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***Ab initio* study of polytetrahedral packing: The Al-Mg system**

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We have performed first-principles local-density-approximation calculations on aluminum-magnesium intermetallic compounds. Experimental studies of this system have shown that complex topologically close-packed structures with large unit cells are favored over simpler planar structures. We show that this is due to the opening of a quasigap in the density of states at the Fermi level; our results for total energies confirm that this lowers the energy. These electronic effects resemble those measured and calculated for quasicrystals which have similar chemical compositions and structures.

In this paper, we undertake an *ab initio* investigation of the hitherto neglected complex binary alloy system of aluminum and magnesium. This also enables us to address wider questions regarding the stability of topologically close-packed structures and their puzzling preponderance in nature.

Being light, strong, inexpensive, and environmentally safe, alloys of aluminum are of enormous technological and commercial importance. Magnesium is one of the most important constituents of these alloys, since adding up to 10% of magnesium to aluminum increases its strength, while retaining the low density of Al.¹ Al-Mg alloys are also corrosion resistant and highly weldable; industrial uses of these Al-Mg alloys include the manufacture of automobile sheets and beverage cans.

The close chemical and structural resemblance between Al-Mg phases and certain quasicrystals² furnishes additional motivation for a study of this system, since it provides a relatively tractable model system that still exhibits features in common with the more complex quasicrystalline phases. Since Al has three valence electrons per atom and Mg has two, Al-Mg phases have an electron-per-atom ratio between 2 and 3, which is the range within which experimentally discovered quasicrystalline compounds fall. Many of these compounds consist primarily of Al and Mg, together with small amounts of a transition or simple metal; thus Al-Mg crystalline compounds can be used as prototypical approximants to these families of quasicrystals. A study of this system also sheds light on long-standing questions regarding the competition between geometrically close-packed (GCP) and topologically close-packed (TCP) structures. This too is relevant to quasicrystals, since TCP structures are similar to quasicrystalline structures in having polytetrahedral (often icosahedral) local order.³

Though configurations obtained by packing together tetrahedral units of atoms are locally favorable, space-filling

requirements prevent such an arrangement for the crystalline phases of elemental metals. However, in the presence of two or more atomic species, some of the frustration introduced by attempts to fill space with regular tetrahedra is relieved, and it becomes possible to have both TCP structures (with polytetrahedral packings) and simpler GCP structures (characterized by the presence of planes of atoms). Examples of the former are the Frank-Kasper phases,⁴ while familiar GCP structures include those derived from the body-centered cubic (bcc) and face-centered cubic (fcc) structures. A typical alloy phase diagram contains both TCP and GCP phases, with very similar compositions, but markedly different properties (e.g., TCP phases tend to be brittle, whereas GCP phases are usually ductile). Though the ability to predict which kind of structure is favored is therefore highly desirable, it is extremely difficult because of the large unit cells involved. Also, quasicrystals and TCP phases usually contain transition elements, which is an added complication for pseudopotential based methods, because a large plane-wave basis is required. As a result, previous attempts at structural prediction for these materials have generally involved making additional approximations at various levels: The technique of plotting "quantum structural diagrams," where compounds are grouped together in a phase space defined by variously specified coordinates, is largely phenomenological.⁵ Calculations using pair potentials derived from *ab initio* pseudopotentials⁶ and effective-medium theory⁷ lend support to the idea that a preference for TCP phases can be interpreted as an atomic-size effect, but do not provide reliable total energies. However, recent advances in computational power and technique now make first-principles calculations of total energies for large unit cells feasible; the other problem—that of the large cutoffs required for transition metals—need not concern us since we are looking at the system comprised only of simple (*sp*-bonded) metals.

Despite the simplicity of the constituents, the Al-Mg

TABLE I. Calculated values of the lattice constant a , the c/a ratio, and the total energies of various phases of the Al-Mg system. Experimental values, where available, are given in parentheses.

Compound	Structure	a (a.u.)	c/a	E_{tot} (Ry/atom)
Al	fcc	7.485 (7.65 ^a)		-4.20701
Mg	hcp	5.85 (6.07 ^a)	1.62 (1.624 ^a)	-1.80869
Al ₃ Mg	Cu ₃ Au	7.64		-3.60853
AlMg	CuAu(I)	7.82	1.0	-3.00921
AlMg	CsCl	6.24		-3.00419
AlMg ₃	Cu ₃ Au	8.03		-2.40865
Al ₁₂ Mg ₁₇	α -Mn	19.4 (19.9 ^b)		-2.80370

^aReference 22.

