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Towards an understanding of liquid-metal embrittlement: Energetics of Ga on Al surfaces

Roland Stumpf and Peter J. Feibelman
Sandia National Laboratories, Albuquerque, New Mexico 87185-1413

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First-principles electronic structure calculations show that Ga wets the low Miller index surfaces of Al. Consistent with a thermodynamic basis for the observation that Ga causes single-crystal Al to crack along (100) planes, the Ga-covered (100) plane has the lowest surface energy. This represents a compromise between weaker Ga binding on closer-packed Al surfaces and higher clean surface surface energies on more open ones. In the second adsorbed Ga layer, on Al(100), several structures lie near the minimum total energy, consistent with rapid diffusion of Ga to a crack tip. [S0163-1829(96)01031-4]

I. INTRODUCTION

The fact that a material's environment can drastically affect its resistance to fracture[1] not only offers a scientific ''handle'' on the factors that determine the stability of solids under stress,[2] but also has serious technological significance. Examples of technological implications are plentiful: Liquid-metals are not allowed on airplanes — spillage could lead to disastrous crack formation. Liquid-metal embrittling agents are used to enhance the speed of drilling. Embrittlement is a key impediment to a ''hydrogen economy.'' Soldered conductors are worth little if the soldering agent causes them to crack.

In this paper, we focus on liquid-metal embrittlement (LME), for which a qualitative explanation has not emerged despite decades of research. Numerous LME couples are known: Ga embrittles Al, Au embrittles Mo, Hg embrittles Zn, Cd embrittles Fe, etc.[3] We wish to understand, on the basis of atomic level parameters, why a particular embrittling species attacks a particular metal, by how much it reduces a metal's strength, and how the embrittled metal will crack, e.g., along what crystal plane or grain boundary.

The Ga/Al system is especially interesting because, although their properties as metals are so different, Ga and Al are neighbors in column III A of the Periodic Table, whose chemistry ought to be similar. In what follows, we present the results of first-principles calculations of the energetics and structure of ultrathin Ga layers adsorbed on Al(111), (100), and (110) surfaces. Consistent with a thermodynamic basis for the observation that Ga causes single-crystal Al to crack along (100) planes,[4,5] we find (1) that Ga binds more strongly to Al than to itself — thus Ga wets Al surfaces, and (2) that the Ga-covered (100) plane has the lowest surface energy, representing a compromise between weaker Ga binding on closer-packed Al surfaces and higher clean surface surface energies on more open ones. We also find that a second Ga adlayer binds relatively weakly to the first. Thus, there are many two-layer Ga adsorption structures with nearly equal energies. This is consistent with low barriers and fast Ga transport to crack tips at room temperature, which are necessary to explain the rapid crack propagation in Ga-induced fracture of Al.[1,3,4]

We describe our calculational methods and give a detailed presentation of our results in the following section of this paper. In Sec. II A, we discuss the details of our first-principles computational method. In Sec. II B, we present results for reference bulk Al and Ga crystals. Section II C concerns the structure and energetics of Ga pseudomorphic 1×1 monolayers on the low Miller index planes of Al. Sections II D and II E treat fractional layer Ga adsorption, in and on Al surfaces. Finally, in Secs. II F and II G, we discuss the adsorption of two Ga layers on an Al surface, in pseudomorphic and quasihexagonal arrangements, whose energies are very close. The discussion in Sec. III of this paper aims at a qualitative picture of what makes Ga an embrittling agent, while Al is a strong metal. Developing more direct calculational support for this, or perhaps an alternative picture remains an important task.

II. FIRST-PRINCIPLES CALCULATIONS OF Ga ADSORPTION ON Al

A. Method

To investigate the properties of clean and Ga-covered Al surfaces, we use the local density approximation (LDA) to the density functional theory.[6] Electron-nucleus interactions are represented by carefully tested pseudopotentials.[7] Because Ga has a shallow $3d$ core level, we use the Louie-Froyen-Cohen nonlinear core correction for Ga.[8] We expand electronic wave functions in a plane wave basis with energies up to 10 Ry.

