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Structural Unit in Icosahedral MnAlSi and MnAl

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Experimental evidence from extended x-ray–absorption fine-structure measurements indicates that a cage of Mn atoms at the vertices of an icosahedron is the structural unit in the icosahedral MnSiAl and MnAl phases. The connections among these icosahedral units and between them and the Al atoms are different in the icosahedral and α phases. It is suggested that the *i* phase grows by the random nucleating together of Mn icosahedra along their twenty threefold directions, as allowed by local steric constraints.

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There has been intense interest in the icosahedral crystals first discovered over a year ago by Shechtman, Blech, Gratias, and Cahn.[1] Theoretical models have been proposed[2–11] which can produce the observed sharp diffraction peaks with icosahedral rotational symmetry, but the atomic structure of these icosahedral crystals has not been determined experimentally and the various proposed models have not been experimentally confirmed. There are basically two types of models, one based on the Penrose tilings[3–6,11] and the other based on icosahedra connected in various ways.[6,9,10] Shechtman and Blech[10] showed that systems consisting of a random packing of icosahedra that maintain orientational order by sharing edges or vertices can give diffraction peaks. Stephens and Goldman,[12] in a recent calculation, indicated varying widths to the diffraction peaks in such a model. It is now clear from experiment[13,14] that models based on icosahedra with Mn at the center surrounded by twelve Al at the vertices (as first suggested by Shechtman and Blech) are not correct for icosahedral MnAl (*i*-MnAl).

Elser and Henley[6] (EH) and Guyot and Audier[9] (GA) have suggested models for the icosahedral Mn-Al and Mn-Si-Al based on the structure of α-MnAlSi.[15] EH suggested that the icosahedral phase may be built from 54-atom icosahedral clusters, first described by Mackay,[16] which consist of 12 Mn atoms and 42 Al atoms. GA built a model, also based on the structure of α-MnAlSi, using double icosahedra which are related to the Mackay cluster. These icosahedra and the way they connect are similar to those in α-MnAlSi, but their number of neighbors is less so that they are arranged nonperiodically, while the EH model does not specify how the Mackay icosahedra are connected.

Experiments have succeeded in clarifying some general features of the structure of the *i* phase but have failed to determine its structure in detail. X-ray[17] and electron diffraction[1,17] have shown that the diffraction peaks can be indexed by six vectors[11,17] which can be associated with the vertices of an icosahedron. The x-ray results have shown that the diffraction peaks in *i*-AlMn have varying widths corresponding to correlation lengths of approximately a few hundred angstroms. High-resolution[18] and dark-field electron microscopy[1] have verified that the structure is not caused by twinning. Mössbauer[13] and extended x-ray–absorption fine-structure (EXAFS) measurements[14] have shown that there are at least two distinct Mn sites in *i*-MnAl. NMR[19] and heat of transformation[20] measurements have suggested that the *i* phase is more glasslike than crystallike. The density[21] of *i*-MnAl is within a few percent of the orthorhombic $MnAl_6$. The *i*-MnAl phase is observed to grow from the melt along its threefold axis.[22] Coexistence and a definite structural interrelationship between Al_4Mn and *i*-MnAl have been reported.[23] Some recent unpublished results have indicated that *i*-MnAlSi is related to α-MnAlSi: EXAFS measurements suggest that the first coordination shells of Al atoms about Mn atoms may be somewhat similar in the two phases[24]; cases have been seen in which the *i* and α phases coexist and are coherently oriented.[25]

We use EXAFS[26] 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 will show in this case, for Mn shells up to 5 Å distant. We report EXAFS measurements of icosahedral $Al_{84.6}Mn_{15.4}$, $Al_{79}Mn_{15.4}Si_{5.6}$, the $Al_{79}Mn_{15.4}Si_{5.6}$ sample annealed for 44 hours at 500 °C in vacuum, and a sample prepared in the α phase with composition $Al_{73}Mn_{16}Si_{11}$. A powder x-ray diffraction scan of the annealed sample indicated that it was also in the α phase. We also measured orthorhombic

Al_6Mn to use as another standard. All the icosahedral samples were made by the melt-spun method.

EXAFS measurements were made at 12 K at the National Synchrotron Light source beam line X-11 in transmission with a Si (111) double-crystal monochromator. The samples were powdered, sieved through 400-mesh screening, and rubbed onto the sticky side of Scotch brand Magic transparent tape. The absorption change $\Delta\mu x$ at the K edge of Mn in a single layer was typically ~ 0.2 and 4–6 layers were used for a total $\Delta\mu x \simeq 1$. The similarity and fineness of the powder of the various samples assures that distortions of the EXAFS due to thickness-effect[27] differences will be about 1%, a negligible error. The usual care was taken to minimize higher harmonics in the x-ray beam.

