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NEUTRON DIFFRACTION STUDIES OF THE ICOSAHEDRAL PHASE OF Al-Mn ALLOYS

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Abstract - Powder neutron diffraction studies were performed on three icosahedral alloys of the aluminum manganese system containing 27, 30, and 34 weight percent manganese. All peaks were found at the angles consistent with the icosahedral indexing with a six-dimensional cubic lattice parameter of approximately 0.65 nm that decreased with increasing Mn content. The relative intensities differ significantly from those found for X-rays. The intensities are not consistent with a quasilattice consisting of the 3-dimensional Penrose tiling with a .46 nm edge length along the 5-fold axis. It is consistent with a 1.0 nm edge along the 3-fold axis quasilattice node separation.

I - INTRODUCTION

Since the discovery of the icosahedral phase in rapidly solidified melt spun ribbons of Al-Mn alloys /1,2/, a number of experimental techniques have been used to determine the structure of these aperiodic systems. In the original work, electron diffraction studies were made on small regions of the ribbon where the icosahedral phase was singly oriented. Further studies showed the presence of other phases coexisting with the icosahedral phase./3,4/ Depending on the concentration of manganese, the cooling rate, heat treatment, etc., one can find the icosahedral phase, the α-aluminum phase, or the decagonal phase /5/ in many combinations. We report here on some powder neutron diffraction studies of the aluminum manganese icosahedral phase since no large singly oriented single phase specimens are available. We studied this phase using powdered specimens of several compositions of the alloys. Other powder diffraction patterns were obtained for powders containing the icosahedral phase and the decagonal phase and for powders annealed to produce the equilibrium orthorhombic Al₆Mn.

II - SAMPLE PREPARATION

Melt spun ribbons were obtained (1) from each of these Al₁₋ₓMnx alloys where x corresponded to 27 (2), 30, and 34 (3) weight percent of the pure starting

(1) We thank Dr. A. Rabinkin of the Allied-Signal Corporation for providing us these samples.
(2) This corresponds to Al₁₄Mn
(3) This corresponds to Al₁₆Mn
The ribbons were then gently powdered so as not to introduce excessive strain and sieved to provide the neutron diffraction samples.

III - EXPERIMENTAL PROCEDURE

Neutron diffraction measurements were performed on the high resolution BT-1 powder diffractometer /6/ at the NBS 20-MWatt research reactor. The diffractometer consists of 5 separate counters, separated by 20°, that can move simultaneously about an axis at the sample position. The 5 counters cover an angular range from 0° to 120° and for our experiments covered from 5° to 120° scattering angle where each counter moved 35°. The wave length used for our experiments was 1.5406\text{\AA} provided by a copper monochromator. An oriented graphite filter was used in the beam to remove higher order wave lengths contamination. The resolution of the diffractometer varies over the scattering angle from 0.31° at 5° scattering angle to a minimum of 0.22° from 40° to 70° and rises to 0.58° at the largest scattering angle.

The powder to be studied is placed in a thin walled vanadium container which can be fixed at the sample position. Vanadium was used since it does not contribute any structure to the diffraction patterns. Diffraction data was taken for each powder in angular steps of 0.05° and for a given monitor count of the incoming beam.

IV - RESULTS

Figure 1 shows a comparison of the diffraction data versus scattering angle for the three alloys with manganese concentration increasing from the top to the bottom graph. The lowest concentration manganese alloy when melt spun under the conditions for our experiment produces the icosahedral phase plus the f.c.c. \textit{α}–aluminum. The \textit{α}–aluminum phase lines in our pattern are narrower than the peaks of the icosahedral peaks but do not completely reflect the instrumental resolution. Their width could arise from particle size broadening or possible broadening caused by non-uniform concentration of Mn in the \textit{α}–aluminum phase. The icosahedral lines although quite sharp compared to other samples we have examined are broadened significantly more than our resolution function. One also notes an oscillatory background under the peaks of the icosahedral phase. This oscillatory background is reminiscent of the behavior of binary alloy systems showing short range order or possibly the presence of an amorphous phase in our system. No amorphous phase was detected by TEM. An examination of the background behavior at the smaller angles seems to indicate a pattern similar to short range order since the curve is tending upward away from zero. An experiment is being designed to probe these smaller angles to attempt to further clarify this point.