We model the Al surfaces via calculations for thin Al slabs, using 5–12 atomic layers for Al(111), 6–14 layers for Al(100), and 8–20 for Al(110). We use orthorhombic supercells in all cases, even the hexagonal Al(111) surface, for which we choose a $\sqrt{3}\times1$ surface cell. The reason is that special k points are more efficient in orthorhombic than in hexagonal cells. We perform k-space averages via a special k-point sample corresponding to between 500 and 200 000 k vectors in the full Brillouin zone (BZ) of a one atom cell.

To analyze the wetting behavior of Ga on Al surfaces, we need a reference energy for pure Ga. For this purpose, we optimize the lattice constants and the positions of the Ga nuclei in the α-Ga crystal structure, i.e., the Ga ground state. Since, experimentally, the lattice parameters a and b in the orthorhombic α-Ga phase are nearly equal (4.51 Å as against 4.52 Å), we simplify the optimization by requiring $a=b$. Our

k-point sample, for α-Ga, constitutes 2048 special points in the full BZ corresponding to a primitive tetragonal cell containing 8 Ga atoms.

Finite slab thickness and k-space sampling are the major sources of numerical inaccuracy in the results reported here. Tests imply that our per-atom energy differences can be trusted to the level of 10 meV. Surface-energy differences are converged to a reliability of roughly 3 meV/Å^2.

B. Calculated properties of bulk Al and Ga

To perform a LDA calculation, one begins by selecting an energy functional to represent the effects of exchange and correlation (XC). Most recent LDA calculations employ the XC energy functional and potential parametrized by Perdew and Zunger,[9] using simulations of the infinite electron gas by Ceperley and Alder.[10] This choice guarantees, in the hypothetical limit that a solid's crystal potential becomes isotropic (the ''Jellium'' limit), that the calculated energetics will approach those of the Ceperley-Alder simulation. However, the goal of the present work is to improve our understanding of the mechanical properties of Al and of liquid-metal embrittlement mechanisms. Accordingly, the asymptotic behavior of Al in the Jellium limit is less important here than Al's response to external stress. We, therefore, use the Wigner interpolation formula[11] for the exchange-correlation energy, which yields Al elastic properties in good agreement with experiment, for example, a bulk modulus of 0.722 Mbar, compared to quoted experimental values of 0.722 Mbar and 0.76 Mbar. The theoretical Al lattice constant, using the Wigner potential, is 4.033 Å , which is 0.4% smaller than the room temperature experimental value. Considering that the theoretical result corresponds to $T=0$, and does not include zero point motion, the calculated lattice constant is actually about 0.5% too big compared to the experimental value. In comparison, the Ceperley-Alder representation of XC gives a lattice constant about 1.5% smaller than experiment, and a bulk modulus 12% larger than the Wigner result.

Ga is a low melting point (29.8 °C) metal. In its $T=0$ phase, known as α-Ga, E_{Fermi} lies in a pronounced dip in the density of states. This occurs because Ga atoms dimerize in the α-Ga structure,[12] i.e., because one Ga-Ga bond in the eight-atom unit cell is especially strong and short. The bonds *between* Ga-dimers are much weaker. This may be the source of the low melting point. More generally, though, structures other than the α-phase structure, including nondimerized phases, are energetically close.[13] For example, our calculations show that fcc-Ga is only 60 meV per atom higher in energy than α-Ga.

A first step in understanding how Al and Ga interact is to compare their bulk properties. As one expects, given their identical Pauling covalent radii,[14] the computed radii of Al and Ga, in comparable crystalline phases, are similar. In a hypothetical fcc phase, our LDA calculations imply that the Ga lattice constant would be 4.239 Å , corresponding to a metallic radius of 1.499 Å . This is 5.1% larger than our result for fcc-Al. Importantly, in α-Ga, we obtain a dimer bond length of 2.50 Å , corresponding to a Ga radius of only 1.25 Å .[15] Thus, we must think of Ga as an atom, whose bonding configuration and radius can vary considerably at very little cost in energy.

TABLE I. Summary of calculated surface energies for clean and Ga-covered surfaces. The indications ''fcc'' and ''hcp'' refer to the two inequivalent threefold hollows on the Al(111) surface.

