SHORT COMMUNICATIONS

STABILITY OF ICOSAHEDRAL UNITS IN QUASICRYSTALS

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FIVE-FOLD rotational axis of symmetry is incompatible with crystalline state since it cannot be combined with the translational symmetry of crystals. But recently formation of the so-called quasicrystals containing 5-fold axis of symmetry has been reported[1-5] in a few alloy systems and notably in Al-14 at % Mn. Extensive electron microscopic studies[2-5] have been performed on this alloy and it has been suggested[6-8] that the structure of quasicrystals is based on orientationally ordered icosahedra. Bursill and Ju Lin[2] have shown that the high resolution electron microscopic images can be projected on to a 2-dimensional Penrose tiling. They have also suggested a possible structural model for Al-14 at % Mn alloy based on edge- and corner-shared icosahedra. The cardinal feature of Al-Mn quasicrystals is therefore the presence of icosahedral units not present in the structures of either Al or of Mn in their known crystalline phases. We discuss here the stability aspect of such icosahedra based on extended Hückel energy calculations on relevant metal atom clusters.

Aluminium is a third group element next to boron. Elemental B exhibits bewildering polymorphism with closely related crystal structures all of which are built with B_{12} icosahedral motifs. The unit cell of a particular modification of B is reported to contain 1708 atoms with an ordered (!) labyrinth of B_{12} icosahedra. The propensity of boron to form icosahedra has been long known to be a consequence of the electron deficiency of third group elements which in turn causes pronounced tendency for overbonding[9].

The sudden disappearance of the tendency for forming icosahedral structures as we move from boron to aluminium in the third group of periodic table is noteworthy. It is also coincident with the appearance of metallicity in Al, boron being a nonmetal. The sudden change in bonding behaviour may be attributed to the rather diffuse 3s/3p orbitals of Al in comparison with 2s/2p orbitals of boron. Diffuse 3s/3p orbitals give rise to large effective radius and elements with larger radii favour non-directional metallic bonding in place of directional covalent bonding[10]. Further, an icosahedron of large atoms is energetically unfavourable due to the presence of a large unoccupied interstitial at the centre of the structure.

However, since icosahedral units are present in quasicrystals of Al-Mn alloys, it is possible that Al_{12} icosahedra are stabilized by the presence of a central Mn atom. Atomic radius of Mn (1.30Å) is lower than that of Al (1.43Å)[11] and hence would stabilize the icosahedron ($r_{Mn}/R_{Al} = 0.91 \simeq 0.902$, required for ideal icosahedral packing). Such a unit may also be resistant to deformation to the geometrically closely related cuboctahedron, ideal radius ratio for which is 1.00. We may also note that deformation of $Al_{12}Mn$ icosahedra to cuboctahedra[12] results in transforming the quasicrystal structure to the regular fcc structure of Al with substitutional Mn atoms. Hence we suspect that the molten state Al-Mn alloys contain $Al_{12}Mn$ icosahedra. Icosahedral packing is also in general favoured in melt structures. Further, loss of cohesive energy of melts due to their typically larger specific volumes as compared to solids is atleast partly mitigated by the formation of tightly packed icosahedral units. We assume that melts containing the icosahedra are quenched into quasicrystals. In short, therefore, we feel that in the presence of an alloying element like Mn, the inherent capacity of Al as a third group element to form icosahedra is buttressed.

In order to quantify these considerations we have performed energy calculations using extended Hückel, EH, method[13] with Slater type atomic basis sets (using 3s, 3p orbitals of Al and 3d, 4s, 4p orbitals of Mn). The candidate structures of atomic clusters are shown in figure 1. The interatomic distances were also optimized

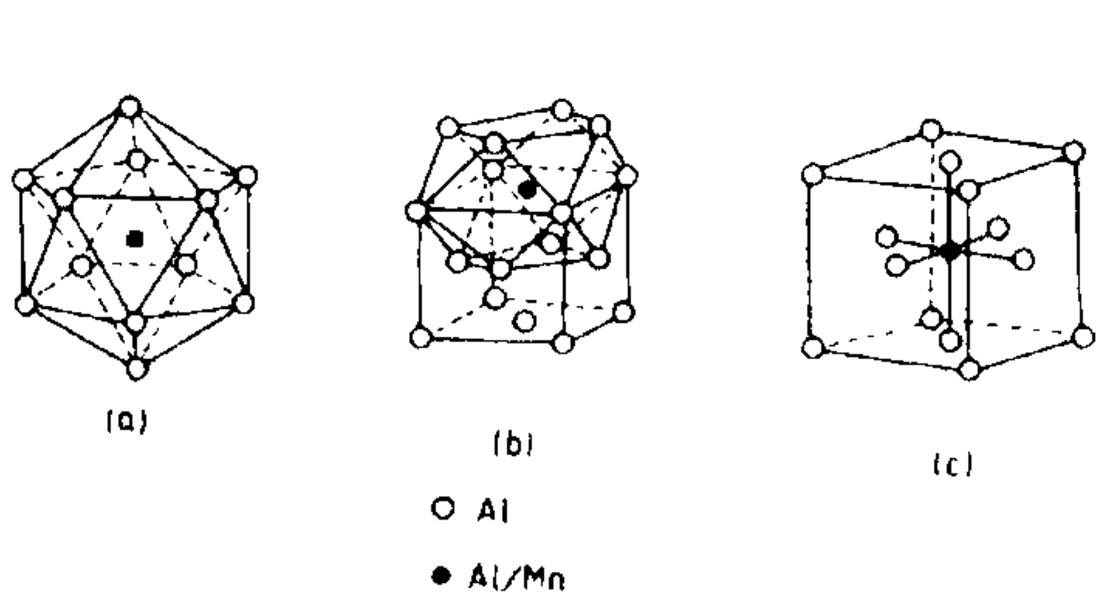

Figure 1. Possible atomic clusters in Al-Mn alloys: (a) icosahedron (b) cuboctahedron (c) interstitial Mn atom in fcc Aluminium.

while calculating the energies which are given in table 1. Energies calculated in EH treatment are known to be only approximate but the relative energies calculated for closely related structures are considered reliable[14,15]. However, in the cluster energy calculations the effect of the long-range interaction cannot be included and to a first approximation we ignore its consequences. It may be seen 'a posteriori' that the approximation is not entirely untenable. Energies have been calculated for Al_{13} and $Al_{12}Mn$ icosahedra (figure 1a) with central Al and Mn respectively along with those of corresponding cuboctahedra (figure 1b). Additionally we have evaluated the energy of $Al_{14}Mn$ cluster (figure 1c) corresponding to interstitial manganese in fcc Al.

From the tabulated values of energies in table 1 (both total energy per atom and binding energy per atom) the following conclusions may be drawn. In pure Al the energy of Al_{13} cuboctahedron is lower than that of Al_{13} icosahedron. Since cuboctahedron is a part of the fcc lattice, we conclude that the known stability of the fcc structure of Al is properly reflected in the calculations. Between $Al_{12}Mn$ icosahedron and $Al_{12}Mn$ cuboctahedron, the icosahedron is energetically more stable, implying that substitutional Mn in an fcc structure to which the cuboctahedron corresponds is less stable. An interstitial Mn in the fcc Al (14 Al atoms are considered in the calculation) is even less stable as expected.

The magnitude of relative stability of $Al_{12}Mn$ icosahedron is only 2% over that of cuboctahedron. The long-range component of interactions neglected in cluster calculations can tip the balance of energy in favour of cuboctahedron because it generates the fcc crystal structure. This we feel is the origin of the metstability of quasicrystals. However as pointed out earlier, due to the absence of long range order in the melt, icosahedral structures may be preferred. It is quite consistent with the fact that rapid quenching is essential for realizing icosahedral structure in solid state and that slow cooling invariably favours formation of crystalline phases.

The stoichiometry of the alloy can be satisfied only when the corners of icosahedra are shared. But in order to generate orientational order unshared corners may be required along with shared edges and faces. One such scheme of icosahedral arrangement has already been suggested by Bursill and Ju Lin[2]. Compositions considerably different from Al_6Mn ($Al_{86}Mn_{14}$) should be quite unstable because in Al-rich compositions nucleation of fcc (cuboctahedron) dominates and in Mn-rich compositions quasicrystalline order would be difficult to achieve since it requires a large measure of edge and face sharing. The latter situation may lead to phase separation.

Thus we conclude that the tendency for overbonding and formation of icosahedral structures which is manifest in B is only latent in Al. Addition of elements like Mn which has the appropriate size revives this tendency. The electronegatives[11] of Al (1.54) and Mn (1.44) also favour a further readjustment of radii, because radius of Mn shrinks a little by flow of electrons towards Al atom and the latter correspondingly swells in size.

Transition metal atoms like iron which stabilize icosahedral structure of Al-alloys may produce similar effects. Other alloy systems in which quasicrystalline phases have been observed may share two important features, namely, dissimilar atomic radii and dissimilar electronegativity, in common with Al-Mn alloys.

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Table 1 *Energies of clusters from EH calculations*

Cluster	R(Al-Al) (Å)	Total Energy per atom (eV)	Binding Energy per atom (eV)
Al_{13} (icosa)	2.9	−33.96	2.86
Al_{13} (cuboc)	2.8	−34.18	3.08
$Al_{12}Mn$ (icosa)	2.5	−36.85	4.04
$Al_{12}Mn$ (cuboc)	2.4	−36.78	3.97
$Al_{14}Mn$ (fcc)	2.6	−35.76	3.18

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