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Effects of Zn additions to highly magnetoelastic FeGa alloys

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Abstract

Fe1−xMx (M = Ga, Ge, Si, Al, Mo and x ~ 0.18) alloys offer an extraordinary combination ofmagnetoelasticity and mechanical properties. They are rare-earth-free, can be processed using conventional deformation techniques, have high magnetic permeability, low hysteresis, and low magnetic saturation fields, making them attractive for device applications such as actuators and energy harvesters. Starting with Fe-Ga as a reference and using a rigid-band-filling argument, Zhang et al. predicted that lowering the Fermi level by reducing the total number of electrons could enhance magnetoelasticity. To provide a direct experimental validation for Zhang's hypothesis, elemental additions with lower-than-Ga valence are needed. Of the possible candidates, only Be and Zn have sufficient solubility. Single crystals of bcc Fe-Ga-Zn have beengrown with up to 4.6 at. % Zn in a Bridgman furnace under elevated pressure (15 bars) in order to overcome the high vapor pressure of Zn and obtain homogeneous crystals. Single-crystalmeasurements of magnetostriction and elastic constants allow for the direct comparison of themagnetoelastic coupling constants of Fe-Ga-Zn with those of other magnetoelastic alloys in its class. The partial substitution of Ga with Zn yields values for the magnetoelastic coupling factor, −b 1, comparable to those of the binary Fe-Ga alloy.

Keywords

Materials Science and Engineering, Magnetostriction, Zinc, Thermoelasticity, Elastic moduli, Single crystals

Disciplines

Engineering Physics | Metallurgy

Comments

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Effects of Zn additions to highly magnetoelastic FeGa alloys

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$Fe_{1-x}M_x$ (M = Ga, Ge, Si, Al, Mo and x ~ 0.18) alloys offer an extraordinary combination of magnetoelasticity and mechanical properties. They are rare-earth-free, can be processed using conventional deformation techniques, have high magnetic permeability, low hysteresis, and low magnetic saturation fields, making them attractive for device applications such as actuators and energy harvesters. Starting with Fe-Ga as a reference and using a rigid-band-filling argument, Zhang *et al*. predicted that lowering the Fermi level by reducing the total number of electrons could enhance magnetoelasticity. To provide a direct experimental validation for Zhang's hypothesis, elemental additions with lower-than-Ga valence are needed. Of the possible candidates, only Be and Zn have sufficient solubility. Single crystals of bcc Fe-Ga-Zn have been grown with up to 4.6 at. % Zn in a Bridgman furnace under elevated pressure (15 bars) in order to overcome the high vapor pressure of Zn and obtain homogeneous crystals. Single-crystal measurements of magnetostriction and elastic constants allow for the direct comparison of the magnetoelastic coupling constants of Fe-Ga-Zn with those of other magnetoelastic alloys in its class. The partial substitution of Ga with Zn yields values for the magnetoelastic coupling factor, $-b_1$, comparable to those of the binary Fe-Ga alloy. [http://dx.doi.org/10.1063/1.4907181]

I. INTRODUCTION

Adding *p*- and *d*-elements such as Be, Al, Si, Ni, Ga, Ge, Mo, Sn, and W to iron has been shown to produce alloys with an increased magnetostriction over that of pure iron, with the exception of Sn. The addition of gallium gives the overall largest increase in the tetragonal magnetostriction, λ_{100}, by over an order of magnitude.[1–4] Recent experiments on binary alloys tested the influence of a higher-than-Ga valence, and the studies showed that increasing the electron valence concentration leads to a decrease in the magnetoelastic coupling constant $-b_1$(Fe-Ga) > $-b_1$(Fe-Ge) and $-b_1$(Fe-Al) > $-b_1$(Fe-Si)) in A2 disordered solid solution. Attempts to further enhance the magnetostriction of Fe-Ga by partially substituting for Ga in ternary alloys have not been successful.[2,4] Restorff *et al.*[2] showed that the first peak in the magnetoelastic curve vs composition for bcc Fe-X, where X is one of the *p*-elements listed above, falls at nearly the same valence-electron to atom ratio (*e*/*a*) which indicates these alloys adhere to Hume-Rothery rules of alloy stability.[5] In addition, Fe-Ga-Ge and Fe-Ga-Al ternary alloys followed the same behavior.[2] A deviation from the rule was observed for Si and the deviation was attributed to the large atomic size difference between Si and Fe, which may play a greater role in phase stabilization. Zhang *et al.*[6] used density functional calculations to show that the large magnetostriction of the Fe-Ga alloys stems from intrinsic electronic factors that are expressed by increases in the strain dependence of the magnetic anisotropy energy, which is proportional to the magnetoelastic coupling factor. With this method, they were able to compute λ_{100} for compositions up to 19 at. % Ga. Using rigid band analysis on the binary Fe-Ga alloy, the trend of magnetostriction against the number of electrons was extracted. Self-consistent calculations for $Fe_{87.5}Ga_{12.5}$, $Fe_{87.5}Ga_{6.25}Zn_{6.25}$, and $Fe_{87.5}Zn_{12.5}$ predicted the ternary alloy to have a magnetostriction constant that is 43% higher than that of the binary Fe-Ga alloy but predicted the Fe-Zn binary alloy to be only slightly higher than that of Fe-Ga binary.