One sees in the neutron diffraction a slight shift in peak positions versus the manganese concentration. This has been observed by both electron and x-ray diffraction./4/ With increasing manganese content there is a change in the amount of other phases present; \textit{α}–aluminum is reduced and the decagonal phase appears. (Neither the \textit{A}_6\textit{Mn} nor \textit{A}_4\textit{Mn} phases were observed.) These changes are observed in the region from 22° to 45° in two theta but can be seen to occur over most of the pattern. We are attempting to prepare a sample in the pure decagonal phase and to measure its neutron, electron and x-ray diffraction patterns in order to analyze completely the diffraction curves with mixed aperiodic phases.
Fig. 1 - The uncorrected neutron scattering intensity of the 3 alloys, Mn(27w/o), AlMn (30 w/o), and AlMn (34 w/o), from top to bottom respectively versus the scattering angle, $\theta$. The vertical lines are the predicted positions of the $Q_0$ series of icosahedral lines for all even values of $N$ between 2 and 106.
Figure 2 shows a comparison of a powder neutron diffraction pattern of the icosahedral phase with the X-ray diffraction pattern /7/ for a similar alloy. The most interesting feature is the difference in the intensities for the same icosahedral peaks. Furthermore, many peaks are observed in the neutron diffraction pattern that seem to be absent in the X-ray pattern, whereas, some strong X-ray peaks are very weak in the neutron pattern. This striking difference in intensity comes from chemical order and the difference in phase of the neutron scattering amplitudes of the manganese atoms which have a negative neutron scattering length relative to that of aluminum.

In the preliminary analysis of the neutron diffraction data for the 27% alloy, we obtained the integrated intensity under all icosahedral peaks positions calculated from the index method we discuss later. To obtain the integrated intensity we did not attempt at this point to fit peak profiles with assumed mathematical forms but subtracted a smooth background from each peak and numerically integrated the resultant intensity. For some positions the intensity differed little from background. These were listed as zero intensity and utilized because they too contain information. In the case of the few overlapping peaks, where the separation could be clearly made, we adjusted each peak's intensity to give it a smooth symmetrical curve whose summed intensity agreed with that observed. Peaks that overlapped with those of other phases were not measured. In order to compare the experimental intensities with our model, we corrected the above integrated intensities by multiplying it by \( \sin^2 \theta \cos \theta \), the applicable Lorentz factor for neutron scattering, where \( \theta \) is one-half the scattering angle. Finally for a comparison with our model we divided each integrated intensity with its multiplicity as determined by the model and normalized these intensities so that the largest one would be unity. For those cases where several nonequivalent peaks had identical \( \theta \), the intensity was divided by the sum of the multiplicities.

![Fig. 2](image)

Fig. 2 - A comparison of the uncorrected neutron scattering intensities, top, to the scattering intensities for x-rays /7/ versus \( Q = 4\pi \sin \theta /\lambda \) where \( \theta \) is one-half the scattering angle and \( \lambda \) is the wave length of the radiation used. The two curves in the neutron data near \( Q=2.3 \) reflect the overlapping range of
V - DISCUSSION

Two aspects of the neutron diffraction results will be discussed; peak positions and how this relates to the icosahedral symmetry, and intensity and how this confirms the emerging model of a structure of parallel large icosahedral motifs stacked aperiodically along their 3-fold axes.