Surface	E_{surf} (meV/Å ^{2})
clean Al(111)	54.9
Ga(1×1)-fcc/Al(111)	40.5
Ga(1×1)-hcp/Al(111)	43.4
clean Al(100)	56.8
Ga(1×1)/Al(100)	29.7
clean Al(110)	65.3
Ga(1×1)/Al(110)	43

Al is considerably more cohesive than Ga. Its measured cohesive energy is 0.56 eV higher, per atom. The calculated difference is 0.86 eV, i.e., somewhat larger. The fundamental reason that Al is more cohesive is that it costs considerably less energy to promote the $3s^2 3p$ Al atom to a $3s3p^2$ state, in which all valence electrons can participate in bonding, than the corresponding $4s^2 4p \rightarrow 4s4p^2$ promotion costs in Ga. (For further discussion of this point, see Sec. III B below.)

These properties of Al and Ga suggest the following: Because of the larger cohesive energy of Al, Ga impurities in Al will tend to segregate to the surface. This agrees with an experimental solubility of Ga in Al of only 2%, and also with our calculations showing that a formation of 3:1, 1:1, or 1:3 Al/Ga alloy, in a fcc matrix, is endothermic by 31 meV, 51 meV, or 58 meV per atom. At the surface, bonds of Ga to Al atoms will be stronger than to Ga neighbors (if the surface structure is not dimerized, anyway). Therefore, Ga adlayers will lower the Al surface energy. Because of the similar sizes of Al and Ga, at least the first adlayer of Ga on Al surfaces will be commensurate.

C. Calculated properties of Ga monolayers on low Miller index Al surfaces

The expectation that Ga binds favorably to Al surfaces is confirmed by our findings. On all three low index Al surfaces, the first ML of Ga binds strongly. The calculated adsorption energies are 3.221 eV and 3.176 eV in fcc and hcp hollows on Al(111), 3.340 eV on Al(100), and 3.380 eV on Al(110).[16] Assuming that the Ga atoms come from a reservoir, whose cohesive energy is that of α-Ga, 3.12 eV, we find that all three Ga-covered Al surfaces have a reduced surface energy.

The most stable surface of clean Al is Al(111). For the low Miller index planes, the computed surface energies are $E_{\mathrm{surf}}(111)=54.9$ meV/Å^2, $E_{\mathrm{surf}}(100)=56.8$ meV/Å^2, and $E_{\mathrm{surf}}(110)=65.3$ meV/Å^2. (For a summary of our results, see Table I). As expected in a valence saturation picture, Ga binds preferentially to less stable surfaces, which are the more open ones. Nevertheless, *Al(100), not Al(110), is the most stable of the Ga-covered, low Miller index surfaces*. This represents a compromise between weaker Ga binding on closer-packed Al surfaces and higher clean surface surface energies on more open ones. Specifically, it means that the stronger bonding of Ga on Al(110) is not enough to overcompensate the lower surface energy of clean Al(100).

To obtain the surface energy of a clean elemental surface from the cohesive energy of an N-layer slab, one uses the formula,

$$E_{\text{surf}}=[E_{\text{slab}}^{\text{clean}}(N)-NE_{\text{bulk}}]/2A_{\text{uc}}, \tag{1}$$

where the energy per bulk layer is obtained from a bulk calculation using the same supercell as for the slab. On the right-hand side of Eq. (1), A_{uc} is the area of the surface unit cell. The factor 2 accounts for the fact that a slab has two surfaces.

The ''surface energy'' relevant to adsorbate-assisted opening of a crack is not given by Eq. (1), but rather by

$$E_{\text{surf}}=[E_{\text{slab}}^{\text{covered}}(N)-NE_{\text{bulk}}-E_{\text{cohesive}}^{\text{adsorbate}}]/2A_{\text{uc}}. \tag{2}$$

The additional term in the square bracket is the energy necessary to remove the atoms to be adsorbed on the new surface from a reservoir. In reality, for liquid-metal embrittlement, the reservoir should be a droplet of the embrittling liquid, and $E_{\text{cohesive}}^{\text{adsorbate}}$ should thus be a per Ga atom heat of sublimation. Not having a LDA-based value of this quantity, and consistent with the fact that all our calculations correspond to $T=0$ K, we use instead the calculated cohesive energy of α-Ga. At 1ML Ga coverage, using Eq. (2), the calculated surface energies are $E_{\text{surf}}^{111}=40.5$ meV/Å^2, $E_{\text{surf}}^{100}=29.7$ meV/Å^2, and $E_{\text{surf}}^{110}=43$ meV/Å^2.

