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Abstract
Iron is a well-utilized material in structural and magnetic applications. This does not mean, however, that it is well understood, especially in the field of magnetostriction. In particular, the rhombohedral magnetostriction of iron, λ111 , is anomalous in two respects: it is negative in sign, in disagreement with the prediction of first principles theory, and its magnitude decreases with increasing temperature much too rapidly to be explained by a power law dependence on magnetization. These behaviors could arise from the location of the Fermi level, which leaves a small region of the majority 3d t2g states unfilled, possibly favoring small internal displacements that split these states. If this view is correct, adding small amounts of Co to Fe fills some of these states, and the value of λ111 should increase toward a positive value, as predicted for perfect bcc Fe. We have measured the magnetostriction coefficients (λ111 and λ100) of pure Fe, Fe97Co3, and Fe94Co6 single crystals from 77 K to 450 K. Resonant ultrasound spectroscopy has been used to check for anomalies in the associated elastic constants, c 44 and c′. The additional electrons provided by the cobalt atoms indeed produced positive contributions to bothmagnetostriction constants, λ111 and λ100, exhibiting an increase of 2.8×10^{-6} per at. % Co for λ111 and 3.8×10^{-6} per at. % Co for λ100.

Keywords
Materials Science and Engineering, Magnetostriction, Elasticity, Fermi levels, Iron, Single crystals

Disciplines
Engineering Physics | Metallurgy

Comments
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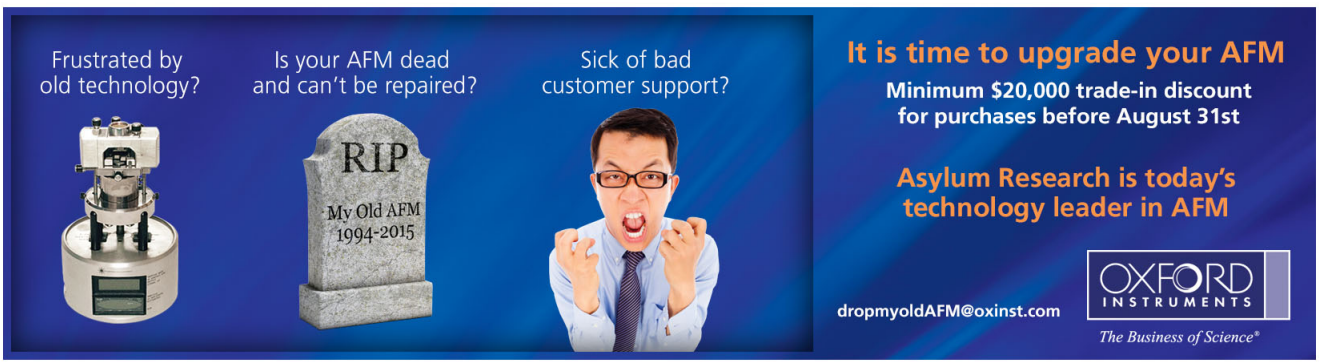

Rhombohedral magnetostriction in dilute iron (Co) alloys

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Iron is a well-utilized material in structural and magnetic applications. This does not mean, however, that it is well understood, especially in the field of magnetostriction. In particular, the rhombohedral magnetostriction of iron, λ_{111}, is anomalous in two respects: it is negative in sign, in disagreement with the prediction of first principles theory, and its magnitude decreases with increasing temperature much too rapidly to be explained by a power law dependence on magnetization. These behaviors could arise from the location of the Fermi level, which leaves a small region of the majority 3d t_{2g} states unfilled, possibly favoring small internal displacements that split these states. If this view is correct, adding small amounts of Co to Fe fills some of these states, and the value of λ_{111} should increase toward a positive value, as predicted for perfect bcc Fe. We have measured the magnetostriction coefficients (λ_{111} and λ_{100}) of pure Fe, $Fe_{97}Co_3$, and $Fe_{94}Co_6$ single crystals from 77 K to 450 K. Resonant ultrasound spectroscopy has been used to check for anomalies in the associated elastic constants, c_{44} and c'. The additional electrons provided by the cobalt atoms indeed produced positive contributions to both magnetostriction constants, λ_{111} and λ_{100}, exhibiting an increase of 2.8×10^{-6} per at. % Co for λ_{111} and 3.8×10^{-6} per at. % Co for λ_{100}. [http://dx.doi.org/10.1063/1.4916541]

