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Mn local structure in the decagonal phase of Al-Mn alloys

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Our extended x-ray absorption fine-structure (EXAFS) results on the decagonal phase of Al-Mn alloys indicate that each Mn atom has on average about eight Al neighbors in the first-neighbor peak, compared to ten in the icosahedral phase. The decrease in the number of neighbors occurs in the low-distance part of the radial distribution function. These differences between the icosahedral- and decagonal-phase nearest-neighbor pair distribution functions, $p(r)$, correlate with the changes in the fraction of magnetic and nonmagnetic sites observed in NMR, suggesting that the sharper part of $p(r)$ is nonmagnetic and the broader part magnetic. These results suggest a model based on Al pentagons or distorted MacKay icosahedra, elongated along a fivefold axis.

I. INTRODUCTION

In a number of rapidly quenched metallic alloys, tenfold rotational symmetry has been observed in x-ray and electron diffraction data, indicating a fivefold symmetry in the material, a point group operation that is inconsistent with simple translational symmetry.^{1,2} Most of these "quasicrystals" have several fivefold axes and appear to be consistent with complete icosahedral symmetry (*I* phase). Several attempts to model such systems^{3,4} have made use of the MacKay⁵ Icosahedron (MI) which, for the Al-Mn systems, consists of two shells.^{4,6} The inner shell is a perfect icosahedron of Al atoms surrounding a vacancy. The second consists of Mn atoms radially situated on each of the inner Al atoms, with an additional Al atom placed between each pair of Mn atoms. The icosahedral Mn-Al system appears to be describable by some random packing of such MI, while an ordered packing gives the α phase of Al-Mn-Si.⁶

For the Al-Mn alloys, the *I* phase (not always single phase) has been observed over a range of Mn concentrations, from roughly 10 at. % to about 25 at. %. In addition, another phase has been observed⁷⁻⁹ for the higher Mn concentrations using a slower quench rate. It is a layered structure^{8,9} with a periodic repeat distance of

12.4 Å and a unique axis perpendicular to the layers. Electron diffraction data exhibit a tenfold symmetry about this axis with two sets of ten twofold axes perpendicular to it. The diffraction data also indicate that six layers exist within the unit cell. Such materials are called the decagonal or *T* phase.

Recently, Pauling¹⁰ has proposed that both the *I* and *T* phases can be explained in terms of multiple twinning of a cubic lattice: twentyfold twinning for the *I* phase and fivefold twinning for the *T* phase. For each case the same unit cell is used ($a_0 = 23.36$ Å). This model suggests that the local structure of the bulk will be the same in both phases.

Here we report EXAFS measurements¹¹ on the decagonal Al-Mn alloys for Al₇₈Mn₂₂, both ribbon and powder, and for Al₈₀Mn₂₀ powder. Comparisons of the Mn local environment in the decagonal materials are made with several compositions of *I*-phase Al-Mn alloys. The near-neighbor environments of Al₈₆Mn₁₄, Al₈₀Mn₂₀, and Al₇₆Si₄Mn₂₀ *I*-phase samples were essentially identical; consequently, data from only Al₈₆Mn₁₄ samples are presented. In contrast, the lower concentration *I*-phase samples with 10 and 12 at. % Mn are slightly different from the above high-concentration samples and are not discussed here. We find the local structure of the *T*- and

I-phase materials to be quite different; specifically, the Mn has, on average, about eight nearest neighbors in the decagonal phase as opposed to about ten in the *I* phase^{12–16} with fewer (five atoms) in the short-distance region of the Mn-Al pair distribution function.

The paper is organized as follows: Sec. II contains a brief discussion of the samples, standards, and experimental details; Sec. III discusses the data reduction and presents both the unfiltered *k*-space and Fourier-transformed *r*-space data; Sec. IV describes the results and makes comparisons with other experiments and theoretical models; Sec. V presents the conclusions.

II. EXPERIMENTAL DETAILS

T-phase samples of Al₈₀Mn₂₀ and Al₇₈Mn₂₂ were prepared by melt spinning in an inert gas atmosphere of alloys prepared from >99.9% starting materials.¹⁷ Alloy structure was ascertained by x-ray diffraction (MoK α); x-ray diffraction (XRD) patterns were compared to a standard *T*-phase pattern. A high yield of *T* phase is obtained only in ribbons 50–70 nm thick; thinner ribbons (cooled at a higher rate) show the icosahedral phase and thicker ribbons contain crystalline phases.¹⁷ Only single-phase material (to the accuracy of about 3% in the XRD phase-analysis method) was selected for EXAFS work.

