Orientation dependences of surface morphologies and energies of iron-gallium alloys

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Abstract

We investigated the surface energies of several low-index surfaces of the D0₃-type FeGa alloys (Galfenol), using density functional theory (DFT) simulations and contact angle measurements. DFT calculations predict that (1) the Ga-covered (110) surface of Galfenol is more stable in the Ga-rich condition, while Ga-covered (001) surface of Galfenol surface become more favorable in Ga-poor condition; and (2) a full Ga overlayer tends to form on top of Galfenol surfaces regardless their orientation, both in agreement with the experimental observation. We also studied Ga segregation in the Fe bcc matrix in order to explore the possibility of Ga precipitation away from Fe. It was found that the Fe-Ga separation is unlikely to occur since Ga diffusion toward the surface is effectively self-stopped once the Ga overlayers form on the facets.

I. INTRODUCTION

Magnetostriction and its inverse effect, i.e., the coupling between magnetization and elastic strain of magnetic materials, have attracted extensive attention in the last half-century due to their significance for both fundamental science and technological applications.¹ Most strongly magnetostrictive materials that are used in sensors, actuators and energy harvesters nowadays involve rare-earth elements, such as Terfenol-D (an alloy of Tb, Dy and Fe, which has a magnetostrictive strain of larger than 1000 ppm).² The shortage of rare-earth supply in the earth crust has inspired a huge interdisciplinary effort in recent years to search for rare-earth free magnetostrictive materials. To this end, Iron-Gallium and related alloys (Galfenol or $\text{Fe}_{100-x}\text{Ga}_x$ with $\sim 12 < x < \sim 35$) are among the most promising rare-earth-free magnetostrictive materials as their tetragonal magnetostrictive strain (λ_{001}) can reach to about 280 ppm, sufficient for many device applications.^{3,4,5,6,7} Nevertheless, the magnetostriction of Galfenol is strongly anisotropic, and its rhombohedral magnetostriction (λ_{111}) is extremely weak.^{8,9,10} Therefore, it is critically important to develop an approach that leads to preferential alignment of most FeGa grains along the tetragonal direction in order to achieve an optimal performance.

It is believed that the alignment of grains in Galfenol films depends on the surface energies (denoted as γ below) of different facets. There are very limited experimental data on surface energies of Galfenol, and special consideration for the effect of orientation and composition on surface energies is more rare. This inspires us to systematically investigate the effect of chemical composition and crystal orientation on surface energies of Galfenol samples. We select the $\text{Fe}_{81.75}\text{Ga}_{18.25}$ alloy, which corresponds to about the highest value of λ_{001} for Galfenol,^{4,7} as our model system and study its surface energetics in different chemical environments. Density functional theory (DFT) simulations suggest that the (110) surface is more stable in the Ga-rich regime while (001) surface becomes more favorable at Ga-poor end for Galfenol, moreover, the cleavage energies of the (001) and (110) surfaces are rather close in vacuum, consistent with experimental measurements. This gives a hope to align FeGa grains along the (001) direction in an appropriate environment. Furthermore, we found that Ga tends to form overlayers on Galfenol surfaces and these overlayers stop further outward segregation of

Ga atoms. Our findings provide useful guidance for the development of high performance Galfenol samples through lamination and other treatments.

II. DFT DETERMINATION OF SURFACE ENERGIES

Our DFT simulations were performed with the Vienna Ab initio Simulation Package (VASP).^{11,12} The effect of core electrons was treated using the projector augmented wave (PAW) method.¹³ Spin-polarized generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was employed to represent the exchange and correlation interactions among valence electrons.¹⁴ The wave functions were expanded with a plane wave basis set with an energy cutoff of 400 eV.

FIG. 1: The $D0_3$ -type $Fe_{81.25}Ga_{18.75}$ bulk structure and other surface models and notations.

