressibility of the metastable icosahedral phase is larger than that of the stable crystalline phase, the $p\Delta V$ term in ΔG will become negative and eventually the icosahedral phase will become stable, $\Delta G > 0$. The current theoretical prediction²⁵ of a smaller bulk modulus for the quasicrystalline state relative to the crystalline state would lead to a stable quasicrystalline phase at high pressure. Unfortunately, the equation of state of *c*-Al-Mn has apparently never been determined. However, we can estimate the bulk modulus of *c*-Al-Mn by assuming that the bulk modulus of the crystalline phase is 4–7% higher than that of the icosahedral phase (i.e., assume it has typical glassy behavior; the shear modulus does appear to follow the same trend as metallic glasses³⁹). Assuming the larger bulk modulus estimate for *c*-Al-Mn, ~ 126 GPa, the $p\Delta V$ term will become positive at about 65 GPa. This indicates that pressure can stabilize the *i*-Al-Mn phase above this region.

(3) Pressure also changes the free energy barrier between the icosahedral phase and the transition state (*)³⁸

$$\Delta G^*(p, T) = U^* + pV^* - TS^* \\ -(U_i + pV_i - TS_i) \equiv \Delta U^* + p\Delta V^* - T\Delta S^*.$$

Since *i*-Al-Mn is metastable at one atmosphere, $\Delta G^* > 0$. Pressure typically decreases the metastability barrier because the transition state usually has a larger volume than the initial state.

The microscopic order in *i*-Al-MN is intermediate between the long-range order of *c*-Al-Mn and the short-range order in the amorphous Al-Mn metallic glass (*g*-Al-Mn) produced at extremely high cooling rates. This makes it interesting to compare the stability of *i*-Al-Mn versus *c*-Al-Mn to the much more extensively studied glass versus crystal case. Although there is no rigorous proof that a glass cannot be the most stable state of a system at finite temperature, all known amorphous solids are metastable with respect to a crystalline phase or a phase mixture.⁴⁰ While most of the known quasicrystalline systems are metastable (with respect to their crystalline phases), both $\text{Al}_6\text{Li}_3\text{Cu}$ and $\text{GaMg}_{2.1}\text{Zn}_3$ appear to be thermodynamically stable at atmospheric pressure;⁴¹⁻⁴³ it would be interesting to determine the stability of these materials versus pressure. We find that quasihydrostatic pressure does not induce crystallization or amorphization of *i*-Al-Mn up to ~ 28 GPa. There are examples of pressure-induced crystalline-to-amorphous transitions in a few systems⁴⁴ and there are many examples of pressure-induced crystallization of semiconductor glasses.⁴⁵ For metallic glasses, which should be the most directly relevant to the metallic quasicrystals, hydrostatic pressure has been shown³⁵⁻³⁷ to retard the temperature dependence of the crystallization by about 15 K GPa^{-1} . This increase in metastability has been attributed to the decreased atomic diffusion coefficients due to the applied pressure.

B. Isotropy

The full elastic tensor for perfect icosahedral quasicrystals has been computed by many groups.¹⁸⁻²³ There are five elastic constants: two associated with phonon

strains, two associated with phason strains, and one connecting the phason and phonon strains. The elastic response is characterized by a short-time phonon response and long-time phason and phonon-phason responses. The phason strains relax very slowly (typically much slower than laboratory time scales) compared to the phonon strains (which relax at the speed of sound). Because of the icosahedral symmetry, the short-time response for perfect quasicrystals is isotropic, but the long-time behavior is anisotropic. In nonperfect quasicrystals with quenched anisotropic phason strains, the phason-phonon coupling will produce anisotropic short-time elastic responses and might lead to a distortion of the icosahedral symmetry in response to an applied hydrostatic pressure. For perfect icosahedral quasicrystals, the bulk modulus is an eigenmodulus of the six-dimensional crystal, and a purely hydrostatic pressure should produce a purely isotropic compression on all time scales. Our observed compression is isotropic to within our measurement error of $\pm 0.3\%$ as predicted by the theory and as expected in general for any system with such a high symmetry.

C. Compressibility

How large should the compressibility of a quasicrystal or of a quasicrystalline glass be? Very naively, we expect that the compressibility is set only by the number of neighbors, the pair potential, and the interparticle spacing. Since the densities of *i*-Al-Mn, *c*-Al-Mn, and *g*-Al-Mn are all very similar, this simple-minded view predicts similar moduli for the three phases. This correspondence is well established for amorphous and liquid metals³⁹ where the 1–2% and 2–3% respective density decreases relative to the crystalline phase produce fractional bulk modulus changes about four times larger: $\Delta K_0/K_0 \approx 4\Delta\rho/\rho$. However, it is well established that the decreases in the shear moduli of metallic glasses relative to the crystalline phases cannot be explained in such a simple way.³⁹

The elastic moduli for metallic glasses are lower than the corresponding moduli for the crystalline phase: the bulk moduli, K_0 , are typically 4–7% lower; the shear moduli, G , are typically 30–40% lower, and the Young's moduli, E , are typically 20–30% lower.³⁹ The corresponding Poisson's ratios range from 0.30–0.40 (Ref. 39). Chen *et al.*¹⁵ measured the Young's moduli for *i*-Al-Mn, 101 ± 2 GPa, and *c*-Al-Mn, 126 ± 3 GPa, and noted that the corresponding 20–30% decrease agrees very well with the usual decrease of glassy materials. Combining their value for the Young's modulus, $E = 101 \pm 2$ GPa, with our value for the bulk modulus, $K_0 = 117.6 \pm 16.8$ GPa, produces a Poisson's ratio estimate for *i*-Al-Mn, $\nu = 0.35 \pm 0.02$.