Ribbon samples were examined for pinhole-free sections, 12–15 mm in length. The powdered samples, embedded in epoxy, were ground to a moderately fine powder as a compromise between attaining a very uniform sample and the concern that grinding introduces stress that can change the structure. Pictures of the x rays transmitted through the samples were taken to check the sample uniformity before making EXAFS measurements. Crystalline Al₆Mn standards, produced by annealing Al₈₅Mn₁₅ *I*-phase ribbons at 580°C for 1 h and by annealing a 6:1 alloy of Al and Mn, were selected in a similar manner. Dilute quenched alloys of 1 at. % Mn in Al were also prepared. Several standards were measured to check consistency from sample to sample and run to run.

We collected transmission and fluorescence x-ray absorption data at both 77 and 4.2 K for powdered and ribbon samples of *T*-Al₇₈Mn₂₂, powdered *T*-Al₈₀Mn₂₀, powdered *I*-Al₈₀Mn₂₀, ribbon *I*-Al₈₆Mn₁₄ and *I*-Al₇₆Si₄Mn₂₀, and the Al₆Mn standards.

III. DATA REDUCTION AND ANALYSIS

The EXAFS data were reduced in the standard way,^{12,18} with care taken to choose the zero of electron kinetic energy, E_0 , consistently for each trace ($\Delta E_0 = \pm 0.25$ eV). Because of a small contamination of iron in one of the *T*-phase samples, the fit to the background in energy space above the absorption edge was restricted to energies below the iron *K* edge, 7112 eV for all the samples, i.e., to a maximum value in *k* space of $k = 12 \text{ \AA}^{-1}$. Examples of the raw *k*-space data, $k\chi(k)$, for three of the samples are shown in Fig. 1 [$\chi(k)$ is defined by the *K*-edge absorption $\mu = \mu_0(1 + \chi)$]. In Fig. 2 the Fourier transform of the data multiplied by k^3 ,

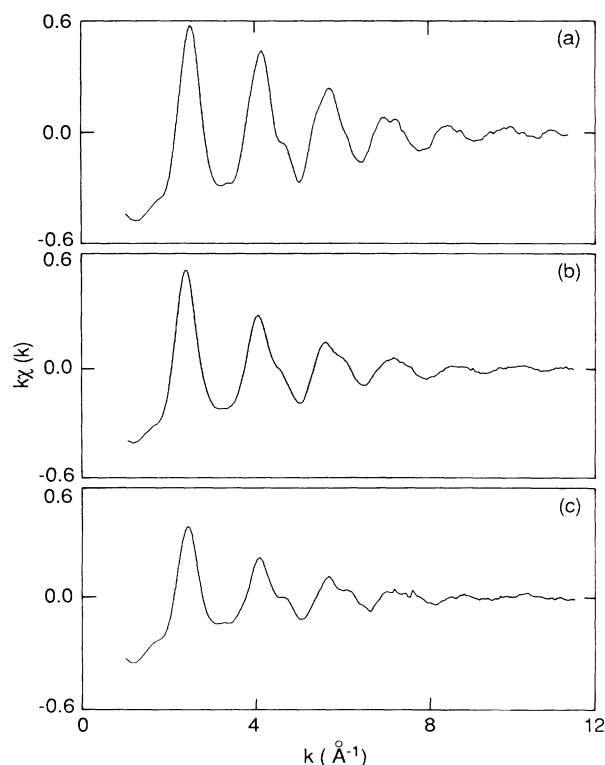


FIG. 1. The Mn *K*-edge *k*-space EXAFS data, $k\chi(k)$, with no smoothing or filtering. From top to bottom o-Al₆Mn (orthorhombic), *I*-Al₈₄Mn₁₆, and *T*-Al₇₈Mn₂₂. Note the decrease in overall amplitude and the change in structure (e.g., at $k = 6 \text{ \AA}^{-1}$).