Using standard analysis techniques, we obtain the normalized EXAFS data $\chi(k)$ for the Mn-Al-Si samples as shown in Fig. 1. The energy origin was chosen so that k has the value of the Fermi wave number at the edge. The magnitudes of the Fourier transforms of $k^3\chi(k)$ of these samples and that of i-MnAl are shown in Fig. 2. Care was taken to transform all of the samples over the same k range, 2.3–11.7 Å^{-1}, so that the magnitudes of their peaks can be directly compared. The high-k limit was determined by the i-MnAl data which were not of as high quality as the other data. The three 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 (Al,Si) atoms and contains the same number of atoms in all phases within 10%. It is not possible to distinguish between Al and Si atoms in our analysis because their atomic numbers are so close. The first shell around Mn in orthorombic[28] $MnAl_6$ is used as the Mn-Al standard, while the α phase 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 Mn atoms. From the known structure[15] of α-MnAlSi, its second shell corresponds to five Mn atoms at an average distance 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 0.083 Å. To interpret these distances it is useful to summarize the structure of α-MnAlSi. If we neglect the (Al,Si) atoms, the Mn atoms form a skeleton consisting of two types of somewhat irregular icosahedra with the Mn atoms at the twelve vertices of the icosahedra. The icosahedra are located at the corners and center of a cube, and are all oriented the same. Each icosahedron is connected to eight neighbors directed along the threefold icosahedra 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. Four of the other five Mn atoms at 4.46 Å are

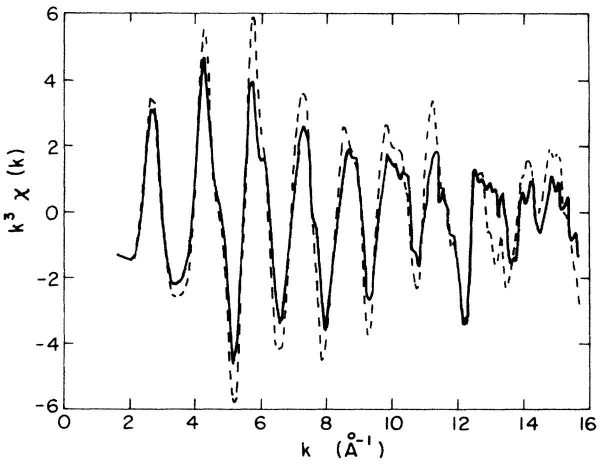

FIG. 1. $k^3\chi(k)$ for α phase (dashed line) and i phase (solid line) of MnAlSi vs the wave number k.

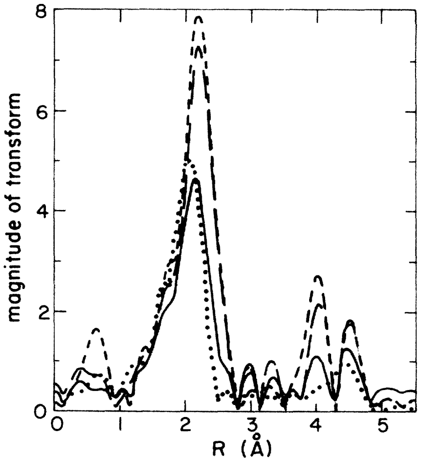

FIG. 2. Magnitude of the transform of $k^3\chi(k)$ over the range 2.3 $\text{Å}^{-1} < k < 11.7$ Å^{-1}. The α phase with composition $Al_{73}Si_{11}Mn_{16}$ (short dashed line), the α phase obtained by annealing of the i phase of MnAlSi (long dashed line), the i phase of MnAlSi (solid line), and the i phase of MnAl (dotted line) are shown. The third peak overlaps for the two α phases.

on connecting, neighboring Mn icosahedra, while the fifth is on a neighboring Mn icosahedron which has no direct connection with the central icosahedra. 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. 2 that the Mn icosahedra change less in the icosahedral phase than do their connections. A quantitative measure of the changes can be obtained by isolating each peak and back-transforming to k space. The logarithmic ratio of amplitudes and difference of phases of each peak are taken between the icosahedral and α phases. The result for the third peak, as shown in Fig. 3, is that the MnAlSi icosahedral phase retains 5 ± 0.25 Mn neighbors at the same average distance within the experimental uncertainty of ± 0.02 Å and is slightly more disordered by $\Delta\sigma^2 = 0.0022(4)$ Å^2. The annealed sample has essentially the same third shell as the sample prepared initially in the α phase. Similar ratios for the second peak indicate that the icosahedral phase has a distribution which cannot be described by a simple Gaussian. The logarithmic ratio versus k^2 for this shell is consequently not a straight line, which makes the interpretation more complicated. The high-k behavior is dominated by the Mn atoms and its limiting behavior of zero slope at a negative value indicates that only e^{-1} of the Mn neighbors have the same distribution as the α phase, which is consistent with the statement that only that fraction of connections with neighboring icosahedra is the same as in the α phase. Since the α phase has eight neighbors, the number of similarly connecting icosahedra in the *i* phase is 2.9. What happens to the missing connections is somewhat uncertain because of the lack of low-k data near the origin and the possible contribution to the low-k data by Al/Si atoms. The possibilities are that these connections either do not exist in the *i* phase, are more highly disordered, or a combination of the two. Thus, the number of connections of 2.9 is a lower limit to the actual number of neighboring icosahedral units.

