Q1
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 $D0_3$-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.

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1. 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 $Fe_{100-x}Ga_x$ with ~12 < × < ~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 rarer. This inspires us to systematically investigate the effect of chemical composition and crystal orientation on surface energies of Galfenol samples. We select the $Fe_{81.75}Ga_{18.25}$ 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

[1] Lacheisserie E., in Magnetostriction: Theory and Applications of Magnetoelasticity. CRC Press, New York (1993).

[2] F. Jerems, C. Mac Mahon, A. G. Jenner and R. D. Greenough. Ferroelectrics 22, 333 (1999).

[3] J. Atulasimha and A. B. Flatau. Smart Mater. Struct. 20, 043001 (2011).

[4] E. M. Summers, T. A. Lograsso, and M. Wun-Fogle, J. Mater. Sci. **42**, 9582 (2007).

[5] S. Guruswamy, N. Srisukhumbowornchai, A. E. Clark, J. B. Restorff and M. Wun-Fogle. Scripta Mater. 43, 239 (2000).

[6] A. E. Clark, J. B. Restorff, M. Wun-Fogle, T. A. Lograsso and D. L. Schlagel. IEEE Trans. Mag. 36, 3238 (2000).

[7] G. Petculescu, R. Q. Wu, and R. McQueeney, *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, New York, 2012), Vol. 20, Chap. 3, pp. 123-223.

[8] A. E. Clark, K. B. Hathaway, M. Wun-Fogle, J. B. Restorff, T. A. Lograsso, V. M. Keppens, G. Petculescu, and R. A. Taylor, J. Appl. Phys. **93**, 8621 (2003).

[9] H. M. Schurter, M.S. thesis, University of Maryland, 2009.

[10] Y.N. Zhang, H. Wang and R.Q. Wu, Phys. Rev. B 86, 224410 (2012).

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.

2. 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.

It is known that many phases such as disordered A2, B2 and D0$_3$ 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 D0$_3$ phase, along with a small amount of B2.[16,17] The structural model constructed for the D0$_3$-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 D0$_3$-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 Fig. 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

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

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 and 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

$$\mu_{FeGa} = 13\mu_{Fe} + 3\mu_{Ga} \tag{2}$$

where μ_{FeGa} is the chemical potential of the bulk D0$_3$-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 Fe$_{13}$Ga$_3$ 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 ($\mu_{Ga} \to 0$) 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/m^2, favoring the later one. The exception occurs at the extreme of Ga poor condition ($\mu_{Ga} \to -3.5$ 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.

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 $\mu_{Ga} > 3.0$ 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 eV $< \mu_{Ga} < 0$), while the (001) configurations favor at the Ga-poor end (-3.5 eV $< \mu_{Ga} < -2.3$). Nevertheless the energy difference between (001) and (110) surfaces is rather small, especially in the Ga-poor end (-3.5 eV $< \mu_{Ga} < -2.3$ 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.

3. 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 g_{sv} (non-oriented) around the melting point.

[11] G. Kresse and J. Furthmu•ller, Comput. Mater. Sci. 6, 15 (1996).
[12] G. Kresse and J. Furthmu•ller, Phys. Rev. B 54, 11169 (1996).
[13] Kresse G, Joubert D, Phys Rev B 54, 1758 (1999).
[14] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[15] Q. Xing, Y. Du, R. J. McQueeney, and T. A. Lograsso, Acta. Mater. 56, 4536 (2008).
[16] O Ikeda, R Kainuma, I Ohnuma, K Fukamichi, and K Ishida, Journal of Alloys and Compounds 347, 198 (2002).
[17] Hui Wang, Y. N. Zhang, R. Q. Wu, L. Z. Sun, D. S. Xu, and Z. D. Zhang, Scientific Reports 3, 3521(2013).

[18] W. R. Tyson and W. A. Miller, Surf. Sci. 62, 267 (1977).
[19] H. M. Lu and Q. Jiang, J. Phys. Chem. B 109, 15463 (2005).