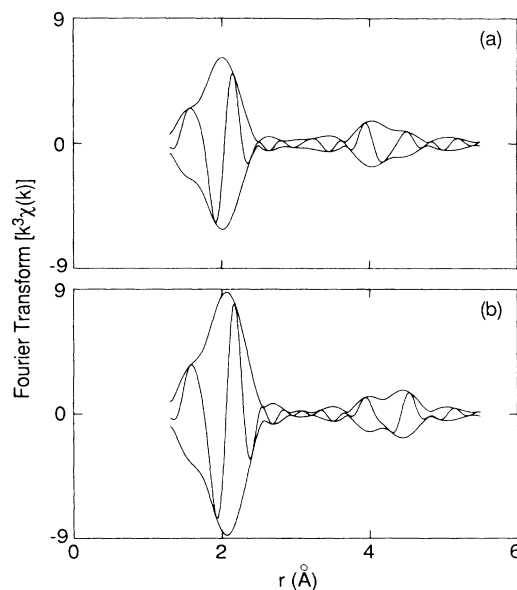


FIG. 2. The Fourier transforms of the EXAFS (amplitude and real part) on the Mn *K* edge, $k^3\chi(k)$, for the decagonal phase (a) and the *I* phase (b), transformed over a range from $k = 2.8$ to $11.2 \text{ \AA}^{-1}$, broadened by a Gaussian of width $0.5 \text{ \AA}^{-1}$. Note the decreased amplitude of the first-neighbor peak and the further neighbor peaks near $4.5 \text{ \AA}$ for the decagonal phase relative to the *I* phase.

i.e., $k^3\chi(k)$, is shown for the *T*- and *I*-phases using a transform range of 2.8 to 11.2 Å⁻¹, broadened by a Gaussian of half-width 0.5 Å⁻¹.

For detailed fits of the Mn nearest-neighbor environment, a single peak Mn-Al standard was extracted from the crystalline Al₆Mn data using the known distribution of nearest neighbors¹⁹ and the assumption that the widths of the four Mn-Al peaks are identical. The expression for $k\chi(k)$ for the Al near-neighbor contribution to the Mn EXAFS is

$$k\chi(k) = T(k) \sum_j N_j \exp(i2kr_j) \exp(-2k^2\sigma_j^2)/r_j^2 \\ = T(k)N \exp(i2k\bar{r})S \exp(-2k^2\sigma^2)/\bar{r}^2, \quad (1)$$

where

$$S = \sum_j (N_j/N)(\bar{r}/r_j)^2 \exp[i2k(r_j - \bar{r})],$$

$T(k)$ is the back scattering amplitude, $\bar{r}$ is the weighted average Mn-Al distance, N is the total number of neighbors, and $\sum_j$ is the sum over the ten Al neighbors at four different distances, r_j . A single-peak signature can be obtained by dividing this $k\chi(k)$ by the multipeak correction S . The resulting single-peak standard was tested using the dilute 1 at. % alloy of Mn in Al. A good fit was obtained, with a narrow width and a nearest-neighbor distance very close to the expected fcc Al distance.

Fits to the data were carried out in r space with E_0 varied; the best fits were obtained for a shift of less than or equal to 1 eV. Because the numbers of neighbors, N_j , are not known, they were varied in the fits along with the changes on the widths squared relative to that of the standard, $\Delta\sigma_j^2$, and the shifts in the peak positions relative to those of the standard, Δr_j . The consistency of the standards was checked by making one Gaussian comparisons of one standard against another. Changes in $\Delta\sigma_j^2$ were negligible, relative shifts were less than 0.001 Å, and the amplitudes were constant to within 5%.

Comparisons of all the *T*-phase data files to each other (including ribbon and powder samples and two different Mn concentrations) showed that the Mn local environment is essentially identical in these samples; the 77 K data were slightly broader than the 4.2 K data, consistent with increased thermal disorder. Attempts to fit the *T*- and *I*-phase data to the single Mn-Al peak standard were unsuccessful, indicating that the local environment is not a single Gaussian peak. However, these one peak fits do suggest a broad distribution for the *T* phase with about eight Al nearest neighbors about the Mn.

These results were confirmed in detailed two-peak fits of the *T*-phase data using two Mn-Al standards which fit the data very well. Our analysis shows that 5.1 ± 0.7 neighbors occur in a sharp peak [$\Delta\sigma^2 = (5.6 \pm 1.2) \times 10^{-3}$ Å² relative to the Al₆Mn standard] at $r_1 = 2.54 \pm 0.01$ Å, very near the mean Mn-Al distance ($\bar{r} = 2.567$ Å) of the ten Al atoms in orthorhombic Al₆Mn.¹⁹ This is essentially the same position as the

