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HAL Id: jpa-00225750
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Submitted on 1 Jan 1986

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THE STRUCTURE OF ICOSAHEDRAL MnAlSi AND MnAl

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Abstract - Extended x-ray absorption fine structure measurements show that in icosahedral (I) (MnAlSi) and (MnAl) there is a structural unit consisting of a cage of Mn atoms on the vertices of an icosahedron with an average distance between Mn atoms of 5 Å. The icosahedra are connected with an average of 3.4 ± 1.0 neighboring icosahedra. It is suggested that the I-phase grows by randomly nucleating together Mn icosahedra along their 20 threefold directions as allowed by steric constraints, but maintaining orientation. The diffraction pattern of a computer simulation of such a model, called a randomly connected icosahedra (RCI) model, is calculated and compared with experiment. Excellent agreement occurs in the peaks when the center-to-center distance between icosahedra is 10.96 Å for I (MnAl). The diffraction widths for the RCI model are finite and vary from peak to peak, indicating an essential difference from models obtained by projection from higher dimensional space. The Hendricks-Teller model calculation is found to be a reasonable approximation to the RCI diffraction pattern. It is argued that the RCI model of a quasicrystal is favored over ones which project from higher dimension.

I - INTRODUCTION

Since the discovery of the icosahedral phase (I-phase) of MnAl by Shechtman at al. [1], there has been an intense effort to determine the atomic arrangement that can produce such noncrystallographic point symmetry yet sharp diffraction peaks. The models proposed can be classified into two categories. One is based on Penrose aperiodic lattices which can be constructed by projection from a six-dimensional space [2-9]. The other is a random connection of icosahedra (RCI) [10].

In this paper we present extended x-ray absorption fine structure (EXAFS) results which clearly indicate for I (MnAlSi) a structural unit of a cage of Mn atoms at the vertices of an icosahedron [Ma, Stern, and Bouldin, unpublished]. This result and those from other experiments suggest an RCI model with connections along threefold icosahedra directions so that all icosahedra are oriented the same. A calculation of the diffraction pattern expected for our RCI model is presented, and it is pointed out that line shapes can be used to distinguish between our RCI and projection models. The experimental results favor our RCI model.

II - EXAFS RESULTS

We use EXAFS [11] measurements of the Mn K-edge to compare the short-range structure of the I-phase with that of the α-phase. EXAFS measures the radial distribution about Mn atoms, not only for the first Al shell but also, as we shall show in this case, for Mn shells up to 5 Å distant. We report EXAFS measurements of icosahedral Al_{84.6}Mn_{15.4}, Al_{79}Mn_{15.4}Si_{15.6}, and the Al_{79}Mn_{15.4}Si_{15.6} sample annealed for 44 hours at 500°C in vacuum. A powder x-ray diffraction scan of the annealed sample indi-
cated that it was in the \( \alpha \)-phase. We also measured orthorhombic \( \text{Al}_6\text{Mn} \) to use as another standard. All the icosahedral samples were made by the melt spun method.

EXAFS measurements were made at the NSLS beamline X-11 in transmission using a \( \text{Si}(111) \) double crystal monochromator. Measurements were made at room temperature and at 12 K. We report here only results for 12 K; the temperature dependence will be given elsewhere.

Using standard analysis techniques, we obtain the magnitude of the Fourier transforms of \( k^2\chi(k) \) of these samples and that of \( \text{i(MnAl)} \) as shown in Fig. 1. Care was taken to transform all of the samples over the same \( k \)-range, \( 2.3-11.7 \text{ Å}^{-1} \), so that the magnitude of their peaks can be directly compared. Not shown in Fig. 1 are the results obtained on a sample formed by annealing the \( \text{i-phase} \) at 550°C for one hour. The magnitude of the transform of this sample has peaks between that of the \( \text{i-phase} \) and the 44-hour annealed sample, indicating a monotonic change in peak height with annealing. The two \( \text{MnAlSi} \) phases overlap their first three distinct peaks, but what is particularly striking is the peculiar sequence of the relative heights of these peaks. In the icosahedral phase the first and second peaks have much larger reductions than the third. This is contrary to the standard situation, in which the first shell is the one least reduced and the more distant ones are progressively reduced by usual reduction mechanisms such as thermal and structural disorder. From the \( k \)-dependence of their amplitudes and phases we determine that the first peak consists of only \((\text{Al},\text{Si})\) atoms and contains the same number of atoms in all phases within 10%. It is not possible to distinguish between \( \text{Al} \) and \( \text{Si} \) atoms in our analysis because their atomic numbers are so close. The first shell around \( \text{Mn} \) in orthorhombic \([12]\) \( \text{MnAl}_6 \) is used as the \( \text{Mn-Al} \) standard, while the \( \alpha \)-phase \([13]\) is used as the standard for the second and third peaks.