It is known that many phases such as disordered A2, B2 and D0₃ may coexist in a Fe_{100-x}Ga_x sample of a composition in the vicinity of x~18.¹⁵ Experimental results and recent *ab initio* molecular dynamics (AIMD) simulations indicate that Fe_{81.25}Ga_{18.75} favors the D0₃ phase, along with a small amount of B2.^{16,17} The structural model constructed for the D0₃-type bulk Fe_{81.25}Ga_{18.75} is shown in the top panel of Fig. 1. Even for this simple model, the surface cleavage may result in several different terminations for each crystal orientation. For example, the (001) surface of the D0₃-type Fe_{81.25}Ga_{18.75} may have two terminations, one with no Ga atoms [S0(001) in Fig. 1] and other with 1 Ga atom [S1(001) in Fig. 1] in the surface layer. Similarly, there are two and three different terminations for (110) and (111) surfaces, respectively. Moreover, it is also possible that the chemical composition at the surface is different from that in bulk as Ga atoms may migrate to the topmost layer, depending on the growth and annealing condition. As depicted in Figure 1, twelve models were adopted to simulate the (001), (110) and (111) surfaces of Galfenol within the limit of unit cell size. They range from no Ga at the topmost layer (S0) to a full monolayer of Ga [S4 for the (001) and (111) surfaces and S8 for the (110) surfaces]. To ensure the adequate convergence of surface energies, all slabs are thicker than 11.5 Å, i.e., 9 atomic layers for the (001) surfaces, 7 atomic layers for the (110) surfaces and 17 atomic layers for the (111) surfaces. In order to avoid spurious interactions between slabs due to periodic boundary condition, a vacuum space of 12 Å was inserted between adjacent slabs.

In principle, the surface energy should be temperature dependent and be calculated from Gibbs free energies of the surface and bulk. However, the temperature factor is typically ignored and Gibbs free energies can be replaced by DFT total energies in ambient conditions without much prejudice to the overall conclusions. Since most of our models have non-stoichiometric compositions, the chemical potentials of the constituents μ_{Fe} and μ_{Ga} must be involved and the equation we used for the determination of surface energies is

$$\gamma(N) = \frac{1}{2A} [E_{slab}(N) / N_{Fe} \mu_{Fe} / N_{Ga} \mu_{Ga}] \quad (1)$$

Here, N denotes the total number of atoms; N_{Fe} and N_{Ga} represent the numbers of Fe and Ga atoms; A is the surface area; and the factor $1/2$ is included to account for the two surfaces created in typical slab models. One should note that μ_{Fe} and μ_{Ga} are not the chemical potentials of Fe and Ga bulks. Instead, they correspond to the alloy environment and are related according to

$$\mu_{FeGa} = 13\mu_{Fe} + 3\mu_{Ga} \quad (2)$$

where μ_{FeGa} is the chemical potential of the bulk D0₃-type Fe_{81.25}Ga_{18.75} (or approximately the total energy of the supercell with 16 atoms). This constraint indicates that the chemical potential of Ga is the only free variable in Eq. 1 and we can use it as a parameter to characterize the annealing and quenching conditions.

We first determined μ_{FeGa} in two approaches: 1) from the total energy of a bulk unit cell as displayed in the top panel in Fig. 1; and 2) from thin film calculations with varying thickness and extrapolate the thickness dependence of energy according to $E_{film}(n) = 2\gamma_{film} + n\mu_{FeGa}$ (n is the number of Fe₁₃Ga₃ units in the film). As a result, the values of μ_{FeGa} obtained from these calculations are rather close, with a difference less than 1%. This also indicates the quality of our calculations and the sufficiency of the slab thickness in our models.