There have been no reports of experimental validations of these predicted ternary results in part due to the challenges of working with zinc metal. A cursory review of the phase diagram reveals that zinc has a large solubility in bcc iron at elevated temperatures, but because its boiling point (907 °C) is much less than the melting point of iron (1538 °C), and due to its high vapor pressure, typical alloying processes such as arc melting or induction melting are not feasible. Corson *et al.*[7] prepared very weakly textured bulk Fe-Zn alloys by loading their sintering ampoule in the presence of a magnetic field and then subjecting the liquid-phase sintered pellet to explosive compaction, followed by a homogenizing anneal. The result was a minimal enhancement in saturation magnetostriction values, on average, large scatter in the data

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and no specific trend vs. zinc composition. The authors attributed this result to compositional non-uniformity and microcracks in the samples. Later, Thuanboon *et al.*[8] obtained similar results, also showing insignificant changes in the magnetostriction with Zn composition, using untextured samples that were liquid-phase sintered only. While the relative densities were comparable to the compacted samples (60%–67%), the distribution of the porosity was found not to be uniformly distributed throughout the sample. Thuanboon concluded that Zn does not influence the magnetostriction in Fe. Our own work has included alloy synthesis by vapor phase diffusion followed by an extended anneal. This process yielded untextured, chemically homogeneous samples with 2.4% porosity comparable to the Thuanboon study. The magnetostriction values were found to be no higher than those of pure Fe. In view of practical applications of these materials, it should be noted that, for bulk polycrystalline alloys, the saturation magnetostriction, λ_{sat}, for cubic systems includes both the tetragonal λ_{100} and the rhombohedral λ_{111} magnetostriction constants, and therefore it is sensitive to crystallographic texture, or preferred orientation. For isotropic polycrystalline alloys, the saturation magnetostriction is influenced more by λ_{111}, according to the equation

$$\lambda_{sat} = (2/5)\lambda_{100} + (3/5)\lambda_{111}.$$

Since λ_{111} is small and often negative for Fe-based systems, unremarkable strains are often reported in polycrystalline measurements.

To validate the theoretical predictions for the tetragonal magnetostriction constant, λ_{100}, oriented single crystal samples are necessary to make strain measurements along the [100] crystallographic direction. Furthermore, single crystals allow the measurement of all the elastic constants of the material which, in turn, allows for the calculation of the anisotropic magnetoelastic coupling coefficient $-b_1$, according to the relationship

$$-b_1 = 3\lambda_{100}(c_{11} - c_{12}),$$

where c_{11} and c_{12} are two of the independent elastic moduli of the crystal. The combination $\frac{1}{2}(c_{11} - c_{12})$ is equal to the shear modulus c' and it is the elastic modulus reported here. The magnetoelastic coupling coefficient is the more appropriate quantity for comparing alloy systems as it accounts for differences in the strain derivative of the magnetoelastic anisotropy between alloy systems. In this study, single crystals of Fe-Ga-Zn have been grown for the first time. Our magnetostriction and elastic moduli measurements enabled the calculation of $-b_1$.

II. EXPERIMENT

Ingots of Fe-Ga of compositions specifically chosen to establish the trend leading up to the first peak[2] in λ_{100} were made by arc melting and drop casting electrolytic iron flake (99.95%) (pre-melted for outgassing) and gallium (99.9999%). An ingot of $Ga_{25}Zn_{75}$ was made by melting gallium and zinc (99.997%), in a sealed quartz tube. A hole was drilled in each Fe-Ga casting, and an appropriate quantity of Ga-Zn was inserted into the hole to achieve the desired compositions. The ingot was placed in an alumina Bridgman style crucible that was placed inside of a secondary container of graphite. The furnace was heated to 200 °C before backfilling to 13 bars with high purity argon. It was then heated to 1575 °C, where it reached a final pressure of 15 bars, before immediately withdrawing at a rate of 5 mm/h. When the thermocouple adjacent to the tip of the ingot reached 900 °C, the translation was stopped and the ingot was annealed for approximately 1.5 days to relieve stress and increase grain size. It was then cooled to room temperature at a rate of 600 °C/h, referred to here as the slow-cooled (SC) condition. Quenched (Q) condition refers to post-growth annealing at 1000 °C or 800 °C, for Fe-Ga and Fe-Ga-Zn, respectively, for 4 h followed by quenching into water.

