Energetics of Icosahedral Phase Stability in Metallic Alloys

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Total-energy calculations based on self-consistent effective-medium theory are used to investigate icosahedral phase stability in aluminum–transition-metal binary alloys. We identify the mechanism of cohesion and explicate trends observed in diffraction experiments.

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The existence of long-range icosahedral order in certain metallic alloys is now an established experimental fact.[1] The crystallographic[2] and metallurgical[3] data base is particularly large for Al-Mn, the subject of the original investigation.[4] Unfortunately, the available evidence[5] does not clearly distinguish between the two most popular structural models of this metastable phase—an icosahedral quasicrystal[6] or an icosahedral glass.[7] On the other hand, both models assign[8] an important role to the Mackay icosahedron,[9] a 54-atom structural unit which appears twice in the unit cell of crystalline α-(Al-Mn-Si). Atomic models for other icosahedral alloys[10] similarly incorporate structural elements from nearby stochiometric crystalline phases. It is noteworthy that the physics of metals plays no role in these analyses. No evidence is offered that the presumed "building blocks" possess any particular stability. The present Letter is intended to open[11] discussion of this subject by means of first-principles total-energy calculations of the cohesive properties of various crystalline phases of aluminum-transition metal alloys. Our results directly bear on the observed trends[12] of icosahedral phase formation in these materials.

The correct ground-state crystal structure of elemental solids regularly emerge from total-energy calculations in the local-density approximation (LDA) to density-functional theory.[13] Regrettably, practical considerations render such computations unfeasible for even moderately complex ordered alloy phases. Approximate methods based on tight-binding theory have been proposed,[14] but at the cost of the introduction of adjustable parameters. A rather different scheme[15] is based on the idea[16] that a metal can be viewed as a collection of atoms—each embedded in an effective medium which reflects its immediate surroundings. The total energy of a collection of atoms located at positions $\mathbf{r}_i$ is written

$$E_{\text{tot}} = \sum U_i(n_i) + \sum\sum \phi(|\mathbf{r}_i - \mathbf{r}_j|). \qquad (1)$$

Here $\phi(R_{ij})$ is a pair potential and $U_i(n_i)$ is an embedding function (different for each element) which depends on the local "background" electron density contributed to site $\mathbf{r}_i$ by the wave-function tails of atoms at sites $\mathbf{r}_j \neq \mathbf{r}_i$. Energy calculations based on Eq. (1) have been notably successful in the prediction of structural properties such as lattice relaxation[17] and reconstruction[18] at metal and alloy surfaces. In all these calculations, the functions $U(n)$ and $\phi(R)$ are determined empirically by fitting to known quantities such as bulk lattice constants, elastic moduli, vacancy formation energies, etc.

Very recently, Jacobsen, Nørskov, and Puska,[19] and Manninen[20] have derived Eq. (1) as a formal approximation to the exact expression given by density-functional theory. For practical application to our problem, we generalize the approach of the authors of Ref. 19 to the case of an alloy to yield a total-energy expression which contains neither adjustable parameters nor any functions to be fitted to experimental data. A key point is that, at the stoichiometries where icosahedral phases generally form, transition-metal atoms are the minority species and are never nearest neighbors. Hence, unlike pure transition metals,[21] cohesion is *not* dominated by large *d*-orbital overlap and the many-body embedding function $U(n)$ is well represented by the energy of an atom immersed in a homogeneous electron gas of density n. This quantity may be calculated exactly within the local-density approximation.[22] The pair potential is identified[19] with the first-order perturbation-theory correction to the homogeneous-electron-gas contribution to E_{tot}.[16] We write it in the form $\phi(R_{ij}) = \alpha_i(12 n_{ij}) n_{ij}$, where $n_{ij}(R_{ij})$ is the electron density contributed to cell i by an atom at site $\mathbf{r}_j$ and $\alpha_i(n)$ is the cell-averaged electrostatic potential produced by the total charge density of an atom of type i immersed in a homogeneous electron gas of density n.[23]

Although our quantitative calculations reported below use Eq. (1), an approximate analysis of this equation is sufficient to expose the qualitative cohesive principles at work in the aluminum–transition-metal alloys of interest. Suppose that, for each atom i, the electron densities n_{ij} contributed by the (twelve) nearest neighbors are all equal. In that case, Eq. (1) reduces to

$$E_{\text{tot}} = \sum [U_i(n_i) - \alpha_i(n_i) n_i] = \sum E_i(n_i). \qquad (2)$$

Figure 1 is a plot of the function $E_i(n)$ for aluminum and the 3*d* transition metals.[24] Obviously, aluminum and manganese atoms have vastly different background density requirements. A compromise is required to minimize the energy. In particular, an icosahedral arrangement of twelve aluminum atoms surrounding a man-

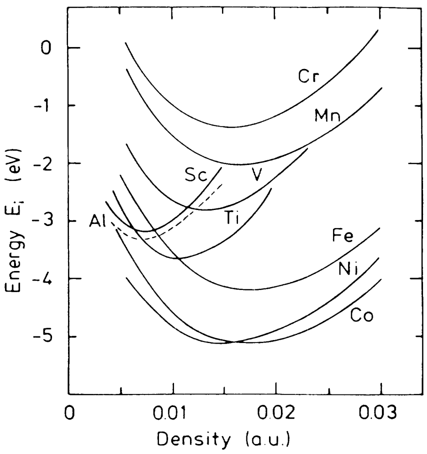

FIG. 1. Plots of the function $E_i(n)$ [Eq. (2)] for aluminum (dashed curve) and the $3d$ transition metals (solid curves). The unit of density is a_B^{-3} (from Ref. 19).