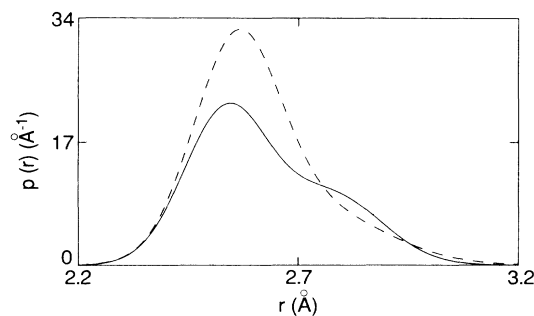


FIG. 3. The pair distribution function, $p(r)$, about a Mn atom for the decagonal phase (solid line) and *I* phase for Al₈₄Mn₁₆ (dashed line).

sharp peak found in the *I*-phase materials¹² but with five neighbors rather than seven. Additionally, a broader peak ($\Delta\sigma^2 = 0.01 \pm 0.004$ Å²) occurs at a larger distance ($r_2 = 2.77$ Å), very close to the high- r peak observed for the *I* phase. More surprisingly, the number of neighbors in the high- r peak is very similar in both the *T* and *I* phase ($N_{2T} \approx 2.78$, $N_{2I} \approx 3.0$) but the *I* phase is broader ($\Delta\sigma^2 = 0.02 \pm 0.003$ Å²). This difference is clearly observed in the plots of the *I* and *T* phase pair distribution functions (Fig. 3), generated as a sum of two Gaussians using the above parameters and an estimated width for the standard at 4.2 K of $\sigma_0 \approx 0.06$ Å. Similar results were obtained for fits to both the Fourier transforms of $k\chi$ and $k^3\chi$. We note that the parameters quoted above are an average of the results from several samples.

These results suggest that an important structural difference between the *T* and *I* phases is a decrease in the number of nearest neighbors for the *T* phase in the low- r part of the distribution function. To test this conjecture further, we used the sum of a *T*-phase distribution and a single Gaussian peak at $r = 2.567$ Å to simulate an *I*-phase distribution for *I*-phase Al₈₄Mn₁₆. We obtained an unusually good fit with essentially no additional broadening or shifts of these two distributions. Again, the number of neighbors that must be added to the *T* phase near $r = 2.567$ Å in order to describe the *I*

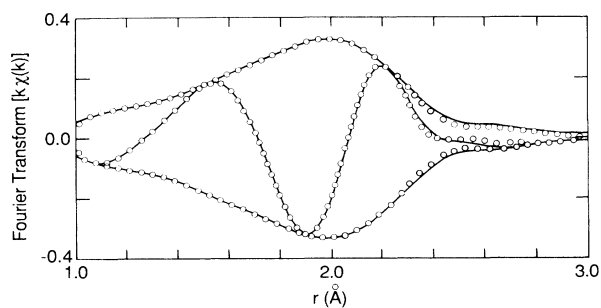


FIG. 4. A fit in r space of the *I*-phase data (Al₈₄Mn₁₆) to the sum of the *T*-phase data plus a single peak Mn-Al standard. To obtain this fit the *T*-phase peak is broadened slightly ($\Delta\sigma^2 = 0.002$ Å²); the single peak corresponds to 2.1 Al neighbors with negligible broadening and an insignificant shift in r of about 0.015 Å.

phase is about two. This fit is compared to the *I*-phase data in Fig. 4. Note that although the fit was done over the range 1.3–2.2 Å, a good fit is also obtained outside this range.

We also considered the further neighbor peaks in the region 3.6 to 4.6 Å in Fig. 2, corresponding to about 4.1 to 5.1 Å in actual distance. This double peak is attributed²⁰ to the Mn neighbors of the central Mn atom and is quite broad, with its centroid at roughly 4.6 Å. Qualitatively there is less weight in the *T* phase at 4.4 Å (about 4.9 Å actual distance) than in the *I* phase. Since this distance in the *I* phase has been attributed to Mn-Mn distances on the same MI,²⁰ our results suggest that undistorted MI no longer exist in the decagonal phase. A quantitative analysis of this part of the Fourier transform [$k\chi(k)$] using a Mn-Mn standard indicates that a two-peak model does not fit the data well. Either additional Mn peaks are present or a significant contribution from second-neighbor Al atoms is present. The *S/N* for the second-neighbor shell is not high enough to warrant a detailed fit to several peaks.