Single crystal disks of Fe-Ga-Zn (see Table I for compositions used in this study along with their respective valence-electron to atom ratios) approximately 6.4 mm in diameter and 2 mm thick, with a {100} face and with the [100] direction marked on the face, were prepared for the measurement of λ_{100} by traditional strain gage techniques.[2] Single crystal rectangular parallelepipeds of approximately $3 \times 2.5 \times 2\,mm^3$, with faces, parallel to {100} planes were used to measure the elastic moduli by resonant ultrasound spectroscopy (RUS).[9] Measurements were performed between temperatures of 7–301 K and magnetic field strengths of 0–15 kOe. Because of segregation during normal freezing crystal growth, the composition varied along the length of the ingots. For this reason, disk and parallelepiped pairs were harvested from the as-grown ingot at the same relative location along the length of the ingot, within our targeted composition range. The disks were harvested first and for some compositions, the grains were not of sufficient size or shape to also harvest RUS samples. The value of c' for these compositions was estimated from the measured ones through an extrapolation in order to calculate $-b_1$ at all compositions where λ_{100} was measured. Because of weight loss during growth and composition segregation, each sample was examined in a scanning electron microscope (SEM) fitted with an energy dispersive spectrometer (EDS) to determine phase purity and composition, utilizing elemental standards.

III. RESULTS

Comparing the tetragonal magnetostriction, λ_{100}, vs. e/a for several binary Fe-X alloys (Fig. 1), one can see that the Fe-Ga alloy has the highest magnetostriction value over the

TABLE I. Room temperature magnetostriction coefficient values and the electron to atom ratios (e/a) (taking Fe = 1, Zn = 2, and Ga = 3) for Fe-Ga-Zn compositions used in this study.

Composition	λ_{100}	e/a
$Fe_{86.34}Ga_{13.02}Zn_{0.64}$	220	1.267
$Fe_{82.6}Ga_{12.8}Zn_{4.6}$	270	1.302
$Fe_{81.5}Ga_{14.4}Zn_{4.1}$	298	1.329
$Fe_{83.2}Ga_{16.3}Zn_{0.5}$	301	1.331
$Fe_{81.2}Ga_{15.3}Zn_{3.5}$	308	1.341

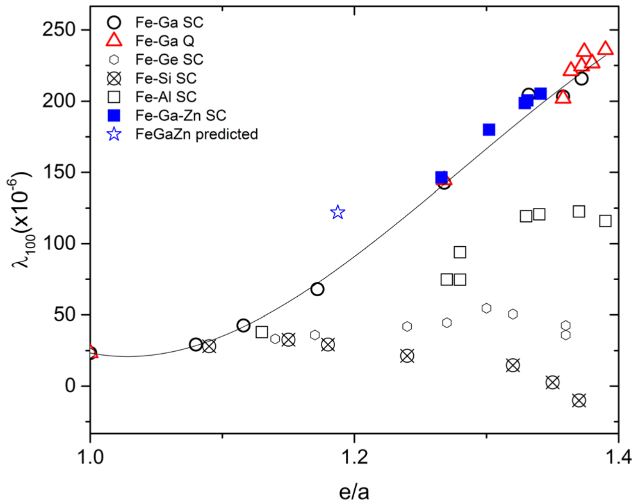

FIG. 1. Magnetostriction, λ_{100}, vs. electron to atom ratio, e/a, for Fe-X alloys. The line is included as a guide to the eye. All binary data are from Ref. 2. Predicted data point is from Ref. 6.

entire e/a range shown. At the highest e/a (red triangles), an extension of the monotonic increase in λ_{100} of Fe-Ga is achieved through annealing and quenching from elevated temperatures.[10] As a result, the e/a first-peak value for Fe-Ga is higher for the quenched than for the slow cooled alloy. This peak shift has been correlated with the ability to retain the bcc phase field in the alloy to higher Ga concentrations.[10] The solid line is included as a guide to the eye. The Fe-Ga-Zn results are shown as blue solid squares and correspond to the slow-cooled condition. The addition of Zn into the binary Fe-Ga results in an increase in λ_{100} by only 7%, which is much less than the predicted 43% increase for the 50:50 Ga-Zn ratio of $Fe_{87.5}Ga_{6.25}Zn_{6.25}$[6] (denoted with a star in Fig. 1).