^bReference 9.

phase diagram is composed entirely of complex TCP phases with large unit cells.⁸ The structure of three of these phases has been determined experimentally: the β phase Al₃Mg₂ has a cubic structure with 1168 atoms in the unit cell, the rhombohedral ϵ phase Al₃₀Mg₂₃ contains 53 atoms in the unit cell, and the γ phase Al₁₂Mg₁₇ crystallizes in the α -Mn structure [a body-centered-cubic (bcc) structure with a 29-atom basis].⁹ Upon examining the polyhedra that constitute the structural units for all three phases, one notices the presence of a large number of icosahedra; the local structure is therefore similar to that of many quasicrystals.

We have performed first-principles calculations on six intermediate Al-Mg phases: the experimentally observed γ phase, Al₁₂Mg₁₇, which has the α -Mn structure; four hypothetical structures: AlMg in the CsCl and CuAu(I) structures, AlMg₃ in the Cu₃Au structure, and Al in the α -Mn structure; and one reportedly metastable phase, Al₃Mg in the Cu₃Au structure. Of these, the α -Mn structure falls into the TCP group of structures, while the remaining phases that we have studied are all examples of GCP structures.¹⁰ We have also performed calculations on pure Al (fcc structure) and Mg (hcp structure) to use as references when comparing energies.

Our calculations have been performed using the local-density approximation (LDA) of density-functional theory. The electron-ion interactions are described by a nonlocal Kleinman-Bylander¹¹ form of Bachelet-Hamann-Schlüter (BHS) pseudopotentials¹² that are expanded in a plane-wave basis set with an energy cutoff of 12 Ry. For simple metals such as Al and Mg, previous calculations^{13,14} have shown that the BHS pseudopotentials describe bulk properties very well, even without correcting for the linearization of the core-valence exchange-correlation term. We use Ceperly-Alder exchange-correlation,¹⁵ and a thermal broadening of the electronic distribution corresponding to a temperature of 100 K. The set of "special" k points that are sampled in the irreducible Brillouin zone (IBZ) depends on the phase being studied; the size of the set varies from 55 points in the IBZ for the α -Mn structures, to 1020 points in the IBZ for hcp Mg.

Values for the structural parameters were determined by minimizing the total energy; Table I shows these results for

TABLE II. Calculated values of the five internal parameters, in units of the lattice constant, for Al₁₂Mg₁₇ in the α -Mn structure. Experimental values from Ref. 9 are given in parentheses; the notation is the same as in Ref. 9.

$x(\text{Mg}_2)$	$x(\text{Mg}_3)$	$z(\text{Mg}_3)$	$x(\text{Al})$	$z(\text{Al})$
0.3276 (0.3240)	0.3568 (0.3582)	0.0409 (0.0393)	0.0912 (0.0954)	0.2782 (0.2725)

seven of the structures that we have studied. (For the eighth structure, Al in the α -Mn structure, we are interested primarily in the shape of the density of states. Therefore in this case we did not attempt to find the most energetically favorable lattice parameters, but fixed the atomic density at that of bulk fcc Al.) For the experimentally observed phases, we compare our results for the lattice constants with those determined experimentally; we find that we underestimate the lattice constant by 2–4%, which is typical of LDA calculations. For the hypothetical phase Al-Mg in the CuAu(I) structure, we obtain the curious result that $c/a=1.0$, even though this is not required by symmetry. For Al₁₂Mg₁₇, in addition to the lattice constant, there are five internal parameters that specify the locations of the four types of sites in the α -Mn structure. We have determined the values of these parameters by minimizing the forces on the atoms; as can be seen from Table II, our results for these vary slightly from the experimental numbers—the largest shift corresponds to an atomic displacement of ~ 0.08 Å. Though these relaxations are small, we find that they lower the total energy significantly; this translates to an even bigger percentage shift in the calculated heats of formation (see below). We therefore emphasize that it is *crucial to permit structural relaxation* (often neglected for large systems) in order to obtain even qualitatively accurate results.

Figure 1 shows our results for the heat of formation ΔH of the intermetallic compounds as a function of composition.