IV. DISCUSSION OF RESULTS

What models or restrictions on models might be inferred from the *T*-phase EXAFS data? First we note that the pair distribution function is an average over the entire sample and might correspond to the weighted sum of many inequivalent sites (see Ref. 12 for a discussion of the EXAFS for this situation). If so, a simple decomposition is not possible. Nevertheless, the EXAFS results provide substantial constraints on the quasicrystal local structure. A difference in the local structure between the *I* and *T* phases is clearly observed in the first-neighbor pair distribution function; consequently, the two phases cannot be explained using the identical unit cell in twinning models as proposed by Pauling,¹⁰ under the assumption that the signal we observe is representative of the bulk. The consistency of the pair distribution function, $p(r)$, from sample to sample supports such an assumption.

Relatively few models for the decagonal phase exist. Biham *et al.*²¹ have considered the stability of quasicrystalline phases to small deformations along a symmetry axis that makes them commensurate. They find that fivefold and tenfold symmetries are possible. Ho²² considered a slight distortion of an icosahedron of 12 *k* vectors, pointing towards the vertices of an icosahedron, to form pentagonal bipyramids. This results in a layered structure in *r* space, with decagonal symmetry about the origin in some layers. Away from the origin, the structure is basically pentagonal in nature.

We consider three possibilities briefly in light of the known layered structure (six layers in a 12.4 Å cell) and the above theoretical considerations. First, we consider the possibility that the local environment is basically the same for all Mn sites with perhaps some minor variations in the high-*r* part in the pair distribution function. Then, the five Al atoms at the same radial distance might correspond to the five points of a triangular bipyramid; such bipyramids could be connected together to form pentagons or decagons with the larger Mn-Al spac-

ings corresponding to connecting atoms. Another interesting possibility is that five Al atoms form a regular pentagonal ring about the Mn atom. Keeping the layered structure^{8,9} in mind, a two-dimensional layer of pentagons could be formed by a random packing which retains long-range orientational order.

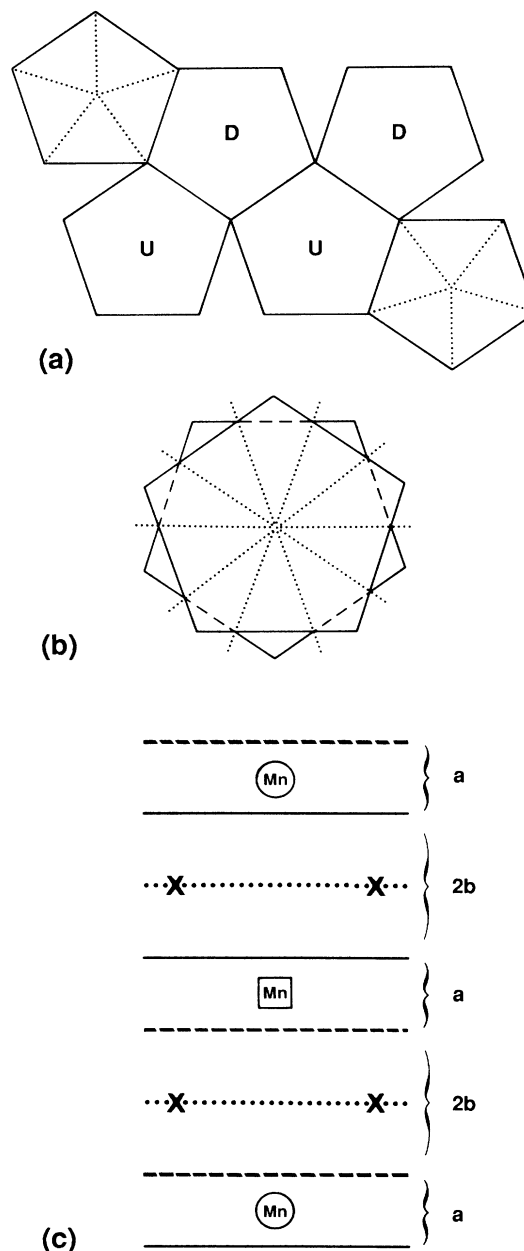


FIG. 5. (a) Part of a random packing of regular pentagons showing the up (*U*) and down (*D*) possible orientations. The two sets of five local twofold axes are shown as dotted lines. (b) Two pentagons in adjacent layers, with a relative rotation of 36°. The additional twofold axes of this local structure are shown as dotted lines. (c) A layered model obtained from a distortion of a MI with pentagons of Al atoms (solid lines), pentagons of Al atoms rotated by 36° (heavy dashed line), layers containing Mn (×) and Al atoms (dotted lines), and Mn atoms on the central axis.

