Direct Measurement of Intrinsic Atomic Scale Magnetostriction

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Using differential x-ray absorption spectroscopy (DiffXAS) we have measured and quantified the intrinsic, atomic-scale magnetostriction of $Fe_{81}Ga_{19}$. By exploiting the chemical selectivity of DiffXAS, the Fe and Ga local environments have been assessed individually. The enhanced magnetostriction induced by the addition of Ga to Fe was found to originate from the Ga environment, where $\lambda^{\gamma,2}(\approx (3/2)\lambda_{100})$ is 390 ± 40 ppm. In this environment, $\langle 001 \rangle$ Ga-Ga pair defects were found to exist, which mediate the magnetostriction by inducing large strains in the surrounding Ga-Fe bonds. For the first time, intrinsic, chemically selective magnetostrictive strain has been measured and quantified at the atomic level, allowing true comparison with theory.

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It is well known that Fe in its pure form exhibits only an extremely small magnetostriction ($\lambda_{100} = 20$ ppm, $\lambda_{111} = -16$ ppm), but experiments performed initially on FeAl alloys [1], and more recently Fe-Ga alloys [2], have revealed that the presence of nonmagnetic metallic elements in the Fe lattice can produce an enhancement in magnetostriction of over an order of magnitude. Compositions of $Fe_{(1-x)}Ga_x$ with around 19 at % Ga have reported magnetostrictive strains of up to 400 ppm [3]. This makes them of interest as candidates for micro- or nano- sensors and actuators, particularly since alloys with larger, or giant magnetostriction (such as the much studied Terfanol-D) commonly contain expensive rare-earth elements and have undesirable mechanical properties for device applications [4,5].

In 2002, Wu proposed a model for the enhancement of magnetostriction in $Fe_{(1-x)}Ga_x$ alloys, deriving magnetostriction coefficients from first principles [6], and suggesting a tetragonal "B2-like" structure in the vicinity of Ga atoms was responsible for the observed enhancement. More recently, Cullen *et al.* [7] have modeled the behavior of the magnetocrystalline anisotropy of $Fe_{(1-x)}Ga_x$, reaching a similar conclusion and stating that such a structure could be formed by $\langle 001 \rangle$ Ga pairs, which could be randomly arranged throughout the material.

Little experimental work has sought to validate such theoretical models, since, in the absence of a local atomic probe, microscopic behavior must be inferred from macroscopic measurements on bulk samples, typically using strain gauge techniques [3,8]. However, the recent development of differential x-ray absorption spectroscopy (DiffXAS), which has demonstrated a sensitivity to atomic strain of the order of femtometres, makes such a direct assessment of local-scale magnetostriction possible [9,10].

In this letter we present the results of DiffXAS measurements of the magnetostriction of $Fe_{81}Ga_{19}$ and the subsequent analysis procedure developed to extract and quantify the atomic magnetostriction coefficients. These coefficients, which provide information from a local perspective, are extremely complementary to those obtained macroscopically, but have the advantage of being a direct measure of atomic strain rather than an inference from some external device. The chemical selectivity of XAS also permits the magnetostriction to be studied from the point of view of different atomic species. A DiffXAS experiment may thus be considered to observe the intrinsic magnetostriction of the sample, which is more readily comparable to theoretical calculations, and which is insensitive to many problems—such as crystal defects, dislocations, and even the process of attaching strain gauges to thin films—that are currently recognized as a significant source of variation in reported coefficient values [11].

Such measurements will therefore be of critical importance in understanding fundamental atomic behavior in systems, including $Fe_{(1-x)}Ga_x$, where sample preparation, and subsequent treatment, are known to play a key role in the development of enhanced magnetostrictive properties. They also pave the way for direct validation of models

describing such behavior, and will aid their future development.