I. INTRODUCTION

First principles calculations incorporating spin-orbit coupling can now reliably predict magnetostriction in elements and alloys[1,2] with one glaring exception: the rhombohedral magnetostriction of iron and its dilute alloys.[3,4] The calculated λ_{111} for pure bcc iron at 0 K is 12×10^{-6} (Ref. 3), whereas its measured values from the current study are negative, -34×10^{-6} at 77 K and -24×10^{-6} at room temperature (in agreement with Ref. 5). The temperature dependence of λ_{111} for Fe is also anomalous, changing much more rapidly with temperature than the usual power law dependence[6] on magnetization.[7] Zhang *et al.*[4] have reported that a displacement of 0.1 Å of the central atom in an Fe bcc unit cell is sufficient to change the sign of the undisplaced atom calculation of λ_{111}, without significantly changing λ_{100} (for which the original calculation agrees with the measurements). They propose that small amounts of residual carbon in experimental samples might cause such a displacement. Alternatively, the particular location of the Fermi level of bcc Fe in a region of majority band t_{2g} density of states (DOS) (Fig. 1) may favor an internal distortion of the bcc lattice, which splits those states electronically. In their discussion of first principles calculations of elastic constants in dilute Fe alloys, Zhang *et al.*[8] suggested a predilection toward a rhombohedral (c_{44}) distortion in these materials. This distortion splits the degenerate t_{2g} at the Fermi level and lowers the band energy. This, or a more complex distortion with the same effect of splitting the degenerate t_{2g} states, either alone or combined with the effects of impurities, might explain the anomalous sign of λ_{111} and possibly its anomalous temperature dependence.

In order to test this distortion hypothesis we have measured λ_{111} and λ_{100} as a function of temperature from 77 to 450 K for single crystals of pure Fe, and Fe with 3 at. % or 6 at. % added Co. The extra electrons provided by cobalt are expected to move the Fermi level to a higher energy, filling more of the majority t_{2g} states, stabilizing the bcc structure and diminishing the assumed distortion. A rigid-band approximation, with the exchange splitting adjusted to keep the Fermi level in the minority states fixed, predicts that, at 12 at. % Co, the DOS will decrease rapidly and that, at 16 at. % Co, all the empty majority d states will have been filled,[9] eliminating the mechanism for distortion.

II. EXPERIMENT

Single crystal samples with nominal compositions of $Fe_{97}Co_3$ and $Fe_{94}Co_6$ were synthesized from high purity Fe (99.95 wt. %) and Co (99.9 wt. %) by repeated arc melting under an argon atmosphere. The resulting buttons were remelted and drop cast into a copper chill-cast mold. The crystal was grown from the as-cast ingot in an alumina

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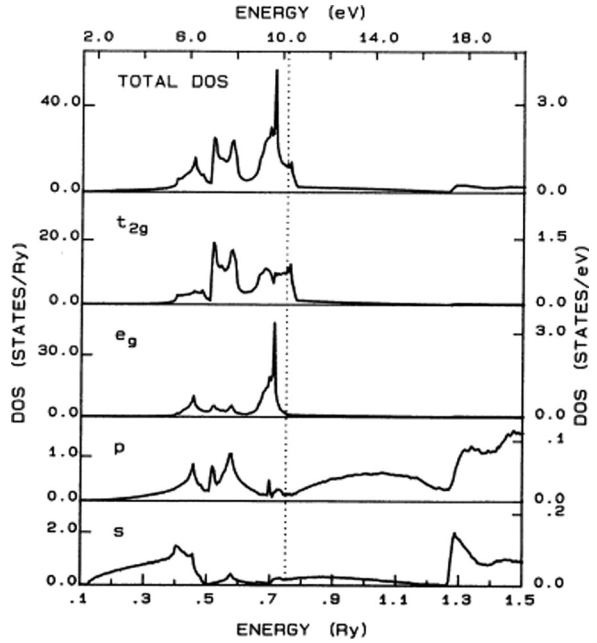