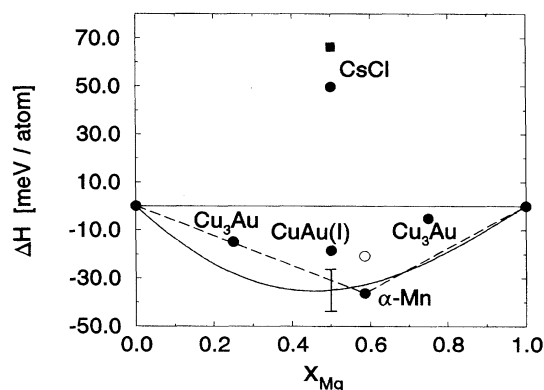


FIG. 1. Heats of formation for Al_{1-x}Mg_x compounds, as a function of Mg concentration x . Labels indicate the structure considered. Filled circles are theoretical values from our calculations, the square is the result from the calculation of Pettifor and Gelatt (Ref. 16), and the solid line is the experimental data (with error bar) for the liquid state. The empty circle shows the theoretical value we obtain for Al₁₂Mg₁₇ when internal structural parameters are not relaxed but are set equal to the experimental values. The dashed lines are tie lines for Al₁₂Mg₁₇ (as a guide to the eye).

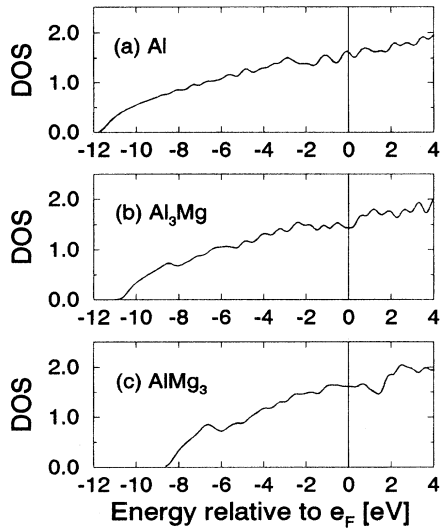


FIG. 2. Electronic densities of states for (a) fcc Al, (b) Al_3Mg in Cu_3Au structure, and (c) AlMg_3 in Cu_3Au structure.

We are aware of only one previous total-energy calculation on an Al-Mg phase: that by Pettifor and Gellat for AlMg in the CsCl structure;¹⁶ like them, we find that this structure has a positive heat of formation, i.e., it is unbound. For the remaining phases, we find a negative heat of formation; note the significant drop in ΔH for $\text{Al}_{12}\text{Mg}_{17}$ upon relaxing the internal coordinates. It is gratifying to observe that ΔH is lowest for $\text{Al}_{12}\text{Mg}_{17}$ in the α -Mn phase, which is the only one of the phases that we have studied whose stability has been confirmed experimentally. Upon drawing tie lines, we find that the formation of the fcc-like phases of AlMg and AlMg_3 is strongly suppressed. There remains the fcc-like phase of Al_3Mg —the value we obtain for its heat of formation lies only slightly above the tie line connecting pure Al and the α -Mn structure. This phase has reportedly been observed in the form of metastable precipitates in Al-rich Al-Mg alloys,¹⁷ thus the large negative value that we obtain for the heat of formation of this phase is confirmation of the accuracy of our approach. Though a slight shift in our value would bring this phase below the tie line, it is also possible that the crystallization of this phase is suppressed by the β or ϵ phase, or by thermal effects. There do not appear to be any reliable measurements of ΔH for solid phases, and our results therefore constitute a theoretical prediction to be confirmed experimentally. For purposes of comparison, we have plotted the experimentally obtained dependence of ΔH on composition in the liquid phase.

Why are the complex TCP phases favored over the simpler GCP phases, and in what way is the electronic structure of these phases similar to that of quasicrystals? Insight into these issues is obtained upon looking at the density of states (DOS) in the different phases. Figure 2 shows the calculated DOS for some of the GCP phases that we have considered, while Fig. 3(a) shows the DOS we obtain for Al in the α -Mn structure (the lattice constant was fixed so that the density is equal to that of fcc Al, and the internal parameters were set equal to those obtained for the γ phase of Al-Mg).

