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Experimental exploration of the origin of magnetostriction in single crystalline iron

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The magnetostrictive atomic strain in a pure Fe single crystal was measured by differential x-ray absorption spectroscopy. The obtained tetragonal magnetostriction constant, $(3/2)\lambda_{100}$, was determined to be 45 ppm, consistent with the previously reported theoretical value calculated from a spin-orbit coupling theory. These results provide a foundation for understanding the origin of magnetostriction in pure Fe as well as Fe-based binary alloys. © *2010 American Institute of Physics*. [doi:10.1063/1.3481083]

Materials with large Joule magnetostriction find wide applications in sensors, actuators, and energy harvesting devices. Understanding the origin of magnetostriction has been a research focus over more than half a century because of both scientific interests and its importance in better control and exploitation of materials for engineering applications. From early theoretical calculations[1] using concepts of magnetic dipole moment and spin-orbit treatments to a recent first-principles calculation[2] based on spin-orbit coupling theory, discrepancies between the theoretical values and experimentally measured macroscopic value[3] for pure Fe have been narrowed but still exist. More recently, Fe-enriched Fe–Ga alloys which are structurally similar to body-centered cubic (bcc) Fe have been studied extensively due to their unique combination of large magnetostriction and mechanical properties. However, the origin of their large tetragonal magnetostriction constant, $(3/2)\lambda_{100}$,[4] remains an open question. Calculations[5] of $(3/2)\lambda_{100}$ in Fe–Ga alloys by a first-principles approach according to spin-orbit coupling theory suggest that the origin of magnetostriction is from intrinsic electronic origins. Neglecting the value of calculated strain, the magnetostriction sign of the Fe–Ga $D0_3$ phase was predicted to be negative, in contrast to the positive strain observed experimentally.[6] Recently, the calculation methods have been improved and these provide better agreement with experimental results,[7] for the discrete structural models employed in the calculations. These structural models provide insight into favored Ga atomic arrangements but do not correctly capture the nature of the experimentally observed nonrandom distributions of Ga atoms present in the bcc lattice. Meanwhile, an extrinsic model states a series of displacive phase transformations account for the large magnetostriction in the Fe–Ga alloys.[8] It is therefore of primary importance to be able to disentangle the contribution of any eventual "extrinsic" effect from the intrinsic mechanism due to spin-orbit coupling.[9] A fundamental step in this direction is to obtain a detailed understanding of magnetostriction in a Fe pure single crystal where strain arises only from spin-orbit coupling, as its high degree of symmetry precludes any origin of the linear magnetostriction other than spin-orbit coupling.

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As spin-orbit coupling is an atomic phenomenon, measurement of strain on an atomic scale in pure single crystalline Fe is highly desirable, as it provides a connection to theoretical approaches for validation and improvement of calculations. These measurements have been made recently possible by differential x-ray absorption spectroscopy (DiffXAS).[10–12] DiffXAS measures strain on an atomic scale by examining variations in a sample's extended x-ray absorption fine-structure (EXAFS) under two different sample magnetization conditions.[10,11] The DiffXAS signal arises from changes in photoelectron scattering paths that surround a central, x-ray absorbing atom, and therefore give strain information on an atomic scale. It is more sensitive to a small atomic strain (down to tens of parts per million[12]) than other x-ray techniques such as conventional x-ray absorption spectroscopy and lattice parameter measurement. Atomic strains are obtained by fitting a DiffXAS signal[13] assuming that the strain is uniform throughout the material and crystal symmetry is not broken. Conventional EXAFS is also required to obtain the local atomic environment for the fitting.

In this work, we measured the atomic strain of a pure Fe single crystal by DiffXAS and obtained $(3/2)\lambda_{100}$. Pure Fe (99.95 wt % purity) single crystals were grown at the Materials Preparation Center, Ames Laboratory[14] and cut into rectangular parallelepipeds ($2\ \text{mm} \times 1.5\ \text{mm} \times 250\ \mu\text{m}$). The sample plane was (100) and the four edges were sectioned along ⟨010⟩. On the sample, a thin window of dimensions $100 \times 85 \times 10\ \mu\text{m}^3$ was prepared by a double window technique[15] to permit DiffXAS measurements in transmission geometry. It was challenging to measure a single crystalline sample, as unavoidable and strong Bragg diffraction from a single crystalline sample corrupts both EXAFS and DiffXAS signals, narrowing the energy range over which useful data can be obtained. Our unpublished work showed that it was difficult to avoid strong Bragg diffraction in the interested energy range for Terfenol-D single crystalline samples with a [112] plane normal. A polycrystalline pure Fe foil was employed for EXAFS measurements so as to extract more accurate parameters from a larger energy range. These EXAFS spectra, which were also used for calibrating the energy scale of the DiffXAS data,[16] were taken at beamline BM29 of the European Synchrotron Radiation Facility (ESRF).