FIG. 1. DOS of majority d states of Fe. Reprinted with permission from D. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986). Copyright 1986 Plenum.[10]

Bridgman-style crucible. It was heated to 1500 °C under vacuum to outgas, then backfilled under a 2800 kPa argon atmosphere to diminish gas pockets and minimize evaporation at temperature. The ingot was homogenized at 1600 °C before directional solidification at 5 mm/h. Grain growth was achieved through *in situ* strain annealing by heating above the fcc transition, then cooling at a rate of 3.33 °C/min into the bcc region to 860 °C and holding there for 5 days, followed by cooling to room temperature at 10 °C/min. This procedure yielded irregularly shaped grains up to ~1–2 cm across. The pure Fe single crystal samples were grown similarly to the Fe-Co samples, but starting with a 99.987 wt. % Fe precursor and proceeding by an arc zone refining technique rather than Bridgman growth. Individual grains were selected and oriented by back-reflection Laue x ray diffraction. Disks ~6.4 mm in diameter and ~2 mm thick with ⟨100⟩ ($Fe_{96.7}Co_{3.3}$ and $Fe_{93.9}Co_{6.1}$) or ⟨110⟩ ($Fe_{96.8}Co_{3.2}$ and $Fe_{94.0}Co_{6.0}$) directions perpendicular to the disk faces were used for magnetostriction measurements. Parallelepipeds with sides between 2 and 3 mm and faces perpendicular to ⟨100⟩ directions were used for elastic constant measurements. Compositions were measured by wavelength dispersive spectroscopy (WDS). For brevity, we will refer to the Co composition for all samples as their value rounded to one significant figure.

The elastic constants associated with λ_{100} and λ_{111} are c' and c_{44}, respectively, and they were measured by resonant ultrasound spectroscopy (RUS) as a function of temperature in a 20 kOe saturating magnetic field. The results for Fe and $Fe_{96.9}Co_{3.1}$ are shown in Fig. 2. For $Fe_{93.6}Co_{6.4}$, however, only the room temperature value was determined. Fig. 2 also shows the Varshni[11] fits for the elastic constants as a function of temperature; these fits were used for the form-factor correction of the measured magnetostriction values (see Sec. III). The fits are given by $c(T) = c_0 - s/[\exp(\Theta/T) - 1]$, where c_0, s, and Θ are fitting parameters and T is temperature. Table I shows the values of the fit parameters. Since the 6% Co sample had only one data point, there was no data to fit. To extend the data, the fit parameters from the 3% Co sample were used, but the fit magnitude itself was scaled to match the 6% Co data value at 300 K. The scaling factors were 1.044 for c' and 0.992 for c_{44}.

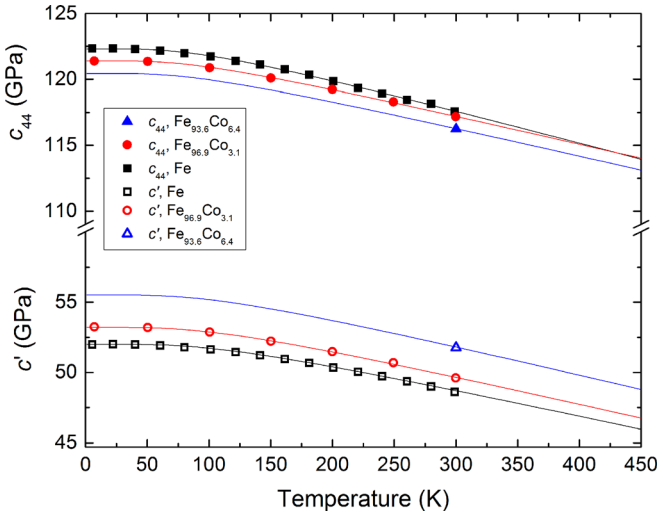

FIG. 2. Elastic constants from RUS measurements (points). The solid lines are Varshni fits to the data. The $Fe_{93.6}Co_{6.4}$ curve uses the $Fe_{96.9}Co_{3.1}$ fitting parameters scaled to agree with the $Fe_{93.6}Co_{6.4}$ data point at 300 K.