D. Submonolayers of Ga on Al surfaces

Since Ga atoms in ''fcc-Ga'' are slightly larger than Al atoms, it is conceivable that 1×1 commensurate Ga adlayers are under compressive stress. To check for such Ga-Ga repulsion, we compute the Ga heat of adsorption for a coverage less than 1 ML. But, comparing per Ga atom adsorption energies, we find that both 1/4 ML and 1/2 ML Ga are quite unstable on Al(111) and Al(100), relative to a full monolayer. *Thus, the Ga-Ga interaction is, in fact, attractive.*

Specifically, in half monolayers of Ga on Al(111), considering two different geometries in a $p(2\times2)$ cell, the adsorption energy per Ga atom is reduced by 65 meV compared to the full monolayer. On Al(100), the reduction is 108 meV. These results show that on-surface Ga will tend to form compact islands. The absence of Ga-Ga repulsion is presumably related to Ga's ability to condense into phases with widely varying bond lengths, but of similar cohesive energies.

E. Ga *in* Al surfaces

Theory implies that clean Al surfaces are under tensile stress.[17] Since the lattice constant of fcc-Ga is slightly bigger than that of Al, the incorporation of Ga into the Al surface layer could relieve such stress and thus be preferred to on-surface Ga adsorption. We test this idea by substituting Ga atoms for 1/4 and 1/2 ML of the outer layer atoms of Al(100) and Al(111). For the Al(100) surface, we also test the results of adsorbing an additional pseudomorphic monolayer of Ga on the intermixed surface layer. This means that we study Ga coverages of 1/4 ML, 1/2 ML, 5/4 ML, and 3/2 ML on Al(100).

We find that each substitutional geometry corresponding to a particular Ga coverage on Al(100) is energetically indistinguishable (within 1 meV per Ga atom) from a combination of nonintermixed phases corresponding to the same coverage. Thus, at Al(100), the energy lost in replacing Al-Al by Al-Ga bonds is compensated by the gain in replacing Ga-Ga by Al-Ga bonds. On Al(111) the intermixed phases are actually slightly favored, though not enough to reverse the ordering of the surface energies of Ga-covered Al(111) and Al(100). At 1/4 ML Ga coverage on Al(111), the Ga atoms prefer a substitutional structure to compact on-surface islands by 9 meV per Ga atom; at 1/2 ML Ga coverage, the difference is 3 meV.

Whether intermixed surface phases are relevant to the embrittlement of Al by Ga remains an open question. Since configurational entropy favors mixed phases, our results imply that the Ga/Al interface layer is intermixed in thermal equilibrium, above $T=0$ K. For nonequilibrium situations, notably a propagating crack, energy barriers might prevent the formation of mixed phases. We have, therefore, tried to estimate a lower limit for the Ga-Al intermixing barrier on Al(100) at various local Ga coverages: For example, an atomic geometry that seems unavoidable in intermixing on a flat Al(100) surface has one Ga atom in a substitutional site in the Al(100) surface layer and the Al atom it replaced in an adjacent four-fold site in the layer above. The difference between the energy for this configuration and the initial nonintermixed state is a lower limit for the energy barrier of the Ga-Al exchange. We calculate this energy difference to be 0.39 eV, if the local Ga coverage is low (1/4 ML). At 1 ML local Ga coverage, this exchange barrier is reduced to 0.28 eV. On the other hand, if the Al surface is initially covered by two pseudomorphic Ga layers, then the exchange of Al and Ga is energetically favorable, by 0.08 eV, and if there is a barrier, it is between the initial and final states of the exchange process.

It goes without saying that it is hard to make anything like a definitive analysis of the barriers to Ga-Al intermixing. The relevant barriers might have nothing to do with flat surfaces. They might be associated with steps or other defects. Intermixing energies computed for a pseudomorphic Ga dilayer may also be irrelevant (see Sec. G, below) for the simple reason that such a structure may never occur. Perhaps most importantly, in a strained system, one in which a crack is about to propagate, one needs to be concerned that barriers will be modified *because of the strain,* and also that the stress applied might provide the energy necessary to overcome whatever barriers do exist. Some of these issues can be addressed by further calculations. However, as we emphasize in Sec. III C, atomic scale structural information on well characterized surfaces would make it much easier to restrict our attention to important Ga/Al configurations. The one conclusion that we can currently draw confidently from our limited investigation of intermixing is that even if Ga and Al mix during crack propagation, it is the intermixed Al(100) surface that has the lowest surface energy. Thus, the Griffith criterion[18] still favors cracking along the Al(100) plane.