D. Comparison with previous experimental work

The experimental results for the compression of *i*-Al-Fe reported by Jaya *et al.*¹³ disagree with our results in two ways: their compression is anisotropic and they find *i*-Al-Fe to be very compressible. Our results are compared with theirs in Fig. 4. The disagreement is probably

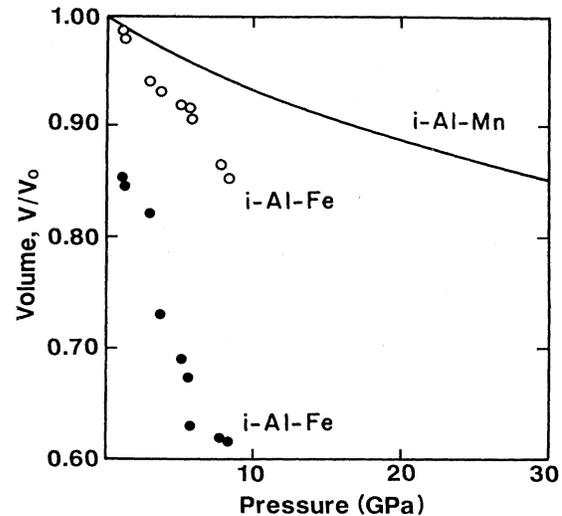


FIG. 4. Comparison of the equation of state determined for icosahedral Al-Mn by the present study with the pressure-volume data for icosahedral Al-Fe determined by Jaya *et al.* (Ref. 13). The solid line is the equation of state for icosahedral Al-Mn. The open circles are the average pressure-volume data reported by Jaya *et al.* for the $d_0 = 2.072, 2.360,$ and 2.610 Å lines; the solid dots are for the $d_0 = 3.310$ Å line. The difference in the compressibility shown by the open circles and the solid dots would indicate that the icosahedral symmetry has been broken by the imposed stress.

too large to be explained as a difference between *i*-Al-Mn and *i*-Al-Fe. In their experiment, they find that three lines with zero-pressure d spacings, d_0 , equal to 2.072, 2.360, and 2.610 Å compressed by about equal amounts, but their fourth line with $d_0 = 3.310$ Å had a much larger compression. If the compression is really so anisotropic, the icosahedral symmetry has been broken and the systems is no longer quasicrystalline, but this seems very unlikely. Also the compression obtained for all of the diffraction lines is unreasonably large: the compression of the $d_0 = 3.310$ Å line is similar to that of lithium³¹ and the compressions of the other three lines are similar to that of indium.³¹ It is impossible to reconcile the extremely anisotropic compression and enormous compressibilities with the behavior expected for an icosahedral phase made from Al and Fe which are individually so much less compressible.³¹ Such a large compression can be explained by the experimental conditions. Their experiment was done using a Bridgman anvil apparatus. A soft hydrostatic pressure medium was not used, instead the sample was mixed with NaCl, which served as the pressure medium and as the pressure standard. In this experimental environment, a very large pressure intensification (described in Sec. III) is expected.³³ If we assume that *i*-Al-Fe has comparable elastic parameters to *i*-Al-Mn, the pressure intensification factor, $\eta = p(i)/p(\text{NaCl})$, for the mixture of NaCl (Ref. 31) and *i*-Al-Fe would be 1.5 to 2.1 and would produce a systematic error in the compressibility of this magnitude. The reported

anisotropic compression cannot be explained simply.

According to Parthasarathy *et al.*,¹² *i*-Al-Mn and decagonal Al-Mn transform to crystalline phases at 9.3 ± 0.8 GPa and 4.9 ± 0.4 GPa, respectively. In their experiments they detected the crystallization indirectly by monitoring the electrical conductivity, and they reported an irreversible transition. They also examined their samples using x-ray diffraction, after the pressure was released, and reported that the material had crystallized. Our *in situ* x-ray measurements did not find any transition in *i*-Al-Mn, and the observed compression was reversible. The disagreement between the two experiments may again be attributed to the very different stress conditions in the samples. Our DAC experiments were conducted with powder samples immersed in a quasi-hydrostatic pressure medium. Their experiments were conducted using a Bridgman anvil apparatus with ribbon samples in a solid pressure medium, steatite (natural rock). Therefore their samples were under extreme shear stress. Under their conditions, the shear stress increases with increasing pressure until the sample yields; this is one method for measuring the yield strength.⁴⁶ It is very likely that the large shear provided the thermodynamic driving force for both diffusion and crystallization. Since their starting material contained *c*-Al-Mn, the nucleation barrier was also eliminated. This would greatly accelerate the shear-induced crystallization.

V. CONCLUSION

Icosahedral Al-Mn does not convert to the crystalline or glassy state for quasi-hydrostatic pressures up to ~ 28

GPa. The *i*-Al-Mn is probably metastable over this pressure range, but may actually become the thermodynamically stable phase at very high pressures. The low-pressure metastability is probably enhanced by the rapid decrease in the diffusion coefficients with pressure. The measured linear compression of the two observed Al-Mn peaks, (100000) and (110001), was isotropic within the measurement error ($\pm 0.3\%$) as expected from the high symmetry. The isotropy of the compression indicates that the applied pressure does not break the icosahedral symmetry through the coupling to quenched anisotropic phason strains. The volume compression of *i*-Al-Mn is well described by the finite-strain equation of state. The measured zero-pressure bulk modulus, $K_0 = 117.6 \pm 16.8$ GPa, and its pressure derivative, $K'_0 = 6.0 \pm 2.4$, are consistent with the known bulk moduli of Al and Mn and similar to Al-Mn alloys.

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