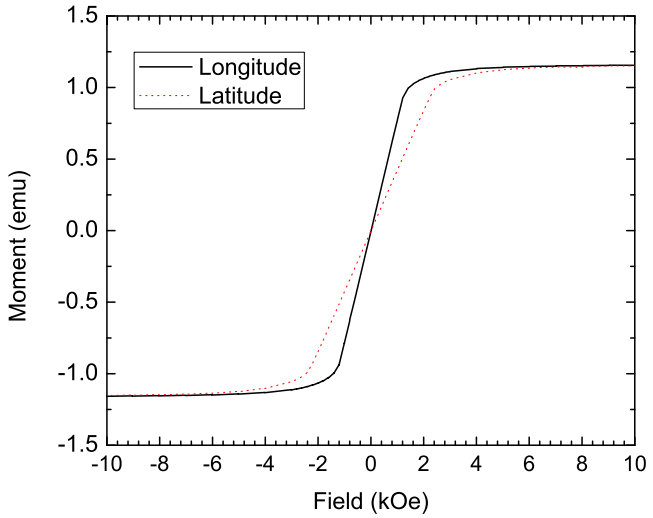

FIG. 1. (Color online) Magnetization measurement showing the sample is saturated at 5.7 kOe. Because of shape anisotropy, the sample was magnetized faster when the magnetic field was applied along the longitude direction.

The DiffXAS measurements were performed at ID24, the ESRF's energy dispersive XAS spectrometer.[17] The full width at half maximum (FWHM) of the incident beam was 5 μm. The acquired DiffXAS signals were normalized by the sample thickness (edge jump) before strain fitting with the DEXA code.[13] The sign of the strain was determined by the direction of x-ray polarization and initial magnetization state of the sample. Simulation of the EXAFS was carried out from *ab initio* theory using the FEFF code.[18] A magnetic field of 5.7 kOe was applied to the sample in its two $\langle 010 \rangle$ directions, parallel and perpendicular to the x-ray polarization vector, in the (100) sample plane during the DiffXAS measurements.

Magnetization measurements at 300 K using a 50 kOe Quantum Design MPMS SQUID magnetometer reveal that the sample was saturated at 5.7 kOe (Fig. 1) and magnetization difference in the two $\langle 010 \rangle$ directions is only 1.3% at 5.7 kOe. Therefore, the shape demagnetization factor of the sample should not significantly affect the strain measurement.

The Fe K-edge EXAFS spectra from simulation, the polycrystalline foil, and the single crystal are consistent, allowing us to extract the static EXAFS parameters from the polycrystalline Fe foil and to use these parameters to fit the DiffXAS signal from the single crystal with the strain variant, $(3/2)\lambda_{100}$. The refined static parameters are tabulated in Table I. These parameters vary with those for background removal, Fourier transform, and backward Fourier transform. However, our results reveal that the variation of the static parameters with reasonable fitting quality does not affect the strain measurement within the error range of about 2 ppm.

TABLE I. Static EXAFS parameters extracted from a polycrystalline Fe foil. The lattice constant $a=2.8665$ Å was employed as a first approximation to the local structure. R_1 and R_2 are the radii of the first and second shells, respectively. σ_1^2 and σ_2^2 are Debye–Waller factors for the first and second shells, respectively.

R_1/Å	R_2/Å	$\sigma_1^2/10^{-3}$ Å^2	$\sigma_2^2/10^{-3}$ Å^2
2.48 ± 0.01	2.866 ± 0.009	5 ± 1	8 ± 2

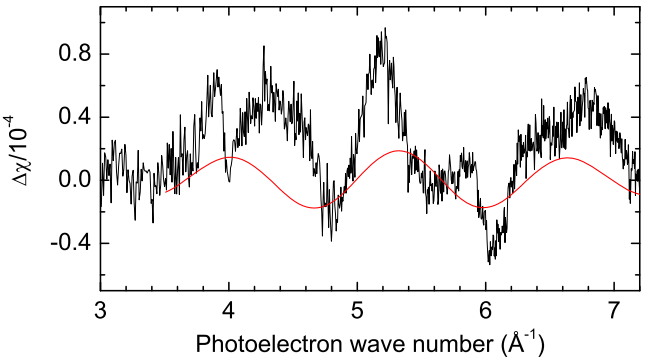

FIG. 2. (Color online) Raw DiffXAS Fe K-edge signal (noisy) from a pure Fe single crystal and scatter contribution from the first two atomic coordination shells that is obtained by Fourier filtration (smooth).

A raw Fe K-edge DiffXAS signal over the range from 3.0 to 7.2 Å^{-1} is shown in Fig. 2. The scatter contribution from the first two atomic coordination shells was extracted by Fourier filtering and subsequently used for the fit of $(3/2)\lambda_{100}$. Contributions from larger coordination shells in Fe were not considered. Figure 3 shows the filtered experimental spectrum and its least square fit from the DEXA code. $(3/2)\lambda_{100}$ was the variant for the fitting and determined to be 46 ± 2 ppm. Detailed fitting procedures were reported previously.[13] We also collected another set of DiffXAS data from a second sample location within the same window and obtained 43 ± 2 ppm for $(3/2)\lambda_{100}$. The average of the two measured values is 45 ± 2 ppm, which is in good accord with the calculated $(3/2)\lambda_{100}$ of 43.5 ppm.[8]

The excellent agreement of $(3/2)\lambda_{100}$ between the measured atomic strain in this work and previously calculated strain based on spin-orbit coupling theory provides the experimental demonstration that the origin of magnetostriction is through spin-orbit coupling. Furthermore, the fact that the magnetostrictive strain is found on neighboring Fe–Fe atomic pairs, provides an experimental basis for future theoretical calculations and may open a window to improve the mathematics of calculation.