VI - COORDINATE SYSTEMS

The geometries of both the direct and reciprocal spaces in three dimensions are conveniently described in terms of a Cartesian coordinate system aligned with one set of three mutually orthogonal 2-fold axes which occur in icosahedral symmetry. Each of the three components of a quasilattice or reciprocal quasilattice vector will be described in terms of two integers e.g., h and h', the magnitude of the component is h + h' and where

\[ \tau = 2\cos(\pi/5) = (1 + \sqrt{5})/2 = 1.618034. \]

A reflection \( Q \) is indexed with six integers \((h + h', k + k', l + l')\) which will be written \((h/h', k/k', 1/1')\). Similarly a translation vector \( X \) will be written \((u/u', v/v', w/w')\). These six integers can also be related to components \((x_1, x_2, x_3)\) of a six-dimensional lattice vector in \( z^6 \) or components \((n_1, n_2, \ldots, n_6)\) of a reciprocal lattice vector in \( z^6 \) by the equations:

\[
\begin{align*}
    h &= n_1 - n_4 \\
    h' &= n_2 + n_5 \\
    k &= n_3 - n_6 \\
    k' &= n_1 + n_4 \\
    l &= n_2 - n_5 \\
    l' &= n_3 + n_6
\end{align*}
\]

with similar equations relating \(u,u',v,v',w,w'\) to the \(x_i\).

Equation (1) can be considered to define a projection of \(Z^6\) onto a three dimensional plane. It will be convenient to let the \((100000)\) vectors in \(Z^6\) and \(Z^6\) have a unit length. Then the corresponding vectors in \(R^3\) along the 5-fold axis \((1/0 0/1 0/0)\) will have a projected length \(1/\sqrt{2}\). We therefore normalize all three-dimensional vectors by a factor of \(\sqrt{2(2 + \tau)}\). In our previous paper \(8/\) the vector \((1/0 0/1 0/0)\) in \(R^3\) was chosen to have unit length. As a result of the redefinition of a unit length formulas for lengths in this paper differ from that of the previous paper by a factor of \(2(2 + \tau)\).

\[
\begin{align*}
    Q &= \sqrt{2(2 + \tau)} ((h + h')i + (k + k')j + (l + l')k) \\
    X &= \sqrt{2(2 + \tau)} ((u + u')i + (v + v')j + (w + w')k)
\end{align*}
\]

Note that \(X (1/0 0/1 0/0) \cdot Z (1/0 0/1 0/0) = 1/2.\) These vectors which were reciprocal to each other in \(Z^6\) have been foreshortened by projection and are no longer reciprocal to each other. To convert these to dimensional quantities \(x\) and \(q\) we will use the six-dimensional cubic lattice parameter \(A\) an reciprocal lattice parameter \(A^* = 1/A\) and let

\[
\begin{align*}
    x &= A X^* \\
    q &= A Q
\end{align*}
\]
For powder diffraction we need only the magnitudes of these vectors. Because 
\( \tau^2 = 1 + \tau \) these become

\[
Q^2 = (N + M\tau)/2(2 + \tau) \quad \chi^2 = (S + T\tau)/2(2 + \tau)
\]  

(3)

and where

\[
N = 2\Sigma h_i^2 \quad S = 2\Sigma x_i^2
\]

\[
M = h^2 + k^2 + l^2 + 2(hh' + kk' + ll') \quad T = u^2 + v^2 + w^2 + \tau^2
\]

(4)

Hence N and S are always even. Furthermore if N (or S) is divisible by 4, so is 
M (or T). If N (or S) is of the form \( 4m + 2 \), M (or T) is of the form \( 4m + 1 \). In 
addition we have

\[-N/\tau < M < N\tau \quad -S/\tau < T < S\tau.\]

(6)

Equation 4 states that all vectors with the same value of N (or S) lie on 
the same sphere in \( \mathbb{Z}^6 \) (or \( \mathbb{Z}^5 \)). The distance \( Q_c \) that a reflection in 
\( \mathbb{Z}^6 \) is from 
the icosahedral cut plane defined by equations (1) is given by

\[
Q_o^2 = \tau(N\tau - M)/2(2 + \tau)
\]