Samples of $Fe_{81}Ga_{19}$ were made from iron and gallium of high purity (>99.9%), initially melted together 5 times using an arc-melting furnace under an argon atmosphere, to produce an ingot of about 6 g mass. Some pieces of mass close to 100 mg were cut from the ingot and remelted to obtain small spherical samples. These were then inserted into an Edmund Bühler splat-cooling apparatus, where the sample is levitated and melted inside an inductive coil. When the current to the coil was deactivated, the liquid fell through a laser detector that caused the drop to be pressed between two opposing copper plates, quenching it at a rate of about 10^6 K s^{-1}. This produced foils of 80 μm thickness, which were then mechanically thinned to 10 μm to allow x-ray absorption measurements to be made in transmission geometry.

XRD and TEM characterization of the foils revealed the existence of crystallites less than 100 nm in size, with the Ga absorbed into the Fe structure to produce a good solid solution in an A2 structure rather than a two phase mixture. XRD revealed that a third of crystallites were orientated with [100] vectors perpendicular to the surface of the foil, a third with [211] perpendicular to the surface, and a third randomly orientated.

DiffXAS spectra were acquired on ID24, the dispersive XAS spectrometer of the European Synchrotron Radiation Facility (ESRF) [12]. We used the same rotating magnet apparatus and measurement procedure as reported by Pascarelli *et al.* [13]. Figure 1 shows the raw, normalized DiffXAS spectra at both the Fe K and Ga K edges. Overlaid on each are the contributions from scattering paths within the first two atomic coordination shells, obtained by Fourier filtering the data to $1.8 \leq R \leq 2.8$ Å at each edge.

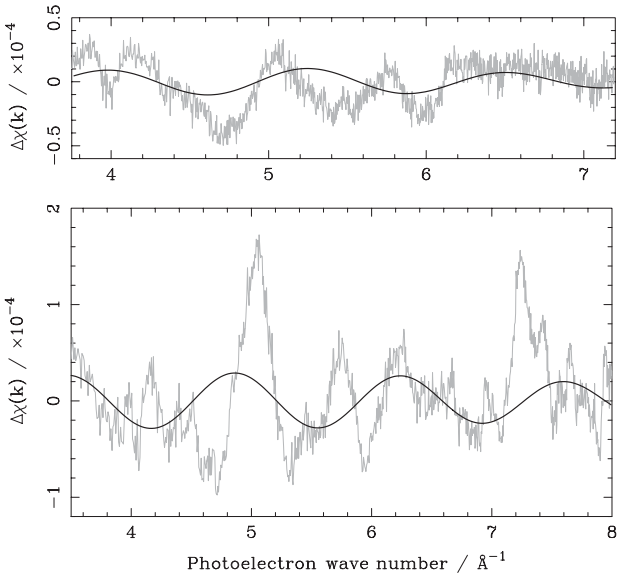

FIG. 1. Raw DiffXAS signals (gray) from $Fe_{81}Ga_{19}$ at the Fe-K (top) and Ga K (bottom) edges. The black plots are the scattering contributions from the first two atomic coordinations shells, obtained by Fourier filtering.

Starting from the magnetostriction tensor $\mathbf{T}$, which is of fourth rank, the strain $\boldsymbol{\epsilon}$ along any given photoelectron scattering leg may be found by contracting the tensor onto the sample magnetization $\mathbf{M}$ and the leg vector $\boldsymbol{\beta}$. Since DiffXAS measures structural changes between two magnetization states, the observed strain $\boldsymbol{\Delta\epsilon}$ is the difference between strains at $\mathbf{M}'$ and $\mathbf{M}''$. Thus,

$$\Delta\epsilon_k = \epsilon_k'' - \epsilon_k' = \sum_{lmn} T_{klmn}\beta_l(M_m''M_n'' - M_m'M_n') \quad (1)$$