ganese atom simultaneously maximizes the density contributed by each Al atom to the Mn atom and minimizes the density contributed by each Al atom to the other Al atoms. This follows from the geometry of an icosahedron: The distance between aluminum atoms is greater than the distance between any aluminum atom and the central manganese atom. Now arrange twelve such icosahedra so that the twelve manganese atoms themselves form an icosahedron. The resulting structure is precisely a Mackay icosahedron encased in a shell of aluminum atoms. It is noteworthy that there is a hole at the center of this structure. The presence of either a Mn or Al atom in the vacancy would contribute excess charge to the immediately adjacent aluminum atoms and destabilize the entire structure. Figure 1 also shows that the icosahedral compromise is unnecessary for, say, an Al-Sc alloy where the minima of the $E_i(n)$ curves nearly coincide. A substitutional fcc structure satisfies both constituents in that case.

The argument given above [based on Eq. (2)] presumably holds rigorously for neither the α-(Al-Mn-Si) structure[25] nor for the $MnAl_6$ or $MnAl_4$ structures which appear in the equilibrium Al-Mn phase diagram.[26] Therefore, we have used the complete energy expression, Eq. (1), to corroborate our intuition. The calculations are self-consistent in the sense that the charge which flows out of a cell into adjacent cells is consistent with the charge which flows into the cell to form the background electron density. Details will be presented elsewhere. For pure aluminum, Eq. (1) is minimized at a lattice constant within 1% of the observed value.[19] Similarly, we find that the minimum energies of substitutional fcc Mn-Al alloys occur at lattice constants in quantitative agreement with experiment.[3]

TABLE I. Total energy of Al-Mn and Al-Sc alloys at various stoichiometries as calculated from Eq. (1). The stoichiometry is given as the atomic percent of the transition metal component.

Structure	Mn or Sc content (at.%)	Total energy (eV/atom)
fcc Al-Mn	12.0	−3.03
$MnAl_6$	14.3	−3.00
fcc Al-Mn	14.3	−2.98
α-(Al-Mn)	17.4	−2.95
fcc Al-Mn	17.4	−2.92
fcc Al-Mn	19.0	−2.89
fcc Al-Sc	15.0	−3.28
α-(Al-Sc)	17.4	−3.18
fcc Al-Sc	17.4	−3.28
fcc Al-Sc	19.0	−3.27

Table I lists the calculated cohesive energies of crystalline α-(Al-Mn), $MnAl_6$, and four substitutional fcc Al-Mn alloys in order of increasing manganese content. The choice of these test structures is motivated by the observed phase diagrams of Al with the transition metals which principally exhibit close-packed and locally icosahedral crystal structures. By using the fcc results to gauge the purely stoichiometric contribution, we find that both $MnAl_6$ (28 atoms/unit-cell) and α-(Al-Mn) (138 atoms/unit-cell) are stabilized by about 0.02 eV/atom relative to the competing substitutional structures.[27] Unfortunately, the detailed crystal structure of $MnAl_4$ is unknown. We presume that its energy is relatively lower than α-(Al-Mn) so that the latter is excluded in favor of the observed phase separation of $MnAl_6$ and $MnAl_4$ at intermediate stoichiometries.[26] Table I also shows a comparison between hypothetical α-(Al-Sc) and nearby substitutional phases. As the simple argument given above suggests, the complex alloy phase with local icosahedral units is much higher in energy than the competing fcc structures.

We now turn to the implications of our results for metastable icosahedral-phase formation. These phases are formed either by rapid cooling from the melt[3,4] or by solid-state interdiffusion.[28] Since the latter process can occur at twice room temperature, we need to identify locally stable configurations of the alloy with energies much less than 0.05 eV above the ground state but with large entropies, i.e., with high probability of formation. Structures which consist of arrangements of Mackay icosahedra (MI) are natural candidates. Each MI (surrounded by aluminum) is a low-energy configuration. The exact placement of aluminum atoms at the connection points contributes a "wall" energy. Our results for α-(Al-Mn) show that there is at least one way to arrange MI so that the total (MI+wall) energy is quite low. However, numerous (noncrystallographic) packing configurations are possible as a result of the many identical faces of a MI and its nearly spherical shape. If, in addition, MI are put together so as to locally mimic α-

(Al-Mn)[7,8] it is very plausible that the wall energies are similarly small. While lower-energy crystallographic structures exist (e.g., $MnAl_6$ and $MnAl_4$), they presumably possess no local structure units (different from MI) which can be rearranged easily without an intolerable cost from the wall energy. Such structures are disfavored at elevated temperature by entropy considerations. With these arguments in mind, it is easy to see from Fig. 1 why aluminum only forms icosahedral binary alloys with transition metals to the right of titanium in the periodic table.[2]

The ideas introduced in this paper lend microscopic support to the suggestion by Villars, Phillips, and Chen[29] (based on a phenomenological analysis) that icosahedral phases are simply a rather exotic sort of alloy structure. The basic physics of cohesion is identical to that of other complex alloy phases. This holds out the promise that a more sophisticated version of the effective-medium theory used here can be successful in (at least) rationalizing the myriad of complex alloy phases observed in nature.[25] For example, we have noted that the α-(Al-Mn-Si) structure contains large holes. This means that the Wigner-Seitz cells associated with neighboring atoms are far from spherical. We have used only the crudest volume correction to account for this effect. Since many large-unit-cell alloy phases exhibit rather "open" structures, a better theory should explicitly calculate the relevant cell volumes. Work in this direction is in progress.

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