(7)

Thus the largest possible value of M for a given N will have the smallest \( Q_c \) and 
usually the greatest intensity. This largest value of M is called \( M_o \). The 
corresponding value of Q is called \( Q_o \) and is a one parameter sequence of 
reflections.

\[
2(2 + \tau) Q_o^2 = \begin{cases} 
N + 4\tau \left\lfloor \frac{N\tau}{4} \right\rfloor & N = 4n \\
N + \tau(1 + 4 \left\lfloor \frac{N\tau - 1}{4} \right\rfloor) & N = 4n + 2
\end{cases}
\]

(8)

where \( \left\lfloor X \right\rfloor \) is the largest integer in X and the corresponding values of \( Q_o \) are

\[
2(2 + \tau) Q_{oo}^2 = \begin{cases} 
4\tau \left( \frac{N\tau}{4} - \left\lfloor \frac{N\tau}{4} \right\rfloor \right) & N = 4n \\
4\tau \left( \frac{N\tau - 1}{4} - \left\lfloor \frac{N\tau - 1}{4} \right\rfloor \right) & N = 4n + 2
\end{cases}
\]

To determine multiplicities of the reflections all nodes in \( \mathbb{Z}^6 \) for \( n_i \leq 7 \) were 
grouped by their length Q and counted.

Table 1 lists for each N, the largest value of M, the indexes in \( \mathbb{Z}^6 \) and \( \mathbb{R}^3 \), 
the multiplicities and the values of \( Q_o \) and \( Q_c \). This same table can be used to 
find those vectors in \( \mathbb{Z}^6 \) for each S that are closest to being parallel to the 
plane \( \mathbb{R}^3 \).
Table Caption

The main distances and/or reflections of the icosahedral quasilattices indexed according to N and M, in Z^6 and in R^3 and in perpendicular space.
VII - PEAK POSITIONS

In figure 1, we compare the experimental diffraction curves with a series of vertical lines at the value of \( Q_0 \) from \( N = 2 \) to \( N = 106 \) with none omitted using \( A = 0.65 \text{ nm} \). Every strong peak attributed to the icosahedral phase coincides with such a position. A few weak peaks were found to line up with the next lower value of \( M \), \( M_1 = M_0 - 4 \). Except for these weak peaks, all peaks fall at angles determined by a single lattice parameter \( A = 0.46 \text{ nm} \) and one other number \( N \) which takes on the value of all positive even integers. In a sense \( Q_0(N) \) is the icosahedral equivalent of the crystallographic rules which determine for powder patterns of crystalline materials where the lines are to be found. As for crystalline materials it has a beginning at \( N = 2 \), and extends monotonically to higher angles. Strictly any list of all peaks must involve two parameters \( N \) and \( M \), and because of the irrational number \( \tau, Q \) can come infinitesimally close to any angle. Only the main \( Q_0 \) sequence has high intensity. This is similar to what occurs with incommensurately modulated phases. However, the strong peaks from an incommensurately modulated phase conform to a periodic lattice.

VIII - INTENSITY

We find that the intensity of neutron diffraction differs significantly from that obtained with X-rays. This indicates a degree of chemical ordering. The intensities are not consistent with a concept of a simple superlattice, since there is no systematic intensity difference correlated with any parity rules on \( N \). In any ordering scheme the \( N = 4u + 2 \) peaks would be superlattice peaks since they all would disappear in any structure that belonged to an icosahedral super group. As in ordinary crystallography, the positions of the reflections depend entirely on the six dimensional lattice and its parameter, only the intensity is affected by other factors. Because the icosahedral phase exists over a range of compositions, as verified by the shift in lattice parameter, there must be substitutions of manganese and aluminum for each other and a certain degree of chemical disorder. In the simplest models, identical single scatterers concentrated on a quasilattice,\(^9\,10\) neutron and xray diffraction would give similar intensities, which would be a known function only of \( Q_0 \).

