Calculated Electronic Structure of Icosahedral Al and Al-Mn Alloys

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Electronic structure calculations on Al and Al-Mn clusters of icosahedral (I_h) symmetry show important differences compared with such calculations on clusters of cubic (O_h) symmetry. Anomalously high state densities at E_F and energy dependence proportional to E^n, $n \geq 1$, characterize the I_h clusters. Highly symmetric molecular-orbital topologies make icosahedral clusters appear like large quasiatoms. Central Mn atoms destabilize I_h clusters.

Icosahedral point-group symmetry had been dismissed as being insignificant to solid-state physics because its inherent fivefold symmetry is incompatible with crystallographic space-filling schemes. However, Frank[1] showed that the icosahedral arrangement of thirteen atoms interacting by a Lennard-Jones pair potential has lower total energy than close-packed crystalline arrangements. This observation fueled the assertion that icosahedral coordination might prevail in densely packed liquid phases and that the icosahedral stability might indeed account for the large amount of supercooling possible in many transition-metal liquids. Notable similarities between the liquid and glassy phases lead naturally to the suggestion of icosahedral short-range order in metallic glasses.[2] Recently, several models have been proposed to account for the possible occurrence of icosahedral structures in noncrystalline states. Nelson and Widom[3] suggest that the glassy phase might bear some resemblance to a structure obtained by projection of an icosahedral structure (polytope {3,3,5}), which tiles a four-dimensional sphere, into three dimensions while accommodating the concurrent strains through a series of wedge disclinations. Steinhardt[4] suggests that a new phase of matter, possessing long-range rotational order, yet lacking traditional crystalline periodicity, could be formed via a quasiperiodic tiling of three dimensions (i.e., by a Penrose tiling). This new phase of matter, dubbed quasicrystal, yields a sharply peaked diffraction pattern with crystallographically "forbidden" fivefold symmetry. The most recent development with respect to icosahedral symmetry has been the observation by Shechtman *et al.*[5] of extended icosahedral rotational order in a rapidly solidified Al-14% Mn alloy. This alloy exhibits a sharply peaked diffraction pattern exhibiting fivefold symmetry which appears to be consistent with the quasicrystal model.[6]

We have calculated the electronic structure and wave-function topology of Al_{13}, Al_{33}, $MnAl_{12}$, and $MnAl_{32}$ clusters in icosahedral symmetry using self-consistent-field, scattered-wave, molecular-orbital cluster calculations (SCF-$X\alpha$-SW). These particular clusters were chosen in order to examine the implica-

tions of icosahedral symmetry on electronic structure and local stability in Al and Al-Mn alloys. SCF-$X\alpha$-SW molecular-orbital cluster calculations[7] have proven useful in the description of electronic structure in both molecules and crystals while given insights into the real-space orbital topology which are often not readily apparent from band-structure calculations. Salahub and Messmer[8] have shown that a 43-atom aluminum cluster, representing up to third-nearest neighbors in fcc aluminum, yields a manifold of energy states having a total band width and energy distributions which are consistent both with band-structure calculations[9] and with measured x-ray photoemission spectroscopy (XPS) data[10] for crystalline aluminum. The merits of this computational approach have also been exploited in the modeling of metallic glasses,[11] where the lack of long-range periodicity precludes the use of Bloch's theorem required for band-structure calculations. Both the presumed icosahedral short-range order in metallic glasses as well as the observed long-range fivefold rotational order in quasicrystals are well suited to the SCF-$X\alpha$-SW cluster calculational approach.