This work clearly demonstrates the capability of DiffXAS in measuring a small atomic strain in a single crystal, as the DiffXAS signal from a strain around 45 ppm is evident (Fig. 2) and the fitting error is only around 2 ppm. A single crystalline sample provides a more rigorous measurement over a polycrystalline sample which is usually textured. For example, the DiffXAS measurement of an Fe-19 at. %

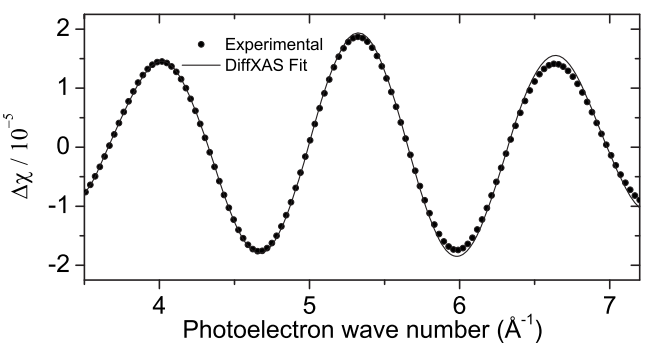

FIG. 3. Experimental DiffXAS Fe-K-edge spectra (solid) and its theoretical fit (dotted).

Ga polycrystalline ribbon gives $(3/2)\lambda_{100}$ to 40 ± 10 ppm between Fe-Fe atomic pairs, and 390 ± 40 ppm between Fe–Ga pairs.[11] These values are close to those macroscopically measured from pure Fe and Fe-19 at. % Ga single crystals,[6] respectively. However, the macroscopic $(3/2)\lambda_{100}$ measured with a miniature capacitance dilatometer is 700 ppm for an Fe-19 at. % Ga polycrystalline ribbon.[19] In principle, the volume fraction of each texture component can be measured and then used to calculate the contribution to the measured strain from each texture component. In practice, there are difficulties in accurately determining the volume fraction of each texture component in the same region measured by DiffXAS, considering the influence of spatial distribution of the texture components on the measurement, and obtaining reliable results from a least-square fit with many variables. In addition, the strain in each grain in a polycrystalline sample is not necessarily identical or the same as that of single crystalline Fe in the same orientation under magnetic saturation, since a grain is constrained by its neighboring grains with different orientations during magnetostrictive deformation. This is equally true for other magnetostrictive alloys, making single crystalline samples attractive for a wide range of DiffXAS applications.

This work on pure single crystalline Fe is not only necessary to validate theoretical work for Fe itself but also important in the context of investigating the magnetostriction physics of Fe-based alloys. Pure Fe is composed of a single atomic species and the crystallographic texture is fixed and controllable. Furthermore the Fe bcc structure is the base structure for each of the phases present in the Fe–X (X =Ga, Al, Ge, Si) magnetostrictive alloys, so understanding the behavior of pure Fe provides the foundation for understanding atomic strains in the Fe–X systems. Recent research efforts have clarified the structure-property relationship in Fe-Ga alloys, finding the magnetostrictive behavior to be phase dependent.[20,21] This phase dependence has also been found in other Fe-based binary systems such as Fe–Al,[22] Fe–Ge,[23] and Fe–Si.[24] Even though the Fe–Ga alloys of interest involve structural changes driven by chemical ordering, there is no relationship between the underlying microstructure and magnetic domains.[25,26] Short-range order (SRO), thought to be a precipitation precursor of long range chemically ordered precipitate, has little effect on the magnetostriction.[27] Together, these experimental results suggest the origin of magnetostriction in these alloys is intrinsic. The sensitivity of DiffXAS to a small strain as demonstrated in this work shows that this technique can be applied to single crystals of Fe–X single crystals in probing the neighboring atomic pairs that show largest and smallest strain. In this work, we showed that Bragg diffraction from the sample can be avoided in the energy range of interest for Fe K-edge DiffXAS on Fe and Fe–X single crystals of similar crystallographic symmetry.

In summary, we have measured magnetostrictive atomic strain in an Fe single crystal by DiffXAS. This is important in the aspects below. First, the measured strain is consistent with the theoretically calculated value, providing the experimental demonstration that spin-orbit coupling is the origin of magnetostriction in pure Fe. Second, this work unambiguously demonstrates the capability of DiffXAS in probing a small atomic strain in single crystals, as a polycrystalline sample may be associated with a large uncertainty in measurement results. Third, it shows that the destruction of DiffXAS signal due to the diffraction from the sample can be avoided in the energy region of interest for measurements at the Fe K-edge on high symmetry structures such as bcc. These results and our approach provide a strong basis for further exploration of the magnetostriction physics.

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