Analysis of the \( k \)-dependence of the back transform of the second and third shells shows that they consist mainly of \( \text{Mn} \) atoms. From the known structure \([13]\) of \( \alpha(\text{MnAlSi}) \), its second shell corresponds to five \( \text{Mn} \) atoms at an average distance

![Fig. 1 - Magnitude of the transform of \( k^2\chi(k) \) over the range \( 2.3 < k < 11.7 \text{ Å}^{-1} \). The \( \alpha \)-phase (long dash) and \( \text{i-phase} \) (solid) of \( \text{MnAlSi} \) and the \( \text{i-phase} \) (short dash) of \( \text{MnAl} \) are shown.](image)
of 4.46 Å with a structural rms deviation of 0.047 Å, and its third shell corresponds to five Mn atoms at an average distance of 5.04 Å with a structural rms deviation of 0.03 Å.

To interpret these distances it is useful to summarize the structure of α(MnAlSi). Neglecting the (Al, Si) atoms, the Mn atoms form a skeleton consisting of two types of somewhat irregular icosahedra with the Mn atoms at the 12 vertices of the icosahedra. One type of icosahedron is located at the corners of a cube and the other is at the center of the cube. The icosahedra are all oriented the same and are connected to eight neighbors of the opposite type directed along the threefold cubic axes which are along the (111) directions of the cube. The neighboring icosahedra do not share vertices but are displaced from one another with their threefold faces parallel and forming two opposite faces of a distorted octahedron.

The five Mn atoms at 5.04 Å are on the nearest vertices of the same Mn icosahedron as the center Mn atom and averaged over the two types of icosahedra. Four of the other five Mn atoms are on neighboring Mn icosahedra of the opposite type through the connecting octahedron bonds, while the fifth is on a neighboring Mn icosahedron of the same type which has no direct connection with the central icosahedron. Thus, in i(MnAlSi) the peak at 4.5 Å in the transform (5.04 Å true distance) is a measure of the rigidity of the Mn icosahedron cage, whereas the peak at 4.0 Å (true distance 4.46 Å) is a measure of the rigidity of the connection between the Mn icosahedra.

Qualitatively, it is clear from Fig. 1 that the Mn icosahedra remain the same in the icosahedral phase while the connections between them are changed. A quantitative measure of the changes can be obtained by isolating each peak and backtransforming to k-space. The ln-ratio of amplitudes and difference of phases of each peak are taken between phases of the icosahedral and α-phases. The result for the third peak is that the icosahedral phase retains 5 ± 0.23 Mn neighbors at the same average distance within the experimental uncertainty of ±0.02 Å and is very slightly more disordered by $Δσ^2 = 0.0006 \text{ Å}^2$. The second peak indicates that the icosahedral phase has a smaller number of neighboring icosahedra than the α-phase.

These results indicate that the Mn icosahedra remain practically unchanged in the i-phase, but their connections are modified. The fact that the coordination for the third peak remains at 5 and the sample peaks monotonically transform to k-space. The In-ratio of amplitudes and difference of phases of each peak are taken between phases of the icosahedral and α-phases. The result for the third peak is that the icosahedral phase retains 5 ± 0.23 Mn neighbors at the same average distance within the experimental uncertainty of ±0.02 Å and is very slightly more disordered by $Δσ^2 = 0.0006 \text{ Å}^2$. The second peak indicates that the icosahedral phase has a smaller number of neighboring icosahedra than the α-phase.

