Effect of Pressure on Magnetoelastic Coupling in 3*d* Metal Alloys Studied with X-Ray Absorption Spectroscopy

S. Pascarelli,[1] M. P. Ruffoni,[1,2] A. Trapananti,[1] O. Mathon,[1] G. Aquilanti,[1] S. Ostanin,[2,3] J. B. Staunton,[2] and R. F. Pettifer[2]

[1]*European Synchrotron Radiation Facility, 6 rue Jules Horowitz, 38043 Grenoble, France*
[2]*Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom*
[3]*Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany*

(Received 12 July 2007; published 6 December 2007)

Using x-ray absorption spectroscopy, we have studied the effect of pressure on femtometer-scale bond strain due to anisotropic magnetostriction in a thin FeCo film. At 7 GPa local magnetostrictive strain is found to be larger than at ambient, in agreement with spin-polarized *ab initio* electronic structure calculations, but contrary to the expected effect of compression on bond stiffness. The availability of high pressure data on local magnetostrictive strain opens new capabilities for validating theoretical predictions and can lead to the development of materials with the desired properties.

DOI: 10.1103/PhysRevLett.99.237204 PACS numbers: 75.80.+q, 61.10.Ht, 75.50.Bb

Owing to spin-orbit coupling and dipole-dipole interaction terms in its Hamiltonian, the spin degrees of freedom in a ferromagnetic or antiferromagnetic crystal are coupled to atomic displacements. The static component of this interaction results in a shift in the equilibrium atomic positions. The simplest aspect of the static interaction is the *external* magnetostriction which is the change in the macroscopic crystal dimensions. From a microscopic point of view there are shifts in the atomic coordinates within each unit cell, and, in some circumstances, this *internal* magnetostriction may differ largely from the *external* magnetostriction [1]. Direct observation of internal distortions is, obviously, more difficult than observation of the *external* magnetostriction. The control of the thermodynamic pressure parameter represents a powerful way to explore this complex magnetoelastic coupling because it acts directly on interatomic distances. Compression modifies all energies in play in a magnetic system—the magnetic isotropic and anisotropic energies, the magnetoelastic and the elastic energies—and can lead to important modifications in structural, elastic, electronic, and magnetic properties of matter [2]. For example, in 3*d* metals and their alloys the effect of pressure is to widen the electronic bands, which in turn leads to a decrease of the density of states at the Fermi level, such that the magnetic state stability condition given by the Stoner criterion is no longer met [3]. In fact, theoretical calculations predict a suppression of magnetism in both Fe and Co with pressure [4,5]. Being able to track the pressure evolution not only of magnetic moments but also of local atomic displacements due to magnetostrictive strain can help disentangle the interplay between magnetic and structural degrees of freedom in magnetic materials. At ambient pressure, anisotropic (Joule) magnetostrictive strains in both Fe and Co are tiny, due to the very weak spin-orbit interaction typical of itinerant 3*d* magnetic systems. However, by mixing them to produce FeCo, local atomic strains induced by magnetostriction are slightly enhanced and can be measured [6]. Anisotropic magnetostriction originates directly from the strain dependence of the magnetocrystalline anisotropy (MCA) energy that can now be calculated for many systems [7,8]. In 3*d* metals, the signs of the magnetostriction constants can be explained through strain induced *d*-band broadening and shifting. MCA of ferromagnetic materials containing transition metals has become the subject of intensive theoretical and experimental research because of the technological implications for high-density magneto-optical storage media. An essential parameter to further increase the recording density in hard disk drives is a large uniaxial MCA. Recent *ab initio* calculations have shown that when the cubic lattice symmetry of ferromagnetic homogeneously disordered alloys is broken, i.e., by imposing a compositional modulation [9] or a tetragonal distortion [10], MCA is largely enhanced. The understanding of magnetostriction, and its theoretical description, still remains a great challenge because it is difficult to determine the magnetoelastic coupling, i.e., the dependence of MCA energy on lattice strain. In this respect, direct measurements of local strain values, as well as their evolution with pressure, can give a fundamental input to gain physical insight into this complex problem. Up to now only *external* magnetostriction measurements were presented in the literature, where microscopic information is lost through averages over different chemical bonds, crystal defects, etc. In this Letter, we present experimental results on the pressure evolution of femtometer local atomic displacements induced by anisotropic magnetostriction and compare them to state-of-the-art *ab initio* calculations. We show that the availability of experimental data on local magnetostrictive strain and its evolution with pressure, coupled to the recently achieved precision of modern calculations, open new capabilities for making theoretical predictions and, perhaps more importantly, provide meaningful physical insights. These models need experimental validation and there is a critical lack of data at high pressures. Furthermore, these experiments open the way to measurements of