Figure 2 shows the shear moduli data, c′, for binary Fe-Ga SC samples that were obtained through RUS.[9] (see Table II for tabular data.) The line is included as a guide to the eye.

TABLE II. Resonant ultrasound spectroscopy elastic constant values at room temperature, with and without an applied magnetic field, for Fe-Ga-Zn compositions used in this study.

Composition	c_{11}	c_{12}	c_{44}	c'	Field	e/a
$Fe_{81.8}Ga_{13.0}Zn_{5.2}$	178.2	127.1	119.9	25.5	On	1.312
	176.5	126.1	119.5	25.2	Off	
$Fe_{83.0}Ga_{14.7}Zn_{2.3}$	188.2	137.2	121.5	25.5	On	1.317
	187.4	136.5	121.2	25.5	Off	
$Fe_{83.6}Ga_{16.1}Zn_{0.3}$	181.5	131.9	122.5	24.8	On	1.325
	178.6	129.1	122.2	24.8	Off	

The c′ values for Fe-Ga-Zn (obtained by the same method) are 4%–7% higher than the binary trend, indicating that the substitution of Zn for Ga stiffens the lattice for that particular shear deformation. From the measured λ_{100} and c′ values, the magnetoelastic coupling coefficient, $-b_1$, has been calculated and is shown in Fig. 3 at the five concentrations where λ_{100} was measured. Compared with the $-b_1$ values for Fe-Ga, the Fe-Ga-Zn data are 2% higher at the lowest e/a value and increase to 6% higher at the highest e/a value. Considering only SC data, an increase in $-b_1$ for the ternary additions suggests that Zn has enhanced the magnetoelastic coupling over the binary alloys, however by very small amounts. This increase in coupling, by itself, would lead to an increase of the magnetostrictive (strain) response, but the effect is being countered by an increase in stiffness. The interplay between elasticity and magnetization is evident even when comparing binary alloys, for example, Fe-Ga and Fe-Al.[11] These two alloy systems have similar magnetoelastic coupling constants but the magnetostriction for the Fe-Al is significantly less than that of Fe-Ga due to its higher stiffness. These results emphasize the importance of measuring both magnetostrictive strains and elastic moduli in order to understand the role that changing the chemistry has on the magnetoelastic response of ferromagnetic alloys. These

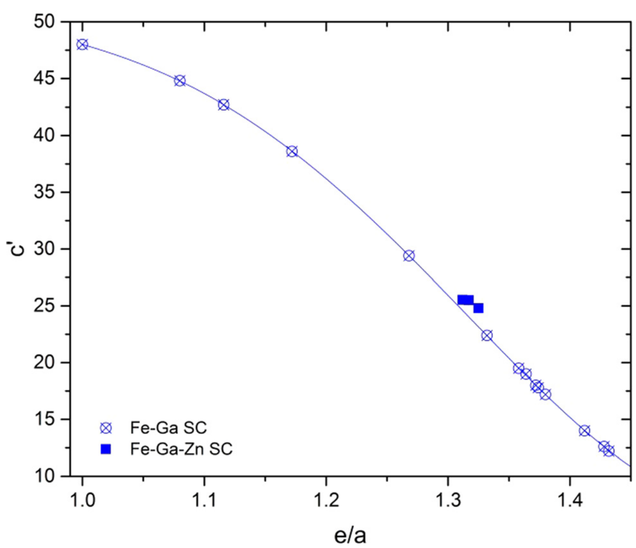

FIG. 2. Shear modulus, c′, vs. electron to atom ratio, e/a, for Fe-Ga and Fe-Ga-Zn. Lowering the e/a by ternary additions of Zn to Fe-Ga slightly increases c′. The line is included as a guide to the eye. Binary data are from Ref. 2.