The number of independent parameters in $\mathbf{T}$ may be significantly reduced by exploiting the crystal symmetry though Neumann's Principle [14]. In the case of cubic crystals, only two Joule magnetostriction coefficients remain [15,16]. These are atomic coefficients, which, although roughly proportional, are not strictly equivalent to the commonly employed macroscopic λ_{100} and λ_{111}. We therefore adopt the notation of de Lacheisserie [17]. The coefficients are then $\lambda^{\gamma,2}$, which describes motion along the cubic [100] axis, and $\lambda^{\epsilon,2}$, for motion along [111]. Using contracted Voigt notation for the subscripts, the tensor, which is symmetric, may then be populated as follows [18]

$$\begin{aligned} T_{11} &= T_{22} = T_{33} = \tfrac{2}{3}\lambda^{\gamma,2} \approx \lambda^{100}, \\ T_{12} &= T_{13} = T_{23} = -\tfrac{1}{3}\lambda^{\gamma,2} \approx -\tfrac{1}{2}\lambda^{100}, \\ T_{44} &= T_{55} = T_{66} = 2\lambda^{\epsilon,2} \approx 3\lambda^{111}. \end{aligned} \quad (2)$$

The Voigt subscripts map onto the tensor subscripts according to $1 \rightarrow 11$, $2 \rightarrow 22$, $3 \rightarrow 33$, $4 \rightarrow 23, 32$, $5 \rightarrow 31, 13$, and $6 \rightarrow 12, 21$. From Eq. (1), the observed strain in a complete scattering path p of atomic coordination shell j, $\boldsymbol{\Delta s}_{j,p}$, may be found by summing contributions from each of the q path legs, $\boldsymbol{\Delta\epsilon}_{j,p,q}$ as follows

$$\boldsymbol{\Delta s}_{j,p} = (\mathbf{P}\cdot\hat{\boldsymbol{\Delta\epsilon}}_{j,p,1})(\mathbf{P}\cdot\hat{\boldsymbol{\Delta\epsilon}}_{j,p,L})\sum_q \boldsymbol{\Delta\epsilon}_{j,p,q}. \quad (3)$$

The vector dot products between the x-ray polarization $\mathbf{P}$ and the first and last scattering legs provide the contrast between measurements taken at $\mathbf{M}'$ and $\mathbf{M}''$, and so give rise to the linear dichroism in the x-ray absorption fine-structure (EXAFS) [9]. The magnitudes of the $\boldsymbol{\Delta s}_{j,p}$ are the strains required in the differential fine-structure function given by Pettifer *et al.* [9]. However, since we use a polycrystalline sample, it is necessary to average contributions from different crystallites, each of which are either orientated at an angle θ about some preferential axis, or randomly in space. The measured, magnetostrictive DiffXAS, $\Delta\chi_m$, is then

$$\Delta\chi_m = \sum_j A_j \cos(s_j k + \Phi_j) k \left\langle \frac{1}{N}\sum_{p=1}^{N} |\boldsymbol{\Delta s}_{j,p}| \right\rangle_{\theta,\phi}, \quad (4)$$

where N is the number of paths in shell j, which must be

handled explicitly since magnetostriction breaks the usual degeneracy that exists when the sample is in an unmagnetized state. $\Delta\chi_m$, and the scattering amplitude A_j and phase Φ_j, are functions of the photoelectron wave vector k.

For disordered samples, as considered here, local component fluctuations may induce structural defects that break the crystal symmetry. Neumann's Principle does not, therefore, strictly hold, and so the observed motion of an atom under magnetostrictive strain may not completely abide with that predicted from a given crystal symmetry alone. There will be some error between an atom's observed and predicted positions. Such errors manifest themselves in the DiffXAS as an apparent change in static disorder and so can be modeled through a change in a scattering path's Debye-Waller factor $\Delta\sigma_j^2$, similar to the thermal case [19].

$$\Delta\chi = \Delta\chi_m - \sum_j 2A_j \sin(s_j k + \Phi_j) k^2 \Delta\sigma_j^2. \qquad (5)$$

The $\Delta\sigma_j^2$ increase in magnitude as any violation of Neumann's Principle becomes more significant, and vanish under strict adherence, making them a good indicator to the validity of a given magnetostriction model.