F. The second layer of Ga on Al

Because atoms in the first Ga layer bind more strongly to Al surfaces than Ga binds to its neighbors in bulk Ga, we

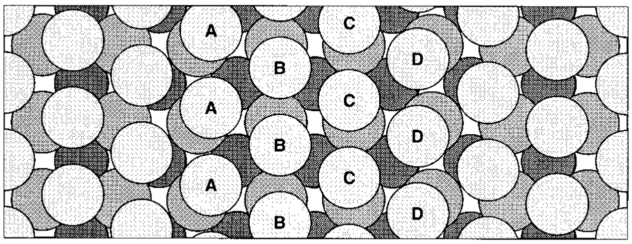

FIG. 1. Schematic top view of two layers of Ga in an 8×1 overlayer on Al(100). Three unit cells are shown. The outer layer Ga atoms, indicated by light gray circles, are arranged quasihexagonally. Because Ga-Al bonds are stronger than the bonds between Ga atoms, the first Ga layer, indicated as medium gray circles, is close to pseudomorphic to the Al substrate, whose outer layer atoms are indicated by the darkest gray circles. The four shortest Ga-Ga bonds (in order) in this 8×1 structure connect the outer layer Ga atoms labeled A, B, C, and D to the atoms almost directly below them in the first Ga layer.

expect that a second Ga layer will be only weakly bound. This proves to be true for two surfaces that we tested, Al(111) and Al(100). The adsorption energy per Ga in a second (1 × 1)-Ga adlayer is lower by 180 meV on Al(111) and 220 meV on Al(100).

A corollary of the second layer's weak bonding is that it resides relatively far outside the first Ga adlayer. On Al(111), the Ga-Ga layer separation is 12% larger than the Al-Al layer separation. On Al(100), it is 14% larger. The two Ga layers bind to each other so weakly that they can be moved relative to each other without significant barriers, i.e., the potential energy surface inhibiting the motion of the second layer is only slightly corrugated.[19] On Al(100), it costs less than about 10 meV to move the second Ga layer from the fourfold hollows of the first Ga-layer to bridge sites. In the bridge geometry, the separation between the Ga layers increases to 120% of the Al(100) interlayer separation.

G. A quasihexagonal Ga layer?

The weak interaction between first and second Ga adlayers on Al(100) suggests that the second layer could prefer a lower symmetry atomic geometry, e.g., a quasihexagonal structure.[20] We study three hexagonal reconstructions: a 4×1 with five second-layer Ga atoms per unit cell, a 6×1 with seven second-layer Ga's, and a 8×1 with nine of them (see Fig. 1). Compared to the 1×1 second Ga layer, the quasihexagonal phases are slightly less stable. The difference per second layer Ga atom is 90 meV for the 4×1 phase, 60 meV for the 6×1 phase, and 40 meV for the 8×1 phase. Since the energy difference between the 1×1 phase and the 8×1 reconstruction is so small, we cannot rule out the possibility that the second Ga layer is actually incommensurate.

Since α-Ga shows a pronounced dimerization, with a short bond of length 2.44 Å and the next six shortest bonds ranging between 2.71 and 2.80 Å, we have been alert for signs of a similar dimerization in adsorbed Ga multilayers. For example, in the energetically relatively favorable 8×1 dilayer on Al(100), we note that four Ga-Ga bond lengths lie between 2.63 and 2.67 Å. As indicated in Fig. 1, these correspond to bonds between four outer layer Ga atoms and Ga's almost directly below them. Two other bond lengths equal 2.71 and 2.72 Å and the rest are greater than 2.80 Å. Most of the inter-Ga bond lengths are clustered around 2.86 Å in the 8×1 structure, but, including each Ga atom's quasihexagonal first-neighbor shell, they range up to 3.15 Å .