In summary, analyses of EXAFS measurements on i(MnAlSi), i(MnAl), and α(MnAlSi) give strong experimental evidence that structural units in the form of a cage of Mn atoms at the vertices of slightly nonregular icosahedra exist in all three with an average Mn–Mn nearest distance of 5.04 Å in the two (MnAlSi) phases and 4.95 Å in i(MnAl). The differences between the three are in the interconnections of the Mn-icosahedra and their connections to the Al atoms. The Mn cage as a structural
The number of randomly connected neighboring icosahedra must vary from an allowed maximum of 8. The fact that the average number is 3.4 indicates quite large fluctuations in the number of neighboring icosahedra. Our model is thus one in which the i-phase grows by randomly nucleating together Mn icosahedra along any of their 20 threefold directions as allowed by local steric constraints of not overlapping. The icosahedra remain oriented. This model is a modification of the original one by Shechtman and Blech [10], which has been further developed by Stephens and Goldman (1).

III - DIFFRACTION PATTERN OF RCI MODEL

The model was computer generated by starting with an icosahedron at the center and attaching icosahedra one by one along the threefold directions randomly. The added icosahedra could attach to the threefold directions of any of the icosahedra present with equal probability. An attachment would remain if it satisfied the steric constraint that it did not overlap any other icosahedra. If it did overlap, it would be removed and a new attachment attempted randomly. The center-to-center distance of any attached icosahedra was fixed at unity, while the dimension of the icosahedra along a threefold direction (face-to-face length) was also set equal to unity.

By this means, clusters of 1,000, 2,000, 3,000, and 4,000 icosahedra were assembled. The diffraction pattern of the centers of these clusters were calculated numerically by

$$|\sum_j \exp(i\mathbf{k} \cdot \mathbf{r}_j)|^2 = I(\mathbf{k})\,$$

where $\mathbf{r}_j$ are the locations of the icosahedra centers. The result for a cluster of 1,000 icosahedra is shown in Fig. 2 for $\mathbf{k}$ along a twofold axis. To improve the statistics, the pattern is averaged over the 15 twofold directions.

Fig. 2. Plot of $I(\mathbf{k})$ versus $\mathbf{k}$ along the twofold axis for a computer simulation of a 1,000 cluster.

The intensity of the diffraction peaks can be divided into two contributions. One contribution comes from the centers of the icosahedra, and the second comes from the average location of atoms about each center, i.e., the structure factor. The structure factor depends on the details of the types of atoms and their relative locations. In this paper our concern is to distinguish between the projection and RCI models and to determine which one best fits the experimental results. The structure factor gives similar contributions to both models and cannot be used to distinguish between them. The distinction occurs in the line shapes. The location of the diffraction lines and their shapes are determined by the position of the icosahedra centers alone, and we concentrate on that portion of the problem here. The intensity of the line shapes can then be calculated by multiplying by the structure factor.

It has been suggested \(^{(1)}\) that the Hendricks-Teller (HT) model \(^{[15]}\) can be used to calculate peak positions and widths. The HT model neglects all short-range correlations between the icosahedra. There is generally some short-range correlation present, and it is expected that the HT model will therefore overestimate the line width because it underestimates the correlation. An HT calculation was made for our RCI model. The peak positions agree with the computer simulation ones, but the HT line widths were too large for the widest peaks. However, they give good agreement for the narrower peaks and are the only reliable means of expected line widths for the very narrowest peaks, where finite-size effects broaden the computer simulation values.

Table 1 shows the summary of peak positions and widths calculated by the computer simulation for a cluster of 3,000 and the HT model, which is for an infinite cluster. The experimental values \(^{[16]}\) are also listed for \(i(MnAl)\). A crude correction for finite-size effects for the 3,000 cluster was made by numerically plotting the number density of the 3,000 cluster as a function of distance from the center and then Fourier transforming the smoothed density curve. A convolution of this Fourier transform with the infinite cluster gives the finite cluster case. The half-width half-maximum (HWHM) of the Fourier transform of the smoothed density function was subtracted in quadrature from the line widths of the 3,000 cluster to obtain an estimate of the infinite cluster line HWHM, as listed in Table 1.