anisotropic magnetostriction in structures that do not exist at ambient pressure and to follow their evolution with pressure and temperature. This opportunity could have far reaching implications in a number of fields and is something important to look at in the future.

We have applied x-ray absorption spectroscopy (XAS) in differential mode to measure the evolution of local magnetostrictive strain in FeCo as a function of pressure. Coupled to high pressure x-ray magnetic circular dichroism (XMCD) [11,12], this new technique has the potential to shed light into the origin of magnetic anisotropy in complex and disordered systems since it gives local atomic information, very complementary to macroscopic (''average'') data obtained using conventional methods. It has the potential to disentangle contributions to strain from AA, BB, and AB bonds in an A_xB_{1-x} alloy, for example. The development of differential XAS (DIFFXAS) techniques to measure tiny displacements was carried out at the energy dispersive XAS beam line of the European Synchrotron Radiation Facility (ESRF), ID24 [13], where a sensitivity to differential atomic motion of one femtometer has been achieved [6]. At ambient pressure and temperature, chemically ordered (disordered) $Fe_{50}Co_{50}$ crystallizes in the PM3-M (IM3-M) structure. No previous work was found in the literature on the structure or magnetic properties of FeCo at high pressures, whereas Fe and Co have been extensively studied both theoretically [4,5] and experimentally [14–17]. Fe is found to lose its ferromagnetic order at the onset of the bcc $\rightarrow$ hcp phase transition, at around 14 GPa [14,15,17], whereas Co remains ferromagnetic up to at least 100 GPa [16,17]. In order to track the pressure evolution of the local structure, the magnetostrictive strain, and ferromagnetism in FeCo, we have coupled high pressure extended x-ray absorption fine structure (EXAFS), DIFFXAS, and XMCD measurements at the Fe K edge. All experiments were carried out on beam line ID24, using a $7 \times 80 \times 80$ μm^3 chip of annealed polycrystalline FeCo of nominal composition 50:50. Our EXAFS measurements are insensitive to chemical order in this system, owing to the similarity of the scattering properties of Fe and Co. High resolution x-ray diffraction, carried out on beam lines ID27 and ID11 of the ESRF, show that some degree of chemical order might be present. This is also confirmed by the intensity and shape of the XMCD signal [18]. The sample was loaded in a nonmagnetic CuBe diamond anvil cell (DAC) equipped with a pair of 350 μm culet diamonds, one of which was perforated to reduce absorption. Placed within a 150 μm diameter hole of a 25 μm thick Inconel gasket, the sample was then surrounded by a 4:1 methanol:ethanol mixture known to provide hydrostatic conditions up to about 10 GPa [19]. The pressure was measured using the ruby fluorescence method [20]. Figure 1 shows an example of Fe K edge XAS and XMCD signals measured at $P = 3$ GPa, as well as the pressure evolution of the integral of the XMCD signal, I. The XMCD at the K edge of transition metals has been shown to scale with the $4p$ conduction band spin polarization [21]. The K edge XMCD signal can be used to track the evolution of the magnetic moment with pressure through modifications of the $4p$ band induced by changes in the $3d$ moment [11,15,17]. Details of the experimental setup and data reduction method for the XMCD measurements may be found in [12]. The presence of a signal up to 8 GPa indicates that ferromagnetism is preserved in FeCo in this pressure range. For the DIFFXAS measurements at high pressure, the DAC was placed at the center of a rotating magnetic field device, composed of 8 NdFeB permanent magnet elements, yielding a 0.5 T field sufficient to magnetically saturate FeCo. The system allows the rotation, via stepping motors, of the magnetic field on a plane perpendicular to the propagation of the linearly polarized x rays. Measurements of the absorption coefficient were made with the magnetic field direction being either parallel or perpendicular to the x-ray polarization vector. Transmitted intensity measurements were made repeatedly at every 90° angle between the magnetization vector and the photon polarization vector. The differential absorption was calculated from the transmitted intensities, averaged over a large number of cycles to improve the signal to noise ratio [12], and normalized by dividing by the edge jump. A fast readout low noise CCD-based detector developed at the ESRF was used, the FReLoN camera [22], allowing the reduction of acquisition time to a few hours for each high pressure DIFFXAS spectrum. Figure 2 shows Fe K edge XAS and DIFFXAS signals at ambient (blue) and at 6.9 GPa (red). The local structure around Fe is preserved in this pressure range, and the shift toward higher energy of the EXAFS oscillations indicates