Considering only the scattering paths within the first two coordination shells of the absorbing atom—all of which were single-scattering Fe-Ga, Ga-Fe, Fe-Fe, or Ga-Ga paths—the A_j and Φ_j in (4) and (5) were calculated from *ab initio* theory using the FEFF code [20]. A conventional EXAFS analysis was then performed, using spectra obtained from BM29 at the ESRF, to determine the structural parameters s_j and σ_j^2. These are shown in Table I. The analysis at the Ga K edge revealed the presence of Ga-Ga pair bonds in the second coordination shell as postulated by Cullen *et al.* [7], and also recently observed in $Fe_{80}Ga_{20}$ melt-spun ribbon samples [21].

With these absolute structural factors known, the only remaining parameters for the DiffXAS analysis were the structural strains themselves: $\lambda^{\gamma,2}$ and $\lambda^{\epsilon,2}$ to obtain the $\Delta s_{j,p}$, and any $\Delta\sigma_j^2$ as necessary. These were fitted to the filtered experimental spectra of Fig. 1 using the DEXA code, which was developed for this project. The results are shown in Fig. 2.

TABLE I. $Fe_{81}Ga_{19}$ structural parameters obtained from conventional EXAFS based upon an A2 cubic model. $s_j = 2R_j$ is the path length, and $\sigma^2{}_j$ the Debye-Waller factor. The path subscripts denote paths in the first and second coordination shells. The Fe-K data ranged between $2.6 \leq k \leq 20.0$ Å^{-1} and the Ga K between $2.6 \leq k \leq 12.3$ Å^{-1}. Contributions at both edges were filtered to $3.6 \leq s'_j \leq 5.6$ Å—which differs slightly from the real s_j due to core potential and scattering phase shifts—and fitted simultaneously such that the Fe-Ga paths at the Fe K edge were reciprocated as Ga-Fe paths at the Ga K edge.

Path	Degeneracy	s_j/Å	$\sigma_j^2/\times 10^{-3}$ Å^2
$Fe\text{-}Fe_1$	5 at Fe K only	4.92 ± 0.01	8.6 ± 0.4
$Fe\text{-}Ga_1$	3 at Fe K, 8 at Ga K	5.085 ± 0.006	12.2 ± 0.3
$Fe\text{-}Fe_2$	5 at Fe K only	5.748 ± 0.008	7.2 ± 0.5
$Fe\text{-}Ga_2$	1 at Fe K, 5 at Ga K	5.86 ± 0.01	17 ± 1
$Ga\text{-}Ga_2$	1 at Ga K only	6.04 ± 0.02	4 ± 2

Each edge was analyzed separately and according to the rules of cubic crystal symmetry. The Fe K edge analysis yielded magnetostriction coefficients of $\lambda^{\gamma,2} = 40 \pm 10$ ppm and $\lambda^{\epsilon,2} = (-32 \pm 5)$ ppm. This is interesting since it represents only a relatively minor enhancement upon the magnetostriction of pure Fe. By contrast, the Ga K edge analysis gave $\lambda^{\gamma,2} = (390 \pm 40)$ ppm—over an order of magnitude greater than pure-Fe, and of the order observed macroscopically—and $\lambda^{\epsilon,2} = (-10 \pm 20)$ ppm. In both cases, including $\Delta\sigma_j^2$ terms yielded no significant improvement to the quality of the fits, thus indicating that Neumann's Principle was not significantly violated.

As a first conclusion, it is clear that the macroscopically observed enhancement in the magnetostriction of $Fe_{81}Ga_{19}$ is driven by atomic strains in the vicinity of the Ga atoms. Strains in the Fe environment are only increased by around a factor of 2. Indeed, since XAS techniques are unable to distinguish between equivalent atomic pairs in inequivalent configurations—such as, say, Fe-Fe in a purely Fe environment, or in an environment containing some Ga atoms—it is possible that the environment devoid of Ga in its immediate vicinity remains unchanged compared to pure-Fe, and that the increased $\lambda^{\gamma,2}$ arises from enhanced strain in environments containing at least one Ga atom.

