Rigid band model for prediction of magnetostriction of iron-gallium alloys

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Using the highly precise full potential linearized augmented plane wave method, we determined atomic structure and the magnetostriction of Fe_{100-x}Ga_x with x<19%. It is demonstrated that the extraordinary enhancement of magnetostrictive coefficient of Fe_{100-x}Ga_x at low concentration stems from intrinsic electronic origins. Moreover, we recognized the potential of using a rigid band model for the prediction of magnetostriction of intermetallic alloys, through studies of ternary alloys with Zn substitution into Fe_{87.5}Ga_{12.5}. © 2010 American Institute of Physics. [doi:10.1063/1.3318420]

It is striking that the tetragonal magnetostrictive coefficient (\(\lambda_{001}\)) of Fe_{100-x}Ga_x alloys (Galfenol) increases monotonically with the concentration of Ga till \(x=18-20\) to as large as 400 ppm.\(^{1-6}\) This offers great opportunities for various applications such as MEMS, sensors, and transducers, and has inspired extensive interdisciplinary activities to search for better magnetostrictive materials.\(^{7,9}\) However, advance in this direction is very limited so far, owing to the absence of predictive theoretical models for the description of magnetostriction in intermetallic alloys. Extrinsic origins including the field-induced rotation of DO\(_3\)-DO\(_{22}\) nanoparticles have been proposed to explain the extraordinary enhancement of magnetostriction in Galfenol.\(^{10,11}\) However, the relevance of this model remains doubtful since most single crystalline samples have no obvious phase stems from intrinsic electronic factors. Furthermore, it was recognized that magnitude and sign of \(\lambda_{001}\) of Galfenol strongly depends on the local arrangements of minority atoms at high concentration.\(^{17}\) The presence of B\(_2\)-like Ga–Ga pairs was reported by several groups,\(^{8,19}\) and was assigned as the main reason for the enhancement of magnetostriction in Galfenol.\(^{20}\) Obviously, more systematic theoretical studies are needed to resolve puzzles in this field.

In this letter, we demonstrate the validity and predictive capability of density functional calculations for the studies of magnetostriction in binary and ternary Fe\(_{100-x}\)Ga\(_x\) alloys. It is clearly shown that the enhancement of \(\lambda_{001}\) in Galfenol with small \(x\) (<19) stems from intrinsic electronic origins. Furthermore, we found that the trend of \(\lambda_{001}\) can be predicted through a rigid band approach, using Fe\(_{87.5}\Ga_{12.5}\), Fe\(_{87}\Ga_{6.75}\Zn_{6.75}\) and Fe\(_{87}\Zn_{12.5}\) as model systems. Our findings provide guidance for the manipulation of magnetostriction in Galfenol, by replacing Ga with Zn or other metalloid elements.

We used the full potential linearized augmented plane wave methods\(^{21}\) to solve the density functional Kohn–Sham equations. The spin-polarized generalized gradient approximation was adopted for the description of exchange-correlation interactions among electrons.\(^{22}\) No shape approximation was assumed for charge, potential, and wave function expansions. The core electrons were treated fully relativistically, while the spin-orbit coupling term was invoked second variationally for the valence states.\(^{23}\) Energy cutoffs of 225 Ry and 16 Ry were chosen for the charge, potential and basis expansions in the interstitial region, respectively. In the muffin-tin region (\(r_{\text{c}}=1.11\) Å and \(r_{\text{Ga}}=1.22\) Å), charge, potential, and basic functions were expanded in terms of spherical harmonics with a maximum angular momentum of \(l_{\text{max}}=8\). The convergence of electronic and magnetic properties against the choice of number of k-points and wave function expansion were carefully monitored. The self-consistency was assumed when the root-mean-square differences between the input and output charges and spin densities are less than \(1.0 \times 10^{-4}\) e/(a.u.)\(^3\). To avoid the complexity of nonuniform distribution of metalloid atoms and local precipitation, we focused on the intrinsic electronic effects on the enhancement of \(\lambda_{001}\) in systems with \(x<19\).