Does this nearly 20% bond-length variation imply that the Ga dilayer is ‘‘dimerized?’’ The answer to this question is somewhat ambiguous. In the 8×1 cell, nine second-layer Ga atoms lie in a quasihexagonal arrangement above a square array of eight first-layer Ga's. The low symmetry of this cell allows the Ga atoms considerable freedom to adopt an optimal adsorption geometry. Thus, one might attribute the existence of bonds that are 0.23 Å smaller than the majority to an energetic preference for dimerization. On the other hand, the fact that the first and second Ga layers simulate being ‘‘out of registry’’ means that unless one of the second-layer atoms is pushed up into a third layer, with a considerable reduction in its coordination, there must be both stretched and compressed bonds.

The result is that we can only draw one firm conclusion from our analysis of the 8×1 adsorption geometry, namely, that the energetic penalty for its wide range of Ga-Ga bond lengths is small. This conclusion is consistent with our earlier finding that the cohesion of the strongly dimerized α-Ga phase is only 60 meV stronger, per atom than in the undimerized fcc-Ga geometry. It is also consistent with other theoretical, as well as experimental findings for pure Ga. Specifically, though dimerization is known to occur in α-Ga, *ab initio* calculations aimed at interpreting STM micrographs of the α-Ga(001) surface[21] suggest that its atomic arrangement resembles that of Ga-III, an undimerized, fcc-like phase.[22] Similarly, although its x-ray structure factor suggests that dimers are present in liquid-Ga,[23] inert gas atom scattering data from the liquid-Ga surface ‘‘do not appear to exhibit any special features that reflect pairing of atoms.’’[24]

III. DISCUSSION

This section focuses on two issues: (A) To what extent do our results help understand the embrittlement of Al by Ga, and (B) how can we account for the fact that Ga and Al, neighbors in the Periodic Table that often behave similarly, e.g., in III-V semiconductors, have such different mechanical properties in their metallic states.

A. Thermodynamics of Al embrittlement by Ga

Brittle fracture is a dynamical effect with a non-negligible temperature dependence. Whether a crack propagates or blunts, i.e., whether a metal is brittle or ductile, depends on as yet poorly known nonlinear interactions in regions of high stress concentration. In the particular case of Ga-induced embrittlement of single-crystal Al, the energy to extend a crack is found to be three to four orders of magnitude greater than the energy needed just to expose fresh Ga-covered Al(100) surface. The reason is that in the macroscopic failure experiment, much of the crack propagation energy is consumed in corollary processes far outside the scope of our idealized theory (e.g., deformation of the sample and its grips, and ductile shear).[4]

These remarks make it plain that the energies that we calculate for Ga adsorbed at 0 K on flat Al surfaces far from ‘‘explain’’ Al embrittlement by Ga. Nonetheless, several features of the LDA energetics are suggestive:

(1) When single-crystal Al is embrittled by Ga, stress cracks expose (100) planes, even cracks deliberately initiated along other crystal directions.[4] Consistent with this result, and with the idea based on the ‘‘Griffith criterion,’’[18] that cleavage occurs on the plane, whose surface energy is smallest, we find that 1×1-Ga/Al(100) has a lower energy of surface formation than either Ga on the more close-packed (111) surface or on the very open (110). The experiments of Old and Trevena imply that surface-energy anisotropy cannot be the source of a propensity to crack along (100) planes, unless $E_{\rm surf}^{100}$ is considerably more than a few percent smaller than $E_{\rm surf}^{111}$.[4] Satisfyingly, we find quite a substantial surface-energy anisotropy for the Ga-covered surfaces,[25] namely (cf. Table I),

$$E_{\rm surf}^{100}/E_{\rm surf}^{110}=0.69 \quad \text{and} \quad E_{\rm surf}^{100}/E_{\rm surf}^{111}=0.73. \tag{3}$$

Thus, our LDA results support the idea that Ga’s tendency to cause failure along Al(100) planes has a thermodynamic basis.

(2) Weak cohesion between the first and second Ga layers on a single Al surface suggests even weaker bonding between two Ga-ML covered Al surfaces. Thus, as soon as a crack opens wide enough to admit two layers of Ga, bonding across the crack will be weak.

(3) Finally, once the crack is wide enough to admit three Ga layers, transport of Ga to the crack tip will become very rapid. The first two layers worth of Ga will cap the exposed Al(100) surfaces. The next Ga’s will ‘‘float’’ between the previously adsorbed Ga layers, moving with extremely low barriers.