Discrete energy levels calculated for the Al_{13} icosahedral cluster are compared in Fig. 1 with those calculated by Salahub and Messmer[8] for a similar cluster in O_h symmetry. Several important features emerge from such a comparison. First, the occupied valence-band width is slightly larger for the icosahedral cluster than for that of O_h symmetry. This former band width is approximately 75% of the occupied band width obtained from an XPS experiment[10] or from band-structure calculation.[9] Secondly, the entire manifold of occupied states in icosahedral symmetry lies at energies approximately 0.06 Ry (0.8 eV) below those of O_h symmetry. This is consistent with Frank's[1] observation of the stability of the icosahedron and can be understood by consideration of the high coordination for surface atoms on an icosahedron. Thirdly, the splitting of h and g states on going from icosahedral to octahedral symmetry has the effect of creating a more dispersed distribution of states in O_h symmetry while the coalescence of these states at the Fermi energy in icosahedral symmetry causes a marked increase in the
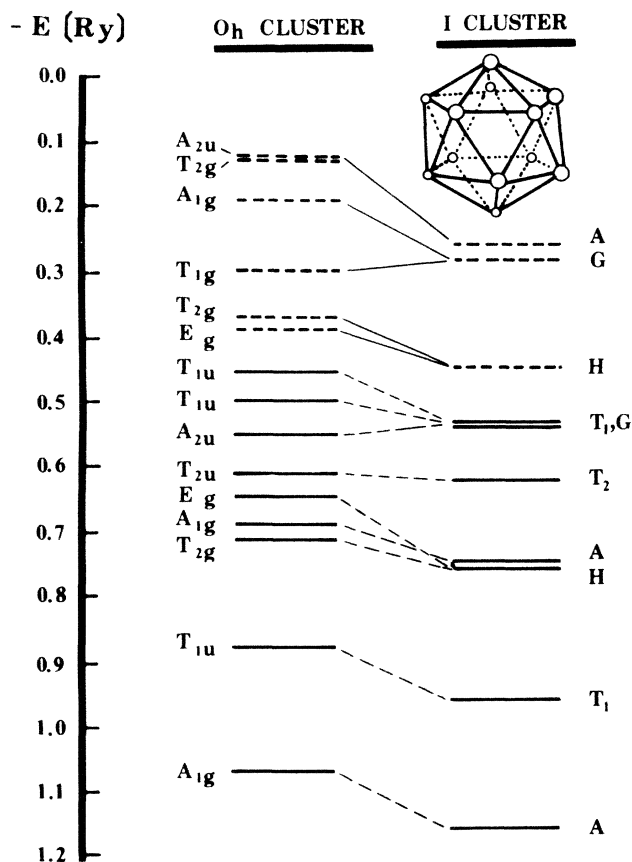
FIG. 1. Discrete-state energy levels for Al₁₃ clusters in O_h and I symmetries. Corresponding states in each symmetry are indicated. Occupied (empty) levels are indicated by full (broken) lines. An icosahedral cluster, minus the central atom, is shown for reference.

density of states there.[12] This is a recurring feature in all the icosahedral clusters examined.

Figure 2 compares the density of states (Gaussian-broadened discrete levels) for all of the icosahedral clusters examined. In addition to the large density of states (DOS) at the Fermi level, several other important features emerge. The effect of cluster size on the computed electronic structure is most noticeable in the total band width which has increased in Al₃₃ to 0.79 Ry (approximately 95% of the total band width for crystalline aluminum). The DOS observed for crystalline aluminum, as well as those calculated by band-structure techniques or cluster calculations (O_h symmetry), uniformly indicate free-electron-like behavior ($E^{1/2}$ dependence). The DOS for icosahedral clusters are of a decidedly different nature, showing more structure and a particularly high peak at the Fermi energy. Furthermore, a positive average curvature is indicative of E^n dependence where $n > 1$. Free-electron behavior in d dimensions leads to an $E^{(d-2)/2}$ dependence of the DOS. This latter feature is particularly interesting in light of the recent observations of Nel-

son and Widom[3] that an icosahedral structure, namely polytype $\{3,3,5\}$, is able to tile a four-dimensional sphere, in which case one would expect a linear dependence of DOS energy. Also, Steinhardt's quasicrystal model[4] indicates that three-dimensional space can be filled densely by a Penrose tiling which preserves icosahedral rotational order and gives a distinct diffraction pattern which may be indexed in terms of six unique vectors. Six-dimensional free-electron-like behavior is expected to show an E^2 dependence for the DOS.

The topologies of the highest occupied molecular orbitals (HOMO) for both Al₁₃ and Al₃₃ clusters are shown in Fig. 3. These states are p orbitals of π-bonding character. In the case of the icosahedral Al₁₃ cluster the HOMO ($2t_{1u}$ orbital) is shown to have a very delocalized bonding character extending over the surface of the first coordination shell. The shape of this $2t_{1u}$ orbital is such that the thirteen-atom icosahedron may act as a large atomiclike packing unit. This is significant in light of intermetallic phases in which icosahedra are found as packing units.[13] The HOMO for the Al₃₃ cluster is the $4h_g$ level which again is p-π-bonding in character. In this cluster the second coordination shell yields bonding in the radial direction and along one of the circumferential directions while a σ^* antibonding relationship exists in the other circumferential direction. (Thus the $4h$ charge distribution resembles the crescent-shaped wedges of an orange.) These spatially extended but spherical $2t_{1u}$ and $4h$ π-bonding topologies contrast dramatically with that seen in octahedral clusters where the p-π-bonding HOMO's are extended in three orthogonal linear chains (and are believed to be related to the superconductivity of pure aluminum[14]).