Magnetostriction constants λ_{100} and λ_{111} were measured by standard strain gauge techniques, rotating the sample 360° about its face normal in a fixed, in-plane, saturating magnetic field. In this paper, λ is the magnetostriction coefficient; (3/2) λ is the measured saturation strain, i.e., $\lambda_{\|} - \lambda_{\perp}$, where $\lambda_{\|}$ and $\lambda_{\perp}$ are the strains with the field parallel and perpendicular to the strain gauge. To evaluate λ_{100}, the disk samples described above with ⟨100⟩ normal to the disc face were bonded with strain gauges aligned along a ⟨100⟩ in-plane direction. To lowest order, peak-to-peak strain values at saturating fields equal (3/2) λ_{100}. To determine λ_{111}, the {110} oriented disks were bonded with a strain gauge aligned along a ⟨111⟩ in-plane direction. The magnetostriction measurements were corrected for the form effect employing Gersdorf's method,[12] using the fitted elastic constants from above and an estimate of saturation magnetization taken from Ref. 13, p. 714, for pure Fe. Measurements from 77 K to 300 K were performed in fields of 20 kOe using Kyowa KFL-1-120-C1-11 strain gauges, and those from 300 K to 450 K were performed in fields of 8 kOe using Micro-Measurements EA-06-031CE-350 strain gauges; despite the difference in the maximum field applied, 8 kOe was also found to be enough to saturate the sample. The

TABLE I. Parameters used for the temperature dependence of the elastic constants. The elastic constants are given in units of GPa.

Material	Elastic constant	c_0	s	Θ
Fe	c'	52.6	6.1	314
Fe	c_{44}	122.3	6.7	265
$Fe_{96.9}Co_{3.1}$	c'	53.2	6.2	303
$Fe_{96.9}Co_{3.1}$	c_{44}	121.4	5.6	254

magnetostriction over the temperature range of 77 K to 450 K is shown in Fig. 3 for Fe, $Fe_{97}Co_3$, and $Fe_{94}Co_6$. The standard deviation for a set of 10 measurements taken in succession at 150 K was measured to be less than 1×10^{-6}. Any abrupt shift in the magnetostriction values with increasing temperature is due to slight changes in the measurement direction caused by strain gauge reapplication. λ_{100} increases with the addition of Co, as expected, since alloys near the 50–50 composition are known to have large ⟨100⟩ magnetostrictions.[14] The negative rhombohedral magnetostriction constant λ_{111} decreases in magnitude more rapidly with Co additions, and the inflection point in the temperature dependence curve moves to lower temperatures, even though the Curie temperature increases.

III. DISCUSSION

Both λ_{100} and λ_{111} of the Fe-Co alloys increase more rapidly with Co additions than would be expected in the low-Co region from the assumed linear interpolation of older work using single crystals at room temperature (see Fig. 4). In addition, λ_{111} moves toward positive values, as calculated for pure Fe from first principles. A linear extrapolation of our data shows the change in sign to a positive λ_{111} is expected at ~9 at. % Co. While some of these values appear to be trending toward higher values than those measured in older publications for the B2 phase region, more recent research has also measured higher values for $Fe_{50}Co_{50}$ and $Fe_{35}Co_{65}$ ($\lambda_{100} = 176$ ppm for 50:50).[14,15]

To reach the positive value predicted by first principles calculations for pure Fe ($\lambda_{111} = 12 \times 10^{-6}$), approximately 13 at. % added Co would be required. By linearly extrapolating our