Using Eqs. (1) and (2) along with the calculated μ_{FeGa} , the surface energies of the (001), (110) and (111) surfaces of Galfenol are shown in Fig. 2 (a), (b) and (c), respectively. For the (001) surfaces the trend is clear: as the Ga rich regime is approached ($\mu_{Ga} \rightarrow 0$) the Ga atoms favors the topmost layers (negative surface energy indicates that condensation of Ga atoms on the surface from the reservoir gains energy). The energy difference from Fe-terminated [S0(001)] to the Ga-covered [S4(001)] surface is as large as 4.3 J/m², favoring the later one. The exception occurs at the extreme of Ga poor condition ($\mu_{Ga} \rightarrow -3.5$ eV), where the S2(001) (with 50% Ga coverage) configuration becomes more stable. Even in the typical Ga-poor condition with $\mu_{Ga} \sim -2.7$ eV, the formation energy of the orthorhombic bulk Ga, the Fe_{81.25}Ga_{18.75} (001) surface is always covered by an

additional layer of Ga.

FIG. 2: The calculated surface energies for (a) the (001) surfaces, (b) the (110) surfaces and (c) the (111) surfaces with different terminations as denoted in Fig. 1. Panel (d) compares energies of the most stable configurations of the three surface orientations. The grey arrow indicates the Ga orthorhombic chemical potential.

A similar trend is observed for the (110) orientation: in the Ga rich condition a full Ga coverage [S8(110)] is more stable. Only when $\mu_{\text{Ga}} > 3.0$ eV the [S4(110)] (with 50% Ga coverage) becomes more energetically favorable. In the case of the (111) orientation, the full Ga coverage [S4(111)] makes the surfaces more stable across the whole chemical potential range. In Fig. 2 (d), we compare the most stable configurations of the three surface orientations, i.e., S4(001), S8(110) and S4(111). It appears that the (110) configurations are more stable in the Ga-rich condition ($-2.3 \text{ eV} < \mu_{\text{Ga}} < 0$), while the (001) configurations favor at the Ga-poor end ($-3.5 \text{ eV} < \mu_{\text{Ga}} < -2.3$). Nevertheless the energy difference between (001) and (110) surfaces is rather small, especially in the Ga-

poor end ($-3.5 \text{ eV} < \mu_{Ga} < -2.3 \text{ eV}$). The (111) surfaces have much higher energies than their (001) and (110) counterparts so the formation of grains with the (111) orientation is effectively suppressed. This is beneficial for the magnetostrictive performance of Galfenol films since λ_{111} of Galfenol is small and sometimes negative. In addition, these results suggest one may need to anneal Galfenol samples in the Ga poor condition to promote grain alignment along the (001) direction.

III. EXPERIMENTAL MEASUREMENTS OF SURFACE ENERGY

It is common to approximate the surface energy of a solid by extrapolation from the surface tension measured in its liquid phase. This is based on the assumption that fusion (close to the melting temperature) does not drastically change the atomic interaction at the surface, and hence one can assign the liquid surface energy to the crystalline phase.^{18,19} Depending on the approach taken to obtain an estimate, the measurements are classified into oscillating (or levitated), pendent and sessile drop methods. These destructive methods are available for estimating surface energy γ_{sv} (non-oriented) around the melting point.

A non-destructive room temperature method has also shown to be effective for determination of the surface energy of many solids. This approach involves measurement of the contact angle between the surface of the solid and a small drop of liquid such as distilled water, glycerol and methylene iodide resting on the solid surface. This works because the shape of the drop depends on material properties, crystallographic orientation and composition. We attempted taking contact angle measurements on the surface of Galfenol using the water drop method with a commercially available goniometer (First Ten Angstroms, Inc. Model: FTA 125).^{20,21} $\text{Fe}_{82}\text{Ga}_{18}$ single crystal samples were prepared with the (001), (110) and (111) facets to evaluate their surface energies, and each sample was fine polished using silica gel with 60-nm size particles to minimize a substantial influence of surface roughness on the accuracy of contact angle measurements. A water drop with a volume of $\sim 15 \text{ }\mu\text{L}$ was placed on the surface of the well-polished sample using a syringe to provide a drop that was symmetric about a central vertical axis. A few images per second were captured with the standard NTSC video camera that was placed to look exactly down on specimens with prisms, where a

prism turns the viewing angle to the normal side view. The software automatically analyzes the drop shape and computes the contact angle. All measurement processes were carried out in a clean room facility to avoid surface contaminations, although we likely were unable to prevent formation of a native oxide layer with a monolayer thickness on the sample surface.