B. Why is Ga an embrittling agent, while Al is a strong metal?

Although these results are consistent with experiment, they nevertheless demand some sort of explanation. Why is it, after all, that Ga is liquid near room temperature, and an embrittling agent, while Al is strong enough for aircraft fuselages? Why does Ga bind strongly to Al and weakly to itself? The notion that the shallow *d* states in the Ga atom must play a role is both obvious and vague. To make it more specific, we start from the simple idea that embrittling agents are species that do not form many bonds. Species that embrittle do not ‘‘glue’’ one side of an opening crack to the other. Hydrogen is a clear example. The crystal structure of α-Ga, an orthorhombic arrangement of Ga dimers, provides a hint that Ga is another. In α-Ga, each Ga atom has a single neighbor only 2.44 Å away and six other neighbors 0.27 to 0.36 Å more distant. The structure of liquid Ga also shows evidence for the presence of Ga dimers.[23]

As noted above, the short Ga-Ga bond in α-Ga is not evidence that Ga is a smaller atom than Al. Energy vs lattice-parameter optimization for a hypothetical fcc Ga crystal yields a Ga nearest neighbor distance of 3.00 Å, a bit larger than the result for fcc Al, 2.85 Å . The fact that the minimum bond length in α-Ga is 0.54 Å shorter than the computed optimum for the fcc structure instead reflects very different bonding of Ga when its coordination is low. In α-Ga, each atom has only one strong bond. In an fcc metal, each atom participates in twelve equivalent bonds, sharing its three valence electrons equally among them.

Why is there a tendency toward dimerization in Ga and not in Al? A reasonable assumption is that what distinguishes the chemistry of Ga and Al is their different $s\rightarrow p$ promotion energies.[26] In both atomic Ga and Al, the electronic ground state configuration is s^2p, and thus, since the valence *s* shell is closed, there is only a single *p* electron available to form a bond. In order to make many bonds, an *s* electron must be promoted to a *p* state, such that the excited atom has three unpaired electrons.[27] If the energetic cost of this promotion is relatively high, and the compensation in the form of hybridization energy is not equally high, $s\rightarrow p$ promotion will not occur. In this case, there will be a tendency to form few bonds.

Atomic spectroscopy reveals that the minimum $s\rightarrow p$ promotion energy in Ga is 4.71 eV. In Al, it is 3.60 eV.[28] Thus, Ga is more stable than Al in singly relative to multiply bonded states. The reason for the higher promotion energy, as anticipated, does ‘‘have something to do with the *d* shell.’’ Because they are not subject to a centrifugal barrier, *s* electrons of any principal quantum number spend an appreciable fraction of their time close to the nucleus. But when a Ga *s* electron is inside the $n=3$ shell, it is attracted by an effective nuclear charge of 21 instead of only 3. A $3s$ electron in Al sees a nuclear charge of 11 when it is inside the $n=2$ shell, not 21, because there is no $2d$ shell. The upshot is that the $4s$ electrons in Ga are bound more tightly than the $3s$’s are in Al.[29]

In contrast to *s*’s, *p* electrons are kept from the core region by the centrifugal force. *p* electron binding in the two atomic species is, therefore, very similar. This can be seen, for example, in the very close values of the first ionization potentials of Ga and Al, 5.999 and 5.986 eV.[28] Since the Al and Ga *p* states are bound essentially equally well, while the *s* electron is held tighter in Ga, the $s\rightarrow p$ promotion energy in Ga is higher, and Ga tends to form dimers, while Al does not.

C. The future

Our results indicate that first-principles calculations based on the local density approximation capture the essential chemistry that underlies the phenomenon of Al embrittlement by Ga. In future calculations, we will address LME with increasing levels of realism. Important features of the problem that seem within our reach at present include a stress concentration at model crack tips, and dislocation emission.

This said, it should be clear that the number of Ga-Al surface atomic arrangements that are plausibly relevant to cracking phenomena is virtually boundless. We would, therefore, greatly welcome the results of structural analysis on well-characterized, Ga-covered Al surfaces. Answers to the simplest questions would help us reduce the dimensions of the Ga/Al configuration space to be explored. Does Ga order on Al(001)? Is the second Ga layer pseudomorphic or not? Is there intermixing in the first or several Al layers? And finally, how do the answers to these questions depend on Ga coverage and temperature? Without proving that we can account for the experimental systematics of Ga adsorption on unstrained, flat Al surfaces, it is hard to imagine a successful attack on possibly much more difficult issues such as the arrangement of atoms near a crack tip, as a function of applied stress.