Table 1. Experimental and theoretical diffraction peaks for \(i(MnAl)\). The experimental peaks and their indexing follow Ref. 16. Column 1 gives the indexing of the peak; column 2 gives the experimental values of peak wave number; column 3 gives the calculated values of peaks in units of \(ka\), where \(a=10.96\) Å is the center icosahedra spacing. The calculated peak HWHM is given in column 4 for the computer simulation and in column 5 for the HT model. The experimental HWHM is in column 6.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Experimental</th>
<th>Calculated</th>
<th>Simulated</th>
<th>HT</th>
<th>Experiment</th>
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<td>18</td>
<td>28</td>
<td>40</td>
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</tbody>
</table>

\(^{(1)}\) By P.W. Stephens and A.I. Goldman [unpublished].
As Table 1 indicates, the RCI peaks all have finite widths which are all less than the measured values. There appears to be another broadening mechanism involved besides the randomness of connections as assumed in the RCI model. The peak positions agree with the experimental values for a center-to-center icosahedra distance of 10.96 Å. Mention should be made of some of the peaks not listed in Table 1, which are weak and broad in both the computer simulation and HT calculations, such as the ones labeled (110001) and (111010) in Ref. 15. In the computer simulation the behavior of these peaks varied in quite an anomalous manner as the cluster size increased from $N=1,000$ to $N=4,000$. The intensity of the peaks increased more slowly than $N$, and their shapes changed from an approximately symmetric single peak to an asymmetric, even double-humped, one. The HT calculation showed a broad but single-peaked shape for these lines. We do not understand the $N$ dependence of these peaks and plan to study them further.

The experimentally measured finite line width has a natural explanation in the RCI model, while the projection method requires an ad hoc deformation and growth faulting. However, the RCI model widths do not agree with the measurements, suggesting the need for another line broadening mechanism in the experiments. The RCI model is physically more pleasing because one expects nucleation and growth to proceed as in the RCI model. Further experimental measurements of line widths on i-phase samples with less strain are required before definite conclusions can be drawn as to which model is correct. A complete detailed determination of the atomic positions awaits a refinement of the structure factor to match experimental intensities. The calculation presented here shows that icosahedral units interconnected along the threefold axes in a random fashion with an average center-to-center spacing of 10.96 Å is consistent with the icosahedral diffraction pattern. As shown by EXAFS, the icosahedral units contain a Mn cage on the vertices of an icosahedron with an average separation of 5 Å between Mn atoms.

There is an apparent paradox in finite line widths for the RCI model. The location of the centers of each icosahedron can be represented as a linear combination of 10 unit vectors along the 10 threefold icosahedral directions. These 10 unit vectors can be obtained by a projection from a 10-dimensional space down to three dimensions. Thus, the centers of the icosahedra can be represented as points on a simple cubic lattice in 10 dimensions. If these points are randomly occupied by icosahedra, then the expected diffraction peaks are sharp and will therefore project as sharp in three dimensions.

The paradox can be resolved by realizing that the points are not occupied randomly. About each point are 20 nearest neighbors, but only a small fraction (of the order of 4) are occupied because of steric constraints. The finite widths can be understood by a two-dimensional analogy. Consider a triangular lattice occupied by large atoms so that steric constraints force the occupation of only one-third of the sites locally, as is the case for Kr gas commensurately adsorbed on graphite. The triangular lattice can be subdivided into three equivalent sublattices A, B, and C. Sharp diffraction peaks occur when the occupied fraction of sites are all of type A. However, if the sites are occupied in domains where one type of site—A, B, or C—is occupied in each domain, then the diffraction peaks will have a finite width corresponding to the average size of domains.

The RCI model explains in a simple physical manner the stability of the i-phase during rapid cooling. During rapid cooling the growth is dominated by local order which favors connections along the threefold directions. Since there are 20 such threefold faces and local constraints limit the number of connections to, at most, 8 and significantly fewer when the connections are made randomly, there is an overwhelming probability that the icosahedral phase will be produced. To produce the ordered α-phase requires the connection to only the 8 faces along the (111) directions for all icosahedra. This coherence requires the operation of subtle long-range forces which do not have time to make their influence felt during rapid cooling. Only annealing for long times permits the cooperative rearrangement of icosahedral connections required for the long-range order into the crystalline α-phase.
Because the RCI model is consistent with the EXAFS and diffraction results and explains in a simple physical manner the formation, growth, and stability of the \( i \)-phase, we favor it over the projection model. If future experiments confirm the RCI model as the correct one, its ascendancy over the projection model can be called a triumph of physics over mathematics.

The samples used in this experiment were kindly supplied by D. Shechtman, R.J. Schaefer, and F.S. Biancanello of the National Bureau of Standards. We are most appreciative of discussions with J.W. Cahn. Measurements were made on beamline X-11 at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. The research was supported partially by the U.S. Department of Energy under Contract DE-A505-80-ER10742.

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