The effect of alloying of icosahedral aluminum with Mn has been examined with calculations on MnAl₁₂ and MnAl₃₂ clusters which represent, respectively, icosahedral Al first and second coordination shells about a central Mn atom. The effect of this alloying on the DOS is shown in Fig. 2. The Mn $3d$ orbitals hybridize with aluminum $3p$ producing a narrow band of localized states of h_g symmetry which are of antibonding nature at the Fermi energy. (This behavior is in general agreement with behavior deduced by Steiner[15] from XPS data on crystalline aluminum with dilute Mn addition.) Both the inherent antibonding nature of the states at the Fermi energy and the fact that the entire manifold of Al states is calculated to be at higher energies than for I_h Al₁₃ and Al₃₃ clusters gives evidence to the instability of a Mn-centered configuration.

The effect of Mn addition is to empty the delocalized p-π-bonding orbitals and replace them by a localized p-d antibonding $4h$ orbital at the Fermi level. (This h orbital is the icosahedral analog of the t_{2g} and e_g orbitals of octahedral symmetry.) Of the five Mn d electrons, four are located in this antibonding orbital;
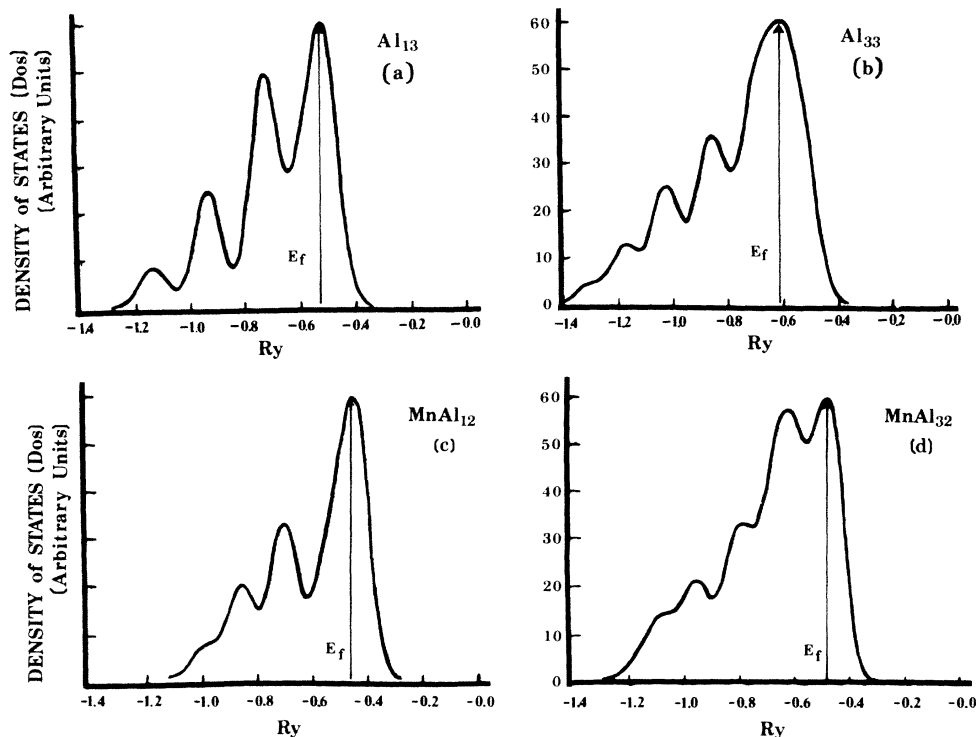
FIG. 2. Gaussian-broadened occupied DOS for (a) Al_{13}, (b) Al_{33}, (c) $MnAl_{12}$, and (d) $MnAl_{32}$ clusters in I_h symmetry.

the remaining electron is located in a low-lying Mn-Al bonding orbital. This disproportionate distribution of d-electron density in antibonding orbitals gives further evidence to the apparent instability of Mn icosahedrally coordinated by aluminum. (Similar behavior is observed for Mn in octahedral aluminum and may be associated with the very low solid solubility of Mn in fcc aluminum.) The instability of Mn-centered icosahe-

dral coordination is consistent with recent Mössbauer[16] studies on Al-(FeMn) quasicrystals which show a quadrupole splitting for Fe which is much larger than expected for a high-symmetry I_h site. Thus, although icosahedral rotational symmetry is seen in electron diffraction, the Mn atoms need not (and probably do not) sit in sites with icosahedral symmetry.