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[1] For a survey, see A. R. C. Westwood, in *Fracture in Metals*, edited by D. C. Drucker and J. J. Gilman (Wiley, New York, 1963) [Metall. Soc. Conf., [Proc.] **20**, 553 (1963)].

[2] B. A. Benson and R. G. Hoagland, Scr. Metall. **23**, 1943 (1989).

[3] For a review, see A. R. C. Westwood, C. M. Preece, and M. H. Kamdar, in *Fracture: An Advanced Treatise*, edited by H. Liebowitz (Academic Press, New York, 1971), Vol. III, Chap. 10.

[4] C. F. Old and P. Trevena, Met. Sci. **13**, 591 (1979).

[5] A. R. C. Westwood, C. M. Preece, and M. H. Kamdar, Am. Soc. Met. Trans. **60**, 723 (1967).

[6] For a review of the LDA, see *The Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum Press, New York, 1983). Also, see, W. E. Pickett, Comput. Phys. Rep. **9**, 115 (1989).

[7] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).

[8] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[9] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[10] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[11] E. Wigner, Phys. Rev. **36**, 1002 (1934).

[12] X. G. Gong, G. L. Chiarotti, M. Parrinello, and E. Tossatti, Phys. Rev. B **43**, 14 277 (1991).

[13] L. Bosio, J. Chem. Phys. **68**, 1221 (1978).

[14] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, NY, 1960).

[15] The experimental dimer bond length in α-Ga is 2.44 Å .

[16] As an atomic reference energy for Ga, we use here and elsewhere in this paper the energy of a non-spin-polarized, quasi-isolated Ga atom, described by plane waves with a cutoff energy of 10 Ry.

[17] R. J. Needs, Phys. Rev. Lett. **58**, 53 (1987).

[18] A. A. Griffith, Philos. Trans. R. Soc. London Ser. A **221**, 163 (1920); for an extended discussion, see B. R. Lawn and T. R. Wilshaw, *Fracture of Brittle Solids* (Cambridge University Press, Cambridge, 1975).

[19] A. R. C. Westwood and M. H. Kamdar, Philos. Mag. **8**, 787 (1963).

[20] This thought comes from the extreme case of adsorbed Xe overlayers, which are hexagonal, independent of the substrate symmetry.

[21] O. Züger and U. Dürig, Phys. Rev. B **46**, 7319 (1992).

[22] M. Bernasconi, G. L. Chiarotti, and E. Tosatti, Phys. Rev. Lett. **70**, 3295 (1993).

[23] Y. Waseda and K. Suzuki, Phys. Status Solidi **49**, 339 (1972).

[24] W. R. Ronk, D. V. Kowalski, M. Manning, and G. M. Nathanson, J. Chem. Phys. **104**, 4842 (1996).

[25] For clean Al, the anisotropy is considerably smaller. In this case, we obtain (cf. Table I) $E_{\mathrm{surf}}^{100}/E_{\mathrm{surf}}^{110}=0.87$ and $E_{\mathrm{surf}}^{100}/E_{\mathrm{surf}}^{111}=1.035$.

[26] For an alternate picture, see J. Hafner and V. Heine, J. Phys. F **13**, 2479 (1983).

[27] See L. Brewer, in *Alloying*, edited by J. L. Walter, M. R. Jackson, and C. T. Sims (ASM International, Metals Park, OH, 1988), pp. 1–28.

[28] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, DC, 1949).

[29] In fact, this argument is not as simple as it seems at first glance, because when a Ga 4s electron moves inside the $n=3$ shell, it screens the interaction between the 3s, p, and d electrons and the Ga nucleus, pushing them farther from the nucleus and reducing *their* binding energy. However, the mutual repulsion of the electrons in the $n=3$ shell diminishes when their orbitals increase in size. The net result is that the occasional plunge of the 4s electron inside the $n=3$ shell is energetically favorable. (A similar discussion pertains for a 3s electron in Al plunging inside the $n=2$ shell.)