We placed iron and metalloid atoms in the bcc lattice, with a 16-atom or 54-atom supercell. The lattice sizes and atomic positions were optimized according to the energy minimization procedures guided by atomic forces. For cases with \(x=12.5\) and \(x=18.75\) that have two and three metalloid atoms in the 16-atom unit cell, we investigated all non-equivalent distribution patterns and calculated their magnetostrictive coefficients with the most preferential configurations. As discussed before,\(^{3,23}\) \(\lambda_{001}\) can be determined from the strain (\(\varepsilon\)) dependences of magnetostrictive anisotropy energy (\(E_{\text{MCA}}\)) and total energy (\(E_{\text{tot}}\)) as

\[
\lambda_{001} = \frac{2 d E_{\text{MCA}}/d \varepsilon}{3 d^2 E_{\text{tot}}/d \varepsilon^2}.
\]

We applied different tetragonal strains along the z-axis with the constant-volume distortion mode (i.e., \(\varepsilon_x=\varepsilon_z=-\varepsilon/2\)). For example, results of \(E_{\text{MCA}}\) and \(E_{\text{tot}}\) of Fe\(_{87.5}\Ga_{12.5}\) are presented in Fig. 1. Both \(E_{\text{MCA}}\) and \(E_{\text{tot}}\) are smooth functions of \(\varepsilon\) and permit reliable polynomial fittings, indicating the high precision of our theoretical data. The value of \(\lambda_{001}\) determined with the slope of \(E_{\text{MCA}}\) and the curvature of \(E_{\text{tot}}\) at \(\varepsilon=0\) is 128 ppm for Fe\(_{87.5}\Ga_{12.5}\), a value that agrees excellently with experimental data. Figure 2 displays the optimal geometries the corresponding \(\lambda_{001}\) of Fe\(_{100-x}\Ga_x\) alloys for \(x=1.85, 6.25, 12.5,\) and 18.75, along with the experimental data. Obviously, density functional calculations reproduce the experimental \(\lambda_{001}(x)\) curve in the entire range of \(x\) explored here. This suggests
that the monotonic increase in $\lambda_{001}$ in this concentration range stems from intrinsic electronic origins, rather than from extrinsic factors such as precipitation. Experimentally, it was also reported that there is no link between the magnetic domains and the magnetostriction enhancement by Ga addition. Furthermore, either slow cooled or rapidly quenched Galfenol samples with $x < 17\%$ show almost identical magnetostriction. Therefore, we may conclude that the magnetic field induced motions of precipitates (if there are any) or domain walls are insignificant for the phenomenal enhancement of magnetostriction of Galfenol, at least for samples with $x < 19\%$. Nonetheless, deviation between theory and experimental data gradually become noticeable at the high-$x$ end in Fig. 2 (to 14$\%$ or $\sim 50$ ppm at $x = 18.75\%$). Therefore, the development of complex local structures is expected to play more important role afterwards. It is believed that the formation of ordered DO$_3$ structure leads to the large dip in the $\lambda_{001}(x)$ curve at $x \sim 24$. The mechanism for the second peak in the $\lambda_{001}(x)$ curve at $x \sim 28$ still remains mysterious. We found that the tetragonal shear modulus of Galfenol decreases almost linearly with $x$, to about 18–20 GPa at $x = 18.75$. These results also agree with experimental data, and suggest that the lattice softening is another important factor for the large enhancement of $\lambda_{001}$ in these alloys.

![FIG. 2. (Color online) Tetragonal magnetostriction constant (3/2) $\lambda_{001}$ as a function of the Ga composition. Circles are the experimental data taken at room temperature and squares are results from the present calculations at 0 K, respectively. Triangles show calculated results for Fe$_{87.5}$Ga$_{6.25}$Zn$_{6.25}$ and Fe$_{87.5}$Zn$_{12.5}$, with either one or both Ga being substituted by Zn in the unit cell. Insets are the atomic configurations used in the ab initio calculations. Blue/dark gray and red/light gray balls are for Fe and Ga atoms, respectively.](image)

Now we discuss the possibility of using the density functional approach along with rigid band model for prediction of magnetostriction in intermetallic alloys. To this end, the strain ($\varepsilon = \pm 2\%$) induced magnetic anisotropy energies of Fe$_{87.5}$Ga$_{12.5}$ are given in Fig. 3(a) versus the number of electrons in the unit cell, $N_e$. Here, moving the position of the Fermi level over the fixed band structure changes values of $N_e$. Note that large $E_{\text{MCA}}$ at the real Fermi level, denoted by the vertical solid lines in Fig. 3, corresponds to strong magnetostriction. It is clear that $\lambda_{001}$ of Fe$_{87.5}$Ga$_{12.5}$ can be further enhanced by taking away about one electron from the unit cell, as shown in Fig. 3(a). Practically, this can be done through Zn substitution for Ga, assuming that Ga and Zn behave similarly toward the hybridization with their neighboring iron atoms.