In addition to this, a further important observation was made with respect to the nature of the magnetostriction surrounding Ga. For data at this edge, the sum over con-

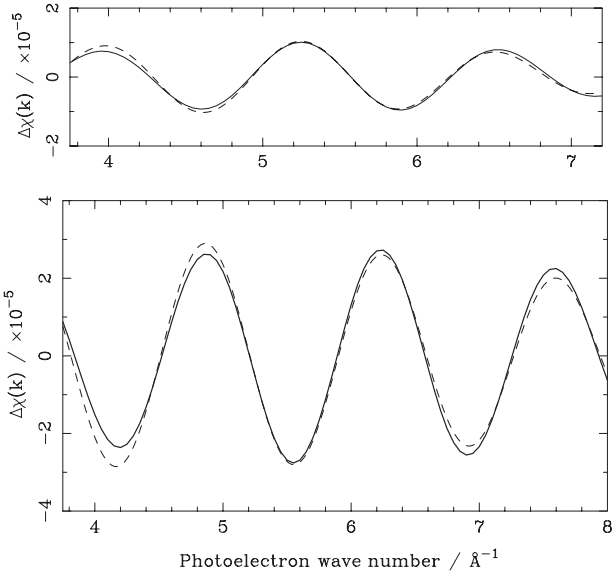

FIG. 2. Theory DiffXAS fits (solid) to the filtered experimental spectra from Fig. 1 (dashed) at the Fe K (top) and Ga K (bottom) edges. At each edge, the fitted parameters were the magnetostriction coefficients $\lambda^{\gamma,2}$ and $\lambda^{\epsilon,2}$.

tributions from scattering paths j in Eq. (4) can potentially include Ga-Fe paths in the first two shells, and Ga-Ga paths in the second shell as listed in Table I. All three were used to model the conventional EXAFS signal. However, including all three in the DiffXAS model, and fitting $\lambda^{\gamma,2}$, resulted in a spectrum with a large spurious phase shift with respect to experiment, indicating a problem with the model.

Removing the contribution from Ga-Ga bonds, and thereby asserting that such bonds do not contribute to $\lambda^{\gamma,2}$, eliminated this anomalous phase shift and provided good agreement with experiment. Since a DiffXAS signal will only record perturbations to the local atomic structure, this indicates that magnetostrictive strain between the Ga-Ga pairs themselves is small and is not the source of enhanced magnetostrictive behavior. Rather, it is exclusively the motion of the Fe atoms surrounding Ga that provides the macroscopically observed enhancement.

Combining this result with those from the Fe K edge and the conventional EXAFS analysis, we can provide experimental confirmation of a number of aspects of the theory put forward by Cullen *et al.* [7]. Firstly, we see the anticipated $\langle 001 \rangle$ Ga-Ga pairs within the sample, and with them the ''B2-like'' coherent defect that forms the core of the proposed model. Separate magnetostriction analyses at the Fe and Ga sites confirm that the macroscopically observed magnetostriction emanates from the Ga environment, with the Fe environment experiencing an enhancement of only a factor of 2 above that of pure Fe. Importantly, the Ga-Ga pairs themselves do not contribute to the enhanced magnetostriction. This confirms the assertion that it is magnetostrictive strain in the vicinity of these defects rather than the defects themselves that are the source of the enhancement.