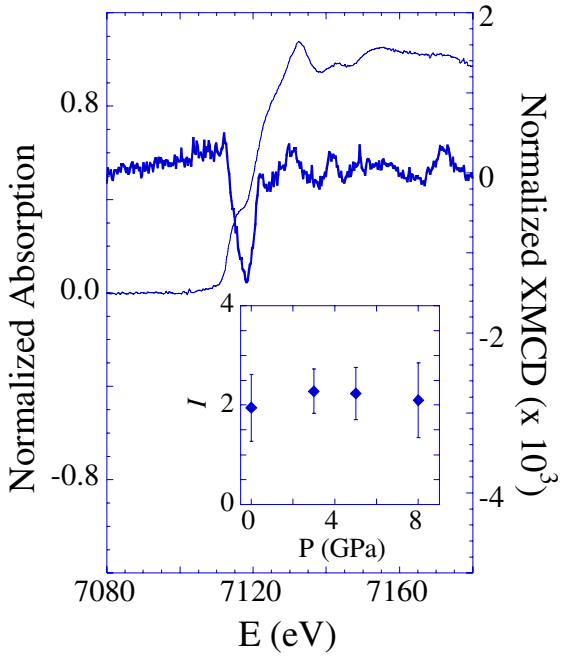

FIG. 1 (color online). Fe K edge XAS (thin line) and XMCD (bold line) signals on FeCo at $P = 3$ GPa. The inset shows the pressure evolution of the integral of the XMCD signal, I.

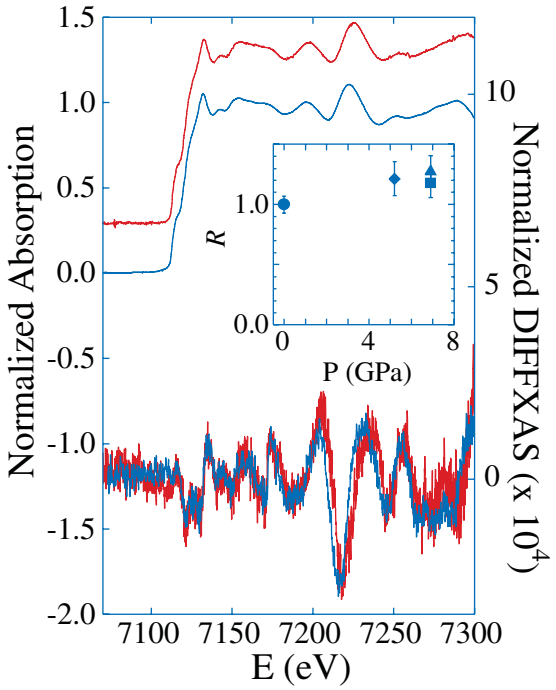

FIG. 2 (color). Fe K edge XAS and DIFFXAS signals on FeCo as a function of pressure. Blue: ambient; red: 6.9 GPa. The inset shows the pressure evolution of the ratio R between the amplitude of the DIFFXAS signal at pressure P and that at ambient (see the text for further details). Data from three independent runs (square, triangle, and lozenge) are compared to data at ambient (circle).