This kind of model is clearly ruled out. More complicated models, involving a quasilattice decorated with identical motifs give rise to a factorable structure factor in which one of the factors gives information about possible quasilattices. This will be discussed next.

VIII - INFERENCE ABOUT THE CUT FUNCTION

A quasiperiodic arrangement of points in \( \mathbb{R}^3 \) with icosahedral symmetry is easily obtained by projecting all lattice nodes in \( \mathbb{Z}^6 \) within a symmetric by a neighborhood of the icosahedral plane and projecting them onto the icosahedral plane. The shape of the neighborhood must conform to icosahedral symmetry. The size and shape of the neighborhood is called the cut function. It determines the density and arrangement of quasilattice nodes. It is worth noting that no points in the quasilattice will be separated by \( X \) if \( X_0 \) can not be fit into the cut function. The shape and size of the cut function can be adjusted to eliminate specific distances in the quasilattice. If each quasilattice node is decorated with the same atomic motif then the structure factor of such a structure is the product of two factors, an intrinsic quasilattice structure factor and one derived from the arrangement of atoms in the motif. The former depends entirely on the cut function. The separation into two factors is an approximation. In the ideal structure there is no quasilattice lattice of points which have strictly identical environments. We assume an approximate repetition of local environment, and use the observed intensity to make inferences about the spacing of quasilattice nodes form the size of the cut.
function. If we assume that the cut function is a sphere we can obtain the quasilattice structure factor $F$ which is only a function of the dimensionless cut radius $R$

$$F = 3\left(\sin\frac{\phi}{3} - \cos\frac{\phi}{3}\right).$$  \hspace{1cm} \text{(10)}$$

where

$$\phi = 2\pi Q_c R$$

$F$ has zeros at $\phi = 4.49, 7.72...$

Fig. 3 - The square root of the relative intensity corrected for multiplicity and the Lorentz factor versus $2(2+\tau) Q_c$. Both the $Q_0$ and $Q_1$ series are shown. The value of $N$ is shown for each reflection. Where no peak was observed the intensity was set to zero. The solid and dashed curves are quasilattice structure factors for spherical cuts for $R = 0.704$ and $1.14$ respectively. The latter is the sphere with the same volume as the cut figure which gives the three-dimensional Penrose tiling.

Fig. 3 plots intensity vs. $\tau(N\tau-M)$ which is $Q_c 2(2+\tau)$. The quasilattice structure factor $F$ is plotted for two values of the dimensionless radius of a spherical cut function $R = 1.14$ and $R = 0.704$. The former has a node in Fig. 3 at 1.65, the other at 2.73. The larger $R$ is a sphere of the size of the tri-icouhahedron that gives the quasilattice of the 3-dim Penrose tiling. For this size the principal node spacing is $0.46\text{nm}$ along the 5-fold axis, corresponding
to \( S = 2, T = 1 \), although it also admits a few of the short diagonals of the oblate tile, \( S = 6, T = 3 \). Because of the many intense reflections near the node of this structure factor we conclude that this is not the size of the cut function, that these distances are not quasilattice vectors, and that this the observed quasilattice is not represented by the 3-dimensional Penrose tiling. The smaller value of \( R \) does indeed give a node at 2.73 where there are no intense reflections. This size cut function rules out \( S = 2 \) and \( S = 4 \) and all \( S = 6 \) except \( T = 9 \), which becomes the shortest distance allowed and is 1.096nm along the 3-fold axis. This is indeed the caliper diameter of a Mackay icosahedron /11/ along its three-fold axis and figures in the model proposed by Henley and Elser /12/, Guyot and Audier /13/, Ma, Stern, and Bouldin /14/. In such a model parallel Mackay icosahedra are placed on nodes separated by 1.096nm along their common three-fold axis forming distorted octahedra where they join. No nodes are closer than this distance. In another paper we describe the construction of a cut-figure which will give a quasilattice with these properties.

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