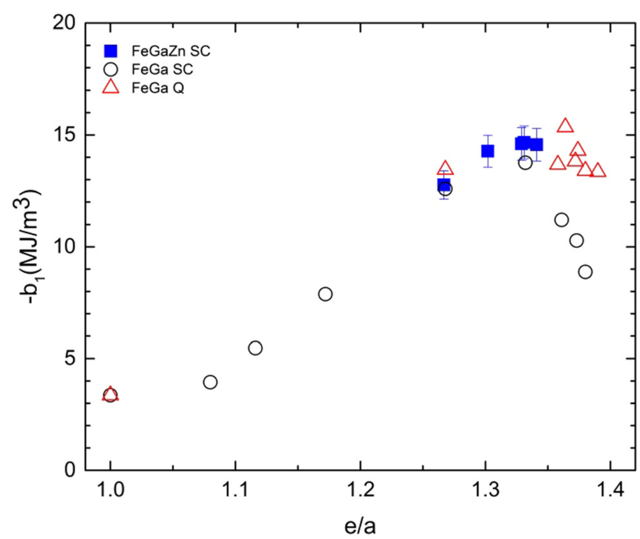

FIG. 3. Magnetoelastic coupling coefficient, $-b_1$, vs. electron-to-atom ratio, e/a, for SC and quenched (Q), (100) single crystal samples. Lowering the e/a by ternary additions of Zn to Fe-Ga slightly improves $-b_1$. Binary data are from Ref. 2.

results also highlight how remarkable and effective gallium is as a softening agent for Fe-based alloys and how this lattice softening effect[12] contributes to the significant λ_{100} magnetostrictive strains observed in Fe-Ga.

IV. CONCLUSION

For the first time, single crystals of Fe-Ga-Zn have been synthesized and the effect of substituting a lower-than-Ga valence atom on the magnetoelastic properties of Fe-Ga was studied. While both the values of the magnetoelastic coupling coefficient $-b_1$ and the elastic modulus c' for Fe-Ga-Zn increase slightly over those of the binary Fe-Ga, their effects work in opposition when one considers the response in the tetragonal magnetostriction constant, λ_{100}. The values of λ_{100} were measured and found to increase only slightly over those of the binary alloys, significantly short of the theoretically predicted value for a composition of $Fe_{87.5}Ga_{6.25}Zn_{6.25}$. The ability to determine the contribution of elastic moduli and magnetostriction constants to the magnetoelastic coupling is essential to understanding the effect of Zn substitution on the magnetoelastic interactions in Fe-Ga alloys.

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[1]A. E. Clark, M. Wun-Fogle, J. B. Restorff, T. A. Lograsso, and G. Petculescu, J. Appl. Phys. **95**(11), 6942–6944 (2004).
[2]J. Restorff, M. Wun-Fogle, K. Hathaway, A. Clark, T. Lograsso, and G. Petculescu, J. Appl. Phys. **111**(2), 023905 (2012).
[3]S. Guruswamy, T. V. Jayaraman, R. P. Corson, G. Garside, and S. Thuanboon, J. Appl. Phys. **104**(11), 113919 (2008).
[4]J. B. Restorff, M. Wun-Fogle, A. E. Clark, T. A. Lograsso, A. R. Ross, and D. L. Schlagel, J. Appl. Phys. **91**(10), 8225–8227 (2002).
[5]G. Petculescu, A. O. Mandru, W. M. Yuhasz, T. A. Lograsso, M. Wun-Fogle, J. B. Restorff, A. E. Clark, and K. B. Hathaway, J. Appl. Phys. **107**(9), 09A926 (2010).
[6]Y. N. Zhang, J. X. Cao, and R. Q. Wu, Appl. Phys. Lett. **96**(6), 062508 (2010).
[7]R. Corson, S. Thuanboon, and S. Guruswamy, in *Advanced Materials for Energy Conversion III, Proceedings of a Symposium Held During the TMS 3rd Annual Meeting*, edited by D. Chandra, P. R. Bautista, and A. Imam (Minerals, Metals & Materials Society, San Antonio, TX, United States, 2006), pp. 221–228.
[8]S. Thuanboon, N. Srisukhumbowornchai, T. V. Jayaraman, and S. Guruswamy, in *8th Global Innovations Symposium: Metal Powders for Energy Production and Storage Applications*, edited by Z. Fang and J. Sears (Minerals, Metals & Materials Society, 2007), pp. 19–25.
[9]G. Petculescu, K. B. Hathaway, T. A. Lograsso, M. Wun-Fogle, and A. E. Clark, J. Appl. Phys. **97**(10), 10M315 (2005).
[10]Q. Xing and T. Lograsso, Scr. Mater. **65**(4), 359–362 (2011).
[11]J. R. Cullen, A. E. Clark, M. Wun-Fogle, J. B. Restorff, and T. A. Lograsso, J. Magn. Magn. Mater. **226**, 948–949 (2001).
[12]J. L. Zarestky, V. O. Garlea, T. A. Lograsso, D. L. Schlagel, and C. Stassis, Phys. Rev. B **72**(18), 180408(R) (2005).