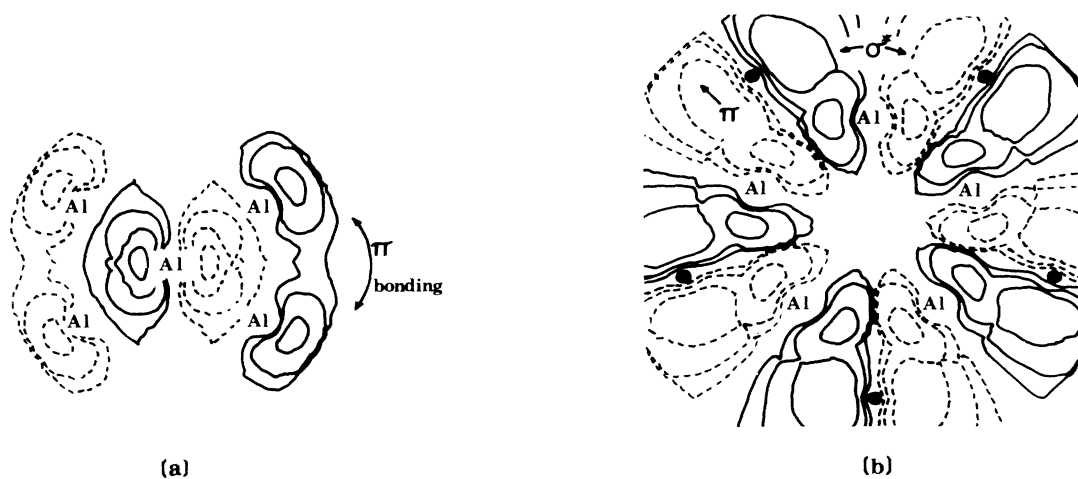In light of the above discussion and as a final note, it

FIG. 3. HOMO's for Al_{13} and Al_{33} clusters in I_h symmetry. (a) $2t_{1u}$ orbital in Al_{13} cluster. This p_x-π-bonding orbital passes through the central atom and four surface atoms. (b) $4h$ orbital in Al_{33} cluster passing ($z = 2.42$ a.u.) through a pentagonal ring of atoms in the first coordination shell. Outer charge density and the resulting π bonding are due to second coordination shell. Filled circles indicate radial positions of second shell atoms lying above the plane.

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is interesting to consider the relative stability of crystalline and glassy or quasicrystalline states in these alloys. On the basis of our calculations, the overriding feature of these structure calculations has been the remarkable density of states at the Fermi energy for all the icosahedral clusters which have been considered. Through the Boltzmann condition, the entropy of a configuration can be related to the number of quantum states available at the Fermi energy. Therefore, it is clear that the icosahedral configurations have associated with them large electronic contributions to entropy compared with the cubo-octahedron. The entropy of quasicrystalline Al-Mn should be between that of the stable crystalline phase and that of either the liquid or glassy phase. It *may* even be possible for such a phase to be truly stable (not simply metastable) at an elevated temperature.

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[12]Group theory alone provides some interesting physical insight into icosahedral clusters. Unlike any of the crystallographic point groups, the icosahedral group has irreducible representations of dimension greater than three, namely the four-dimensional g representation and the five-dimensional h representation. This has important implications for the splitting of spherical harmonics in an icosahedral crystal field. Spherical harmonics of $l = 2$, which correspond to d-wave functions, are completely degenerate in an icosahedral crystal field while the f-wave functions ($l = 3$) are split into a fourfold (g) and threefold (t_2) degenerate level (unlike the splitting associated with crystal fields with the symmetry of any of the crystallographic point groups). These observations have important implications for the electronic structure of $3d$ or $4f$ metals in icosahedral symmetry. Specifically, the d orbitals of Mn in an icosahedrally coordinated aluminum matrix would be completely degenerate and thus contribute a sharp peak to the density of states.

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