bond contraction. A complete EXAFS data analysis will appear elsewhere. At 6.9 GPa, the overall shape of the DIFFXAS signal is similar to that at ambient, although its frequency is slightly reduced to account for bond compression. We have shown [6] that this signal can be well reproduced by including all photoelectron scattering paths up to quintuple scattering for a cluster of radius 7.5 Å, and assuming that the interatomic strains scale directly with the macroscopic strain. At ambient pressure, the average value of local bond displacements due to magnetostriction is found to be of the order of a few fm [6]. The amplitude of the DIFFXAS signal is proportional to the sum, over all paths, of the amplitude of the corresponding EXAFS signal multiplied by the magnitude of path length changes [6]. Our EXAFS analysis shows that the amplitude of the signal at 6.9 GPa is equal to within a few percent of that at ambient. This is consistent with previous high pressure EXAFS work on Fe [23]. Therefore, any DIFFXAS amplitude variation in this pressure range is to be attributed to modifications in atomic displacements. As a first approximation, we quantify the amplitude by taking the peak-peak (P-P) value where the signal to noise ratio is highest, i.e., around $E = 7210$ eV. We have shown [6] that this large oscillation mostly arises from the photoelectron undergoing single scattering from the second neighbor shell, in the [100] direction. In FeCo, this is the crystallographic direction where magnetostrictive strain is largest, with a linear magnetostrictive constant $\lambda_{100} \sim 200$ ppm at ambient pressure.

In a cubic crystal, λ_{100} is related to the derivative of the MCA energy versus tetragonal strain, B_1, and to the elastic constants C_{11} and C_{12} [24]: $\lambda_{100} = -(2/3) \times [B_1/(C_{11} - C_{12})]$. This expression shows clearly how magnetostrictive strain results from an equilibrium between elastic energy and the strain dependence of MCA energy. Using experimental and theoretical data available from the literature on bcc Fe [25], the denominator term $C_{11} - C_{12}$ is found to increase approximately 15–20% between ambient and 10 GPa. This leads to smaller magnetostriction at high pressure and somewhat reflects the commonly accepted expectation that compression leads to shorter and ''stiffer'' bonds, therefore more difficult to deform. The pressure evolution of the numerator is unknown. An increase in B_1 could, of course, compensate or exceed that of the denominator, therefore changing the expected trend on bond strain dictated only by elasticity considerations. In the inset of Fig. 2 we plot the amplitude evolution as a function of pressure obtained from our experiments. The data shown here are relative to three different runs to check reproducibility, where each run corresponds to the loading of a fresh sample in the DAC. The DIFFXAS signal is seen to increase with pressure, and at 7 GPa its amplitude is about $(20 \pm 10)\%$ higher than at ambient. We therefore attempted a calculation of the pressure evolution of B_1 in bcc FeCo. Since magnetocrystalline anisotropy is caused largely by spin-orbit coupling it receives an *ab initio* theoretical description from the relativistic generalization of spin density functional theory [26]. Typically, the total energy, F, is calculated for 2 or more directions and then the MCA is obtained from the difference, ΔF. ΔF is typically small, ranging from meV to μeV, and high precision in calculating the energies is required [8,9]. We have calculated the total energy difference *ab initio* of a compositionally disordered 50:50 FeCo alloy when magnetized along $(1, 0, 0)$ and $(0, 0, 1)$ directions in the body centered tetragonal lattice for different volumes, compatible with the pressures used in the experiments, and different tetragonal distortions, c/a. We used the spin-polarized, relativistic, Korringa-Kohn-Rostoker (KKR) multiple scattering method where the disorder was treated with the coherent potential approximation (CPA) [8,9]. We found the magnetic moment on Fe and Co to be rather insensitive to pressure in the pressure range up to 8 GPa. Figure 3 shows the magnetocrystalline energy, $\Delta F = F(0, 0, 1) - F(1, 0, 0)$, versