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Local atomic environments in periodic and aperiodic Al-Mn alloys

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We have applied Wigner-Seitz constructs to several known crystal phases of Al-Mn and to two independent descriptions of the Al-Mn icosahedral phase for which all the atomic positions are available. The resulting measures of local atomic environments for the icosahedral phase are in agreement with one another and with experiment: broad distributions in site metrics and volumes of both Mn and Al sites, none of which have local icosahedral point symmetry, and a similar radial distribution function.

A year and a half ago, Shechtman and co-workers reported[1] evidence of a new rapidly solidified Al-Mn crystalline phase (*i*-Al-Mn) displaying an icosahedral point group symmetry which is inconsistent with long-range translational order. Since that time, other alloy systems have also been observed[2] to display icosahedral order. In this paper, we consider the local atomic environments in the Al-Mn systems for which we have two independent descriptions[3,4] of the atomic positions from which the local environments may be inferred.

One approach to understanding the structural ordering of icosahedral materials has involved[5,6] tiling, where a system is constructed with space-filling tiles which are fitted together according to specific aperiodic rules. These models describe overall symmetry rather well, but there is a paucity of estimates of where the atoms are. There are, however, experiments,[7] e.g., extended x-ray-absorption fine structure (EXAFS), Mössbauer spectroscopy, and NMR, which have been used to sensitively probe the local atomic environments.

What constitutes the local environment of an atom? In periodic crystals, an important attribute of the local environment of an atom is its point symmetry within the space group to which the structure of the crystal belongs. The use of Wigner-Seitz (WS) cells will give additional information[8,9] in this case. For aperiodic (e.g., icosahedral) crystals, for which there is yet no appropriate crystallographic description, the WS cell is the only way to study the local environment. One measure of the local environment is the coordination number, i.e., the number of "nearest" neighbors, which may be defined as those contributing faces to the atomic Wigner-Seitz (Voronoi)[10] polyhedron. A better measure, which provides some sense of the local topology, is a count of how many nearest neighbors are *common* to a near-neighbor pair (which is indicated by the number of edges on the WS cell face associated with the pair) and what types of pairs occur. For example, the (0,0,12,0) polyhedron of Fig. 1 is the dodecahedron, having twelve five-edged faces, appropriate to some sites in the Frank-Kasper structures. Local environments catalogued in this way have a variety of uses. (i) They provide elementary "tiles" in descriptions of glasses; for example the (0,3,6,0) is associated with the capped bipyramidal Bernal environment which is presumed[11] to be a basic building block of transition metal-metalloid glasses. (ii) Systems nominally having the same crystal structure but *different* internal coordinates (within the unit cell) can have different sets of such WS cells which are indicative of different intrinsic structure.[12] (iii) Invoking higher-dimensional space, Nelson[13] has related certain faces to disclinations in this space and, in turn, has related threads of these disclinations to the Frank-Kasper and glassy systems. (iv) These disclinations have been related[8,9] to the magnetism in αMn and the hard magnets[8] and to a unique definition[9] of the asymmetric units appropriate to certain crystals.

Turning now to the two Al-Mn descriptions, one is based[3] on a mass-density wave (MDW) where atomic sites are attributed to the peaks of a mass-density wave, $\sum_{i=1}^{6}\cos(\mathbf{q}_i\cdot\mathbf{r})$. In the vertex version, the sum is taken to

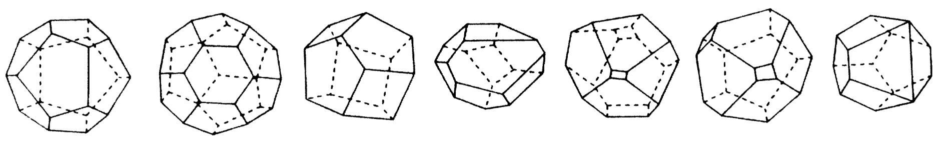

FIG. 1. Some local atomic environments (WS cells) of Mn sites in Al-Mn alloys listed in Table I. ($V_3, V_4, V_5, V_6, \ldots$) indicates a polyhedron having V_i faces with i edges. Areas of faces in other phases may differ, depending on the distances and radii of the neighbors. (0,0,12,4) together with (0,0,12,0) are examples of the polyhedra common to the Frank-Kasper phases. (0,3,6,0) is a Bernal type polyhedron. (0,6,4,0) is a nontriangulated polyhedron having more than three faces meeting at one vertex.

span the six independent q vectors of that model (i.e., they are directed to the vertices of an icosahedron). Given the $|q|$ as measured[14] by x-ray diffraction, the set of peaks is cut off so as to avoid an unrealistically high atomic density. (About 10% of the lowest-amplitude peaks were thus cut off.) The other description is derived directly from electron diffraction data from which the same six independent q vectors were derived.[4(a)] Using traditional methods for the analysis of modulated crystals, a sliding origin (SO) model for the Al-Mn icosahedral phase was generated. This description requires *interpenetrating* rather than space-filling rhombohedral "tiles," where modulations take place along four nonintersecting $\langle 111 \rangle$ directions of cubes. Rules for the occupancy of atomic sites are based on a layering-modulation pattern over a reference skeleton. In both the MDW and SO descriptions, the modulated (aperiodic) atomic motifs fill space—there are no holes or gaps.

Applying the WS constructs, we have found that the local environments in the two descriptions have important features in common: (i) There is a distribution of Mn site WS cell topologies and an even broader one of Al site topologies. There is a wide range in site metrics and volumes. The volumes were found to span those appropriate to Mn and Al and they tend to fall into two well-defined groups with $\sim$20% characteristic of Mn. (This was used in the MDW description to determine which sites are occupied by Mn.) In the SO description, the sites occupied by Mn are determined by layering along the modulation directions, and this was found to be consistent with the same volume considerations used in the MDW description. (ii) No sites were found to be (0,0,12,0) or $(0,0,12,V_6)$, $V_6=2$, 3, or 4, for either of the descriptions. Cells with these topologies are the building blocks of the Frank-Kasper structures. [Incidentally, some (0,0,12,0) were found for a face model, as against the vertex model, in the mass density description.] (iii) The radial distribution functions (RDF) for the two descriptions show nearest neighbors lying between 2.5 and 3 Å in a bimodal distribution. The SO description's RDF was inspected at larger distances and narrow peaks were observed at $\sim$6 Å. This implies long-range positional correlations characteristic of a crystal and inconsistent with a glass.

The Mn site WS cells found in crystalline Mn-Al systems are compared to each other and the SO and MDW description in Table I. (Unfortunately the structure of $MnAl_4$, which is near the composition of greatest interest, has yet to be solved.) There is a significant distribution in crystalline cells indicating that Mn and Al accommodate one another in a variety of ways. This is evident in the range of volumes per atom that is seen for these alloys and is a manifestation of flexibility in bonding conditions. While Mn may occur in (0,0,12,0) sites, none of the crystalline systems in this table are Frank-Kasper phases (where all sites are in $(0,0,12,V_6)$ $V_6=0$, 2, 3, or 4, environments). The $(0,4,4,V_6)$, $(0,3,6,V_6)$ and $(0,2,8,V_6)$ with $V_6 \neq 0$ form a family of polyhedra shared by some of the crystal structures and by the two icosahedral descriptions. (This family is also seen in many crystalline structures of alloy systems which are glass formers.) The main difference between the MDW and the SO icosahedral descriptions is the MDW's somewhat higher average coordination number (i.e., the total number of faces of a cell), $\sim$12.5 versus $\sim$12. The crystalline environments, ranging from 9 to 13, span this range.

TABLE I. The Wigner-Seitz polyhedra appropriate to the Mn sites in the crystalline Mn-Al systems and the principal Mn polyhedra obtained for the icosahedral descriptions. The average Mn site coordination number, n, is indicated.

Crystalline		
$MnAl_{12}$	(0,0,12,0)	$n=12$
$MnAl_6$	(0,6,4,0)	$n=10$
Mn_4Al_{19}, α(Mn-Al-Si)	(0,0,12,0), (0,2,8,1)	$n=11.5$
Mn_3Al_{10}, β(Mn-Al-Si)	(0,0,12,0)	$n=12$
Mn_4Al_{11}	(0,2,8,2), (0,3,6,4)	$n=12.5$
$Mn_{12}Si_{43}Al_{45}$	(0,2,8,0)	$n=10$
$Mn_3Zn_2Al_{11}$	(0,2,8,1), (0,3,6,0), (0,0,12,0) (0,8,2,2)	$n=11.4$
Icosahedral descriptions		
Mass density (Ref. 3)	(0,3,6,4), (0.3,6,3) plus a few (0,5,6,2), (0,2,8,4)	$n=\sim12.5$
Sliding origin (Ref. 4)	(0,3,6,3), (0,4,6,2) (0,5,6,1), (0,4,4,3)	$n=\sim12$

Mossbauer and NMR results suggest that there are broad distributions in quadrupole fields at both Mn and Al sites in the icosahedral phase with few, if any, sites having the zero (or near zero)-valued fields characteristic of local icosahedral (or near icosahedral) environments. (The magnitude of the average Mn site field is on the large side of field gradients observed in metals.) Both the MDW and the SO icosahedral descriptions have[15] distributions of sites, with a range in aspherical character, consistent with experiments. The EXAFS results also indicate that there is substantial variation in the near-neighbor environment of Mn atoms. The results of Heiney *et al.*[7] and one of the atomic distributions suggested by Sadoc *et al.*[7] have identified the bimodal distribution of nearest neighbors required by both the MDW and the SO descriptions.

For glasses, it has proven[9] useful to invoke a model[16] where the local atomic environments of relevant crystalline structures are taken as the building blocks. Similarly, Elser and Henley have suggested[16] a tiling for icosahedral phases in which the Al-Mn-Si and Al-Mg-Zn crystalline systems are chosen as models of possible tiling appropriate to the icosahedral phases. While the tiles are similar, they require *different atomic decorations* for the two crystals. It was conjectured that the same holds for their icosahedral counterparts. Other studies have made[17] an analogy between the icosahedral phase and the Frank-Kasper structures[18] which have icosahedral and near-icosahedral local environments. While analogies to Frank-Kasper structures may be germane to the tiling framework of an icosahedral phase, the present two descriptions and experiments indicate broad distributions of local site environments in *i*-Al-Mn, with local site symmetry at a substantially lower level than icosahedral.

The local environments obtained in the vertex model MDW description or in the SO description derived for *i*-Al-Mn, and also probably for *i*-Al-Mn-Si are not necessarily the only local environments appropriate to icosahedral systems. This implies more than one type of icosahedral phase. WS cells which accommodate atoms with larger (smaller) atomic volumes will, in general, involve larger (smaller) numbers of nearest neighbors. In the case of icosahedral Mn-Al, the minority Mn is the small site and has the lower number of nearest neighbors. There are other icosahedral phases,[2] such as Pd-U and Mg-Al-Zn, where the minority component is the larger atomic species, suggesting a *different* distribution in local environments and, to this extent, a different icosahedral ordering than in the case of Mn-Al (and Ru-Al). The proposals by Elser[6] of the same crystalline tiles for Al-Mn-Si and Al-Mg-Zn, but requiring different atomic decoration, are consistent with this view.

In this paper we have considered the local environments as measured by WS cells relevant to the icosahedral phases. Such a study requires a description of where all the atoms are and we have made use of two models for which this information is now available. The local environments for both models were found to be not icosahedral. Although the two models have some differences, they share important common features with one another and with experiment. It is reasonable to expect that these features will be shared by any physically reasonable construct for icosahedral Mn-Al.

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