Figure 3 shows example photos of the measured contact angles between water and samples. In this set of images, the contact angles are 76.13° , 87.01° and 63.11° for the (001), (110) and (111) surfaces, respectively. The FTA125 software analyzed images and provides values of the measured contact angle that they indicate is accurate to within two decimal places, however the variability from test to test for 20-30 contact angle measurement of 17.9at % Ga single crystals on (001), (110) and (111) surfaces was quite large, leading to contact angles (mean $\pm$ one standard deviation) of $72.2 \pm 5.3^\circ$, $80.9 \pm 5.4^\circ$ and $78.0.9 \pm 2.5^\circ$ respectively.

These contact angles should be inversely proportional to surface energies within the range of $0 \sim 90^\circ$. The measurements indicate that the surface energy of a (110) surface has the lowest surface energy as expected, however the mean relative magnitudes of angles for (001) and (111) surfaces was reversed from what DFT predicts, however with the large standard deviations it is difficult to draw conclusions from these experiments. The trend of the (110) surface energy being lowest also agrees with the Girifalco-Good-Fowkes-Young (GGFY) model that provides an estimate of γ_{sv} , using:²²

$$\gamma_{lv}(1 + \cos\theta) = 2\sqrt{\gamma_{lv}\gamma_{sv}} - \pi \quad (3)$$

Where for this experimental set up, the vapor pressure term π is approximately zero, and γ_{lv} and γ_{sv} are the interfacial energy densities between the liquid and the vapor, and the solid and the vapor, respectively. We want to also point out that the absolute values of the surface energies γ_{sv} determined using Eqn. 3 and the angles in Fig. 3 ($\gamma_{110} = 0.0199 \text{ J/m}^2$, $\gamma_{001} = 0.0277 \text{ J/m}^2$ and $\gamma_{111} = 0.0380 \text{ J/m}^2$) are too small to be correct. The values are almost two orders of magnitude smaller than expected when compared to literature γ_{sv} values

for α -Fe in its crystalline phase [$\gamma_{110}(\alpha\text{-Fe})=2.054 \text{ J/m}^2$] and in its polycrystalline phase around its melting point [$\gamma(\alpha\text{-Fe}) = 1.880\text{-}2.123 \text{ J/m}^2$].^{18,23} This problem arises when measuring the surface energy of metals with water drops because of the large difference in surface energy values. For water, $\gamma_{sv} = 75.64 \text{ mJ/m}^2$. The water drop method works well for determining the surface energy of solids that are of a similar magnitude (e.g. glass with $\gamma_{sv} = 58.95 \text{ mJ/m}^2$ or polyethylene with $\gamma_{sv} = 36.72 \text{ mJ/m}^2$) but fails for metallic solids, where the drop surface energy is several orders of magnitude lower than that of metals.

FIG. 3: Photos of contact angle measurement with water drops on the (001), (110) and (111) surfaces of single crystal Galfenol.

IV. DFT DETERMINATION OF SEGREGATION ENERGY OF GA

The qualitative agreement between theory and experiment for the trend of γ_{sv} supports the use of DFT calculations for studying energy minimization associated with different scenarios for the crystallographic alignment of grains in Galfenol. Now it is clear from the data in Fig. 2 that the surface energy of D0₃ Fe-Ga alloy is minimized when Ga atoms

occupy the topmost sites on almost all Gallenol surfaces. It is therefore important to investigate the energetics of the outward diffusion of Ga atoms, in order to obtain information for the control of surface configurations. For simplicity, we focus on the migration energy of one Ga atom (denoted as Ga_d) in the bcc Fe matrix toward the low-index (001), (110) and (111) surfaces along the path of green balls in Figs. 4(a), 4(b) and 4(c), respectively.