For the pentagonal model, the pentagons within a single layer will have two possible orientations, 36° apart, which correspond to a pentagon pointing up or pointing down, as shown in Fig. 5(a). Areas in which "up" pentagons overlap give one set of five twofold axes, while the regions in which "down" pentagons overlap give another equivalent set, rotated by 36° , for a total of ten twofold axes. This is essentially twinning on a very microscopic scale. In regions where overlapping pentagons are alternately rotated by 36° as shown in Fig. 5(b), another set of ten twofold axes (perpendicular to the tenfold axis) exists locally. These two sets of ten twofold axes could correspond to the two sets of axes observed by Bendersky⁸ and by Fung *et al.*⁹ However, if the Mn atoms are coplanar within the Al pentagons, it is not clear how the fundamental repeat distance of 12.4 Å, implied by the electron diffraction pattern,^{8,9} could be achieved with the measured distances.

Second, we assume that there are two types of Mn sites, possibly corresponding to the sharp and broad parts of the distribution function. Then the additional constraints on the possible structure of the decagonal phase, suggested by the recent NMR results of Warren *et al.*,²³ can be incorporated. These experiments indicate that a fraction of the Mn atoms are strongly magnetic and do not contribute to the NMR signal for high Mn concentrations in both the *I* phase and decagonal phase. Furthermore, for approximately 20 at. % Mn, the number of nonmagnetic Mn atoms is smaller in the decagonal phase (40%) than in the *I* phase (60%). Comparing these results with the smaller number of neighbors in the low-*r* part of $p(r)$ for the *T* phase relative to the *I* phase suggests that the sharper part of $p(r)$ corresponds mainly to nonmagnetic, less-disordered Mn sites, while the broader part of $p(r)$ corresponds to the magnetic, more-disordered Mn sites. One way to account approximately for the decreased average number of Al nearest neighbors in the decagonal phase and the percentages of nonmagnetic Mn atoms above is to assume that the disordered magnetic sites have considerably fewer Al nearest neighbors, perhaps six to seven, while the more ordered sites have ten to twelve neighbors.

Finally, we consider the following question. If we assume that the *I* phase can be described by some arrangement of MI, is there a simple way to distort a MI to form a 12.4 Å unit cell with six layers, such that ordered and disordered Mn sites will occur? One speculation corresponds to a distorted MI expanded along a fivefold axis, with an additional Mn atom inserted at the center, and the outer ring of Al atoms redistributed to form a "glue" between the rodlike structures. We retain the upper and lower pentagonal pyramids (but slightly

compressed) formed by a ring of five Al atoms with a Mn atom at the peak. Then one obtains a set of layers as shown in Fig. 5(c). The Mn atoms on the central axis are the most ordered sites and are indicated by circles or a square; the latter corresponds to the Mn atom inserted at the center of the elongated MI. Solid lines correspond to regular pentagons of Al atoms (up or *U* pentagons) about the axis; the heavy dashed lines correspond to similar pentagons but rotated by 36° relative to the upper two (down *D* or pentagons). The regions identified by *X*'s and a dotted line correspond to planes with both Mn and Al atoms present. Thus each unit cell will have six planes of Al atoms with Mn atoms either in the plane (the $\times$ layers) or between planes. To obtain the measured repeat distance of 12.4 Å the sum of the distances shown in Fig. 5(c) must satisfy $a + 2b = 6.2$ Å. Rods formed by stacking distorted MI's are then packed together to form the Al-Mn *T* phase. We note that if the faster quench rates form primarily *I*-phase packings of MI because MI precursors exist in the melt, then the lower quench rates required to form the decagonal phase are consistent with the additional rearrangements and atomic ordering needed for this phase.

V. SUMMARY

Our EXAFS data indicate a reduction in the number of Al nearest neighbors to the Mn atoms in the decagonal phase relative to the *I* phase, with the decrease occurring in the sharper low-*r* part of the distribution function. The differences between the *I*- and *T*-phase nearest-neighbor pair distribution functions correlate with the changes in the fraction of magnetic and nonmagnetic sites observed in NMR, suggesting that the sharper part of $p(r)$ is nonmagnetic and the broader part magnetic. The combined second- and third-neighbor peak is more complicated in the *T* phase and does not decompose uniquely into two Mn-Mn peaks. This suggests that undistorted MI likely do not exist in the *T* phase.

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