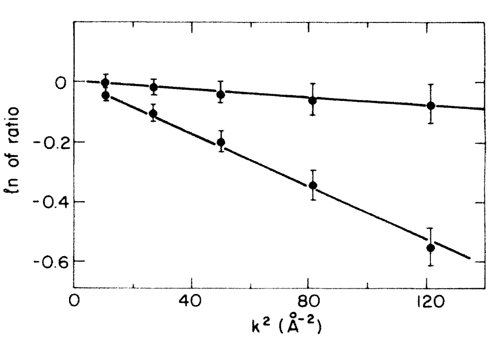

FIG. 3. The logarithm of the ratio of the amplitude of the third shells of the *i* phase (lower line) or of the α phase obtained by annealing of the *i* phase (upper line) to that of the α phase of MnAlSi, vs k^2.

Note from the straight line in Fig. 3 that the third shell always differs by a Gaussian factor even for the two α phases. The Gaussian difference indicates that the third shells in the α phase and in the *i* phase are very similar, differing by only a small Gaussian disorder in the distance distribution of the Mn-Mn distances. In the α phase this Mn-Mn distance has intervening Al/Si atoms which are almost collinear. As Teo[29] has pointed out, the large multiple scattering introduced by such intervening atoms gives EXAFS a sensitivity to bond angles in addition to radial distances. Thus, the fact that the *i* phase and α phase only differ by a Gaussian factor in this third shell indicates not only that both phases have the same number of Mn neighbors with only a slight disorder in the Mn-Mn distance, but that their angular orientations relative to the intervening Al/Si atoms are also closely the same in the two phases.

The transform of *i*-AlMn in Fig. 2 shows only two of the first three distinct peaks in the MnAlSi phases and at somewhat shorter distances. The third peak indicates the presence of 4.8 ± 0.5 Mn at an average distance of 4.95 ± 0.05 Å with an increased disorder of $\Delta\sigma^2 = 0.003$ Å^2 relative to the α phase. This result is consistent with a cage of Mn atoms at the vertices of an icosahedron being also the structural unit in *i*-MnAl. The peak that is missing corresponds to the Mn atoms connecting the Mn icosahedra. From this we conclude that the *i*-MnAl phase has its icosahedra connected differently, but because the second peak is lost in the background we cannot quantify how this change occurs. Growth of the various phases from the melt[23,25] along threefold directions suggests that the Mn icosahedra are also connected along threefold axes in the two *i* phases, as they are in 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 distorted 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. Whatever the connection rules are in the two icosahedral phases, the experiments suggest that the icosahedra do not share vertices. For *i*-MnAlSi the evidence is that the number of connecting icosahedra is less than in the α phase and their connections are more disordered. A decreased number is also consistent with the smaller density of *i*-MnAl relative to α-MnAlSi (3.28 compared with 3.62 g/cm^3). The Mn cage is part of the Mackay icosahedral cluster suggested by EH as the structural unit in *i* phases. However, the nearest Mn-Mn distances are around 5.0 Å instead of 4.6 Å as suggested by EH. Neither the GA nor the EH model predicts the distortion in the connections.

The experimental results indicate that the number of neighboring icosahedra may vary widely about an average from an allowed maximum of eight. Our model is thus one in which the *i* phase grows by the randomly nucleating together of oriented Mn icosahedra along any of their 20 threefold directions, as allowed by local steric constraints. As pointed out by GA, the steric constraint is that connections only occur through threefold faces which do not share edges. This model is a modification of the original one by Schechtman and Blech[10] which was further developed by Stephens and Goldman.[12] It was shown by the latter[12] that this disordered packing model gives good agreement with the measured diffraction patterns[17] of the *i* phase. We have also shown[30] independently that such a model can fit the diffraction data[17] with a center-to-center distance between icosahedral units of 11.0 Å, the same as in the α phase.

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