FIG. 4: Panels (a), (b) and (c) show the structural models of the low-index surfaces of Fe (grey balls). For each orientation the left and right models show the clean and Ga-covered surfaces, respectively. The red balls represent the Ga_o atoms in the overlayer and the green balls show the sites for the diffusing Ga_d atom. Panel d) and the inset show the segregation energies for Ga_d toward the clean and Ga-covered surfaces, respectively. z measures the distance between Ga_d and the center of slabs.

We set the energy for the configuration with Ga_d at the surface site as the reference (zero energy) for each case. To reduce the density of Ga atoms that undergo simultaneous segregation, we expand the unit cell to a 2×2 supercell in the lateral plane (a 3×3 supercell was tested and no significant difference was found). We found that the surface relaxations of Fe are somewhat recovered by the Ga_o layer, e.g., from -2.4% for Fe(001) to -1.7% for Ga/Fe(001). As shown in Fig. 4(d), the energy gain by moving Ga_d from the interior sites (site 4 or 5) to the surface (site 1) is around 1 eV for all orientations. Although the energy shows a small fluctuation around the bulk-like value for Ga_d in the intermediate sites, it is obvious that Ga_d can easily segregate to the surfaces. On the other hand, it also suggests a possibility that Gallium may form precipitates on Galfenol surfaces.

We also performed calculations for the segregation of Ga_d to Fe surfaces that are already covered by a layer of Ga (denoted as Ga_o) atoms, as depicted by models in the right side of Fig. 4(a), 4(b) and 4(c). If the site 1, now right below the Ga_o , is still energetically favorable, a phase separation is likely to occur. As shown in the inset of Fig. 4(d), the energy profiles are now very different, depending on the surface orientations. For the Fe(110) surface, the energy change is extremely small for Ga_d hopping on different sites. In this case, Ga_d has almost equal probability to segregate inward and outward and the chance of having Ga separation away from Fe is little. For the Fe(001) surface, the Ga_d atom actually prefers the interior site, with an energy gain of 0.45 eV. This suggests that once the Ga overlayer is formed, the outward segregation of Ga_d stops. This self-stopping phenomenon doesn't happen on the Fe(111) surface but this is insignificant for Galfenol since the populations of (111)-oriented grains is small, according to discussions in Section II. Considering possible depletion of Ga from the bulk region, we suggest to make Galfenol samples with x slightly larger than 19% before rolling and other treatments for the best performance. Alternative methods for introducing surface conditions that promote this self-stopping phenomenon should also be considered.

V. DISCUSSIONS

Now we need to understand the DFT results on surface energies of Galfenol and

segregation energies of Ga_d in the Fe lattice. The formation of Ga overlayer on all Galfenol surfaces can be attributed to the large surface energy difference between Fe and Ga. Gallium is a liquid metal at 30 °C and has delocalized 3p valence states. It can easily adjust the distribution of its valence electrons in different environments and, as a result, its surface energy is rather small, 0.88-1.10 J/m.^{2, 24, 25} In contrast, each Fe atom has eight directional bonds in its bulk. Either the cleavage of surfaces or the substitution of Ga cuts those bonds, which may lead to peculiar mechanical properties.^{26, 25} The S8(110) surface terminates the least number of Fe-Fe bonds and this is the reason why it is the more preferred configuration of Galfenol surfaces in the range of Ga rich end. We perceive that the surface energies of Galfenol still tend to follow the simple rule by counting the number of dangling Fe-Fe bonds.

FIG. 5: Panel (a) shows the local symmetry for the Ga_d atom and the notations of its neighbors, with the same color code as in Fig. 4. Panels (b), (c) and (d) show the projected density of states (PDOS) of these Fe atoms. Panels (e) and (f) show the top and side views of charge transfer between Ga_d and Fe in the range of $\pm 0.05 e/\text{\AA}^3$. Blue and red colors represent electron accumulation and depletion, respectively.