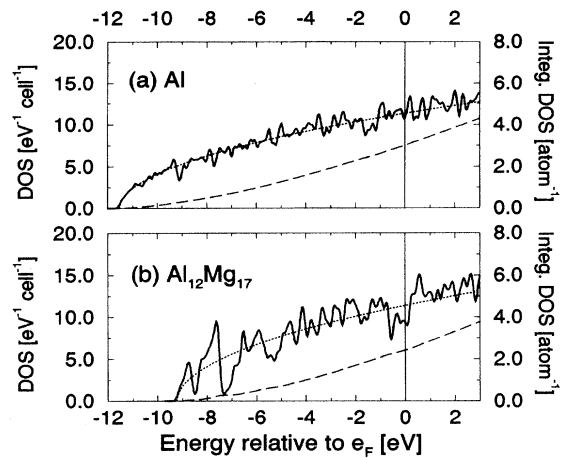


FIG. 3. Electronic DOS in the α -Mn structure for (a) Al and (b) $\text{Al}_{12}\text{Mg}_{17}$. Solid lines are calculated DOS, dotted lines free-electron DOS, and dashed lines calculated integrated DOS.

Notice that the DOS is essentially free-electron-like, with little structure apart from small peaks and dips. This is in marked contrast to the DOS that we obtain for $\text{Al}_{12}\text{Mg}_{17}$ in the α -Mn structure, which we show in Fig. 3(b). The structure seen in the DOS is now much more dramatic, and the Fermi level is found to lie in a relatively deep trough or quasigap (or pseudogap).¹⁸ The opening up of the quasigap lowers the energy by the Hume-Rothery mechanism,¹⁹ and this explains why this structure is favored over the others that we have considered. The stability of quasicrystals has been attributed to this same mechanism; quasigaps at the Fermi level are pronounced features in the calculated DOS of quasicrystals and their crystalline approximants.²⁰ However, in these previous calculations, it was not possible to compute the total energy and prove that the quasigap is in fact associated with greater stability.

A comparison of Figs. 3(a) and 3(b) shows that the rigid band model must be used with some caution, since the two DOS curves differ significantly in shape. However, we can still use our results for Al in the α -Mn structure to identify and predict singular points in the DOS curve, though the strength of these features may be greatly modified upon introducing different atomic species. Examining the section of the DOS curve of Fig. 3(a) that corresponds to an electron-per-atom ratio in the range between 2.0 (valency of Mg) and 3.0 (valency of Al), we see that the Fermi level would fall in a small dip in the DOS if there are 2.4–2.5 electrons/atom. Indeed, $\text{Al}_{12}\text{Mg}_{17}$ has 2.41 electrons per atom, and Fig. 3(b) shows that the magnitude of the dip in the DOS is in fact increased by the presence of the Mg atoms; i.e., both the structure factor and the atomic form factor pieces are responsible for the strength of the quasigap. The latter is significant—a lowering of the DOS by approximately a fifth of the free-electron value—even without the high degeneracy in reciprocal space that is usually cited as being responsible for the large quasigaps observed for quasicrystals. This approach can now be used to identify possibly stable intermetallic compounds with complex structures by performing cal-

culations on some prototypical material²⁰ and then demanding that the Fermi level fall at a minimum in the DOS. Even small concentrations of transition-metal atoms can be introduced in this way, merely counting the number of electrons they contribute, thereby sidestepping the problem of the high plane-wave cutoffs required when they are included in the total-energy calculations.

We note that similar issues, for compounds of Al with transition metals, have been dealt with in a paper by Carlsson.²¹ By comparing the energies of two structures, the Cu₃Au structure and the icosahedral-like Al₁₂W structure, he shows that atomic size is not an important effect. For those cases where the Al₁₂W structure is favored, he too finds that the DOS at the Fermi level is lowered with respect to the free-electron value.

In summary, we have shown that it is feasible to perform first-principles LDA calculations on complex ordered alloy phases. We have carried out such an investigation of the Al-Mg intermetallic system (which is unusual in containing only polytetrahedrally packed phases), considering hypo-

thetical planar structures as well as an experimentally observed topologically close-packed structure. We have confirmed that the latter is energetically favored, and show that this can be attributed to the opening up of a quasigap in the density of states at the Fermi level. This is the same mechanism that appears to account for the stability of quasicrystalline phases. Thus, the structural and compositional similarity between topologically close-packed crystals and quasicrystals is manifested in their electronic structures too; and these electronic effects are responsible for their stability.

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