In summary, we have firstly demonstrated the ability of DiffXAS to measure atomic magnetostriction in $Fe_{81}Ga_{19}$, and, through subsequent analysis, provide quantified magnetostriction coefficients. The experimental and analysis procedures are entirely general and may be applied to the study of magnetostriction in any given system. The technique may furthermore be applied to other studies (such as electrostriction, piezoelectricity, elastic compliance, etc.) simply by inserting the appropriate tensor into Eq. (1). We have also shown the power of element selectivity, inherent to XAS techniques, in determining the intrinsic source of magnetostrictive strain. Combining these results with conventional EXAFS observations, we have then provided direct experimental verification of a number theoretical proposals concerning the enhancement of magnetostriction in $Fe_{(1-x)}Ga_x$ alloys.

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[1] R. C. Hall, J. Appl. Phys. **28**, 707 (1957).
[2] A. E. Clark, J. B. Restorff, M. Wun-Fogle, T. A. Lograsso, and D. L. Schlagel, IEEE Trans. Magn. **36**, 3238 (2000).
[3] 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).
[4] S. Guruswamy, N. Srisukhumbowornchai, A. E. Clark, J. B. Restorff, and M. Wun-Fogle, Scr. Mater. **43**, 239 (2000).
[5] R. A. Kellogg, A. M. Russell, T. A. Lograsso, A. B. Flatau, A. E. Clark, and M. Wun-Fogle, Acta Mater. **52**, 5043 (2004).
[6] R. Wu, J. Appl. Phys. **91**, 7358 (2002).
[7] J. Cullen, P. Zhao, and M. Wuttig, J. Appl. Phys. **101**, 123922 (2007).
[8] R. A. Kellogg, A. B. Flatau, A. E. Clark, M. Wun-Fogle, and T. A. Lograsso, J. Appl. Phys. **91**, 7821 (2002).
[9] R. F. Pettifer, O. Mathon, S. Pascarelli, M. D. Cooke, and M. R. J. Gibbs, Nature (London) **435**, 78 (2005).
[10] M. P. Ruffoni, R. F. Pettifer, S. Pascarelli, A. Trapananti, and O. Mathon, in *13th International Conference on X-ray Absorption Fine Structure*, edited by B. Hedman (American Institute of Physics, New York, 2007), p. 838.
[11] R. Grössinger, R. Sato Turtelli, N. Mehmood, S. Heiss, H. Müller, and C. Bormio-Nunes, J. Magn. Magn. Mater. **320**, 2457 (2008).
[12] S. Pascarelli, O. Mathon, M. Muñoz, T. Mairs, and J. Susini, J. Synchrotron Radiat. **13**, 351 (2006).
[13] S. Pascarelli, M. P. Ruffoni, A. Trapananti, O. Mathon, G. Aquilanti, S. Ostanin, J. B. Staunton, and R. F. Pettifer, Phys. Rev. Lett. **99**, 237204 (2007).
[14] J. F. Nye, *Physical Properties of Crystals: Their Representation by Tensors and Matricies* (Oxford University Press, Oxford, 1985), p. 20, ISBN 0-198-51165-5.
[15] E. du T. de Lacheisserie, *Magnetostriction: Theory and Applications of Magnetoelasticity* (CRC Press, Boca Raton, FL, 1993), p. 130.
[16] A third parameter, $\lambda^{\alpha,2}$, is neglected since it describes volume magnetostriction and so does not contribute to the DiffXAS.
[17] E. du T. de Lacheisserie, *Magnetostriction: Theory and Applications of Magnetoelasticity* (CRC Press, Boca Raton, FL, 1993).
[18] E. du T. de Lacheisserie, *Magnetostriction: Theory and Applications of Magnetoelasticity* (CRC Press, Boca Raton, FL, 1993), p. 161.
[19] M. P. Ruffoni, R. F. Pettifer, S. Pascarelli, A. Trapananti, and O. Mathon, J. Synchrotron Radiat. **14**, 421 (2007).
[20] J. J. Rehr and R. C. Albers, Phys. Rev. B **41**, 8139 (1990).
[21] S. Pascarelli, M. P. Ruffoni, R. Sato Turtelli, F. Kubel, and R. Grössinger, Phys. Rev. B **77**, 184406 (2008).