The self-stopping effect of the segregation of Ga at the Fe(001) surfaces also deserves

attention. Without the presence of the Ga overlayer, the local environment of a Ga atom is shown in Fig. 5. The Ga_d at an interior site eliminates eight Fe-Fe bonds, four more than the number when it sits at the surface. In addition, Ga_d has more room to expand on the surface, which significantly reduces the local stress around it. Both factors favor the outward segregation of Ga_d . When a Ga overlayer is placed at the top of Fe(001), the segregation of Ga_d needs to overcome repulsion from Ga_o atoms on top. As established in our previous studies, Ga atoms transfer their electrons to Fe in Galfenol so they are mutually repulsive. As a result, Ga_d at site 1 is even about 0.3 Å below the topmost Fe plane in Ga-covered Fe(001).²⁷ This suggests that additional surface stress is produced by the Ga_o layer and explains the self-stopping effect on the outward segregation of Ga_d . Obviously, the strength of repulsion depends on the degree of charge transfer from Ga_o to the Fe substrate, which leads to the orientation dependence as displayed in the inset of Fig. 4 (d).

To appreciate the role of Ga overlayer, Fig. 5 shows the projected density of states (PDOS) for three neighboring Fe atoms to Ga_d , namely the first neighbor (1N), the second neighbor along the vertical direction ($2N_v$) and the second neighbor in the lateral plane ($2N_p$), without (clean) and with (Ga-M) the presence of the Ga overlayer. Since Fe(1N) atoms are in the subsurface layer, the Ga overlayer doesn't noticeably affect them. The main influence of the Ga_o atom is on the Fe($2N_p$) since they directly contact with the Ga overlayer. The non-bonding peaks of Fe($2N_p$) in the spin-down channel are removed around the Fermi level and the bulk-like feature is restored when the Fe(001) surface is covered by Ga. Since Ga_o also pushes down the Ga_d atom by 0.35 Å, the PDOS of Fe($2N_v$) is noticeably altered. The charge transfer from Ga_d to its Fe neighbors is displayed in Fig. 5 (e) and (f). It is clear that Ga_d donates its electrons to the surrounding Fe atoms. Ga_o atoms also donate their electron to the interfacial Fe atoms (not shown here) so the presence of the Ga overlayer somewhat reduces the charge loss of the Ga_d atom.

VI. CONCLUSION

We investigated the low-index surfaces of the D0_3 -type $\text{Fe}_{81.25}\text{Ga}_{18.75}$ using both

experimental and theoretical approaches. In almost all cases, a full Ga coverage at the topmost layer was found to be energetically favorable. The Ga-covered (110) surface of Galfenol is preferential in the Ga-rich range, while the Ga-covered (001) surface of Galfenol becomes more favorable in the Ga-poor condition, consistent with experimental results. Our results indicate that the formation of (111) grains is suppressed, and (001) grains have more chance to form in Galfenol samples if we use reservoirs that attract Ga atoms. Furthermore, the presence of a Ga overlayer on the surfaces, particularly along the (001) orientation, may effectively block the further outward segregation of additional Ga atoms. Therefore, Galfenol samples are expected to have a thin Ga overlayer but the gradual separation between Fe and Ga is unlikely to occur. Our findings provide useful guidance to attain optimal performance of Galfenol through appropriate treatments. We are working on studies beyond the vacuum environment, e.g., with the presence of O₂, O atoms, H₂O and H₂S, and the results will be reported elsewhere.

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- ²⁷ After structural optimization, we found that the presence of Ga_d causes significant local deformation. For example, the Ga_d-Fe(1N) and Ga_d-Fe(2N_v) distances are 2.52 Å, and 2.98 Å for Ga_d at the site 1 on Fe(001), much larger than the corresponding values (2.49 Å, and 2.83 Å) in the unrelaxed structure. For Ga_d on Ga/Fe (001), these distances are reduced to 2.40 Å and 2.63 Å, respectively. In addition, the Ga_d-Ga_o distance is 2.7 Å.

Graphical abstract

Left panel shows the contact angle measurement with water drops on the (001), (110) and (111) surfaces of single crystal GaFeInol. Middle panel gives the atomic structures of these surfaces with the lowest surface energies, which are given in the right panel for varying annealing conditions.