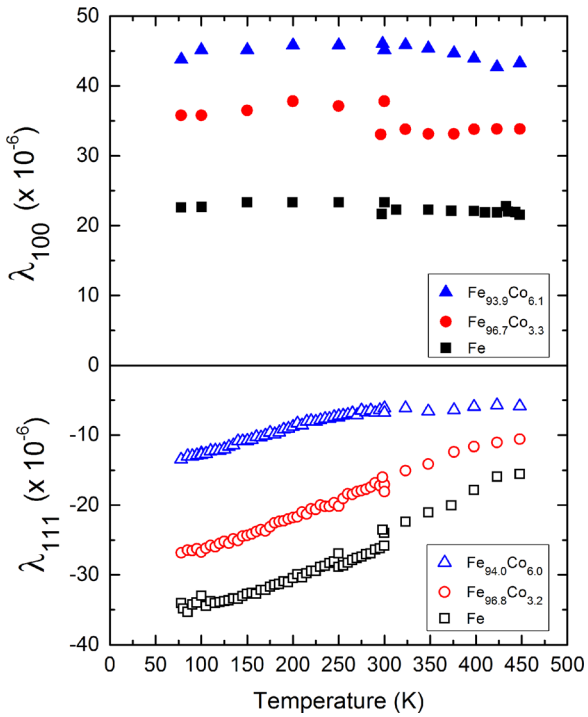

FIG. 3. Single crystal magnetostriction constants of Fe, $Fe_{97}Co_3$ and $Fe_{94}Co_6$ vs. temperature. The saturation strains are (3/2) of the plotted λ_{100} and λ_{111}. The discontinuities in the data at 300 K are the result of using different experimental setups and the reapplication of strain gauges.

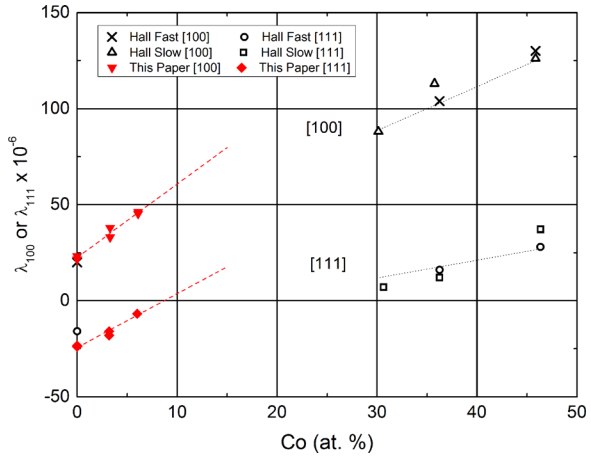

FIG. 4. Our room temperature single crystal magnetostriction constants plotted with data from Hall.[5] The saturation magnetostrictions are (3/2) of the plotted λ_{100} and λ_{111}.

measured values of λ_{100} and λ_{111} to higher Co contents, we can calculate the polycrystalline isotropic magnetostriction value, λ_S, using $\lambda_S = (3/5)\ \lambda_{111} + (2/5)\ \lambda_{100}$, for 10 at. % Co at room temperature. This gives $\lambda_S = 27 \times 10^{-6}$ in comparison with the experimental value reported in literature,[16] $\lambda_S = 18 \times 10^{-6}$.

The temperature dependence of λ_{111} for the 3 at. % and 6 at. % Co samples shown in Fig. 3 remains anomalous. On average, λ_{111} decreases by about half between 77 K and 300 K. From the rigid band approximation described in the Introduction, one can calculate that the broadening of the Fermi level produced by a temperature increase of 300 K is of the same order of magnitude as the positive energy shift in the Fermi level produced by the addition of 3 at. % Co (~0.03 eV). By this simple argument, both the change of λ_{111} toward positive values through Co additions and its anomalously rapid change with temperature may be consistently explained as being a consequence of the Fermi level falling in a region of majority t_{2g} states, which "encourages" the dilute Fe-Co alloy to form a slightly distorted structure (and split the t_{2g} band) in order to reduce its energy.

IV. CONCLUSIONS

The magnetostriction and elastic constants of pure iron and two compositions of single crystal Fe-Co alloys (low Co concentration) have been measured. By adding small percentages of Co to the Fe matrix, the [100] and [111] magnetostrictions increase (in the positive direction) more than what can be estimated by a linear interpolation between pure Fe and 30+ at. % Co alloys. This rapid change pushes λ_{111} toward pure Fe's theoretical value, as predicted by first principles calculations. The discrepancy between experiment and theory for pure Fe is suggested to be due to a small displacement of specific Fe sites. By adding electrons, through Co additions, the need for this energy-reducing distortion is decreased, and the bcc phase is stabilized without the need for distortions, promoting agreement between theory and experiment. The anomalous drop-off in the temperature dependence of magnetostriction (along *only* the [111]

direction) remains at 6 at. % Co, although the inflection point of the drop-off has decreased in temperature.

The elastic constants have been used to obtain the form effect corrected magnetostriction values and do not show any anomalies in the temperature range studied herein.

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