To verify the applicability of this approach, we did self-consistent calculations for Fe$_{87.5}$Ga$_{6.25}$Zn$_{6.25}$ and Fe$_{87.5}$Zn$_{12.5}$, by replacing one or two Ga atoms with Zn. Interestingly, the three sets of $E_{\text{MCA}}(N_e)$ curves in Fig. 3 are very similar. The Fermi level of Fe$_{87.5}$Ga$_{6.25}$Zn$_{6.25}$ locates right at the peaks of the $E_{\text{MCA}}(N_e)$ curves in Fig. 3(b), which leads to $\lambda_{001}$ = 183 ppm, 43$\%$ larger than that of Fe$_{87.5}$Ga$_{12.5}$. Also as predicted according to the rigid band analysis, further reduction of $N_e$ decreases $\lambda_{001}$, to 134 ppm for Fe$_{87.5}$Zn$_{12.5}$. Moreover, curves of density of states in Fig. 4 also indicate that substitution of Zn for Ga mainly causes band shift against the Fermi level but hardly changes the band structure. Therefore, the applicability of the rigid band model can be established for the prediction of magnetostriction of these alloys in a reasonable range of $N_e$. Synergistic experimental/theoretical studies along this direction are very promising for the design of excellent magnetostrictive materials. So far, experimental studies showed that most ternary additions such as Al, Cr, Co, and Ni typically result in reduction in magnetostrictive performance of Galfenol, except Sn.

We found that Fe atoms nearest to Ga give the largest contributions to the magnetoelastic coupling, i.e., the strain dependence of $E_{\text{MCA}}$. Since the Fe–Ga hybridization is much weaker than that between Fe–Fe, the $d_{xz,yz}$ states become “dangling” bonds and shift in energy from the edges to the center of Fe 3$d$-band. As highlighted by the arrow in Fig. 4, Galfenol has high peaks right above $E_F$ in the minority spin

![FIG. 3. (Color online) The calculated $E_{\text{MCA}}$ against the band filling, $N_e$, for Fe$_{87.5}$Ga$_{12.5}$, Fe$_{87.5}$Ga$_{6.25}$Zn$_{6.25}$, and Fe$_{87.5}$Zn$_{12.5}$ with $+2\%$ and $-2\%$ lattice distortions along the $z$-axis.](image)
channel, in contrast to the valley at the same place for the pure bulk Fe. On the other hand, tetragonal lattice strain alters the energy position and occupation of $e_g$ states. The strong spin-orbit coupling interaction between $d_{xz,yz}$ and $e_g$ states across the Fermi level gives rise to the large magnetostriction.\(^2\) For instance, the negative contribution of $\langle z^2|L_z|xz,yz\rangle$ to $E_{\text{MCA}}$ under the tetragonal stretch was assigned as the main reason for the large magnetostriction in the $\text{DO}_3-\text{Fe}_{75}\text{Ge}_{25}$ alloy.\(^1\) Obviously, changing $N_e$ alters the occupation of states and thereby the leading pairs of states across the new Fermi level to attain. Large magnetostriction, we want to capture the pair of states across $E_F$ that are close in energy for strong spin-orbit coupling interaction.

In summary, high-quality density-functional calculations are reliable for the determination of $\lambda_{\text{MCA}}$ of Fe$_{100-z}$Ga$_z$ alloys with $z < 19\%$. Furthermore, we demonstrated the capability of using the rigid band model to predict magnetostrictive coefficients and explained the physical origin. Zn is proposed as a good substitute for Ga for the further enhancement of magnetostriction of Fe$_{87.5}\text{Ga}_{12.5}$, due to the change in the number of valence electrons. Density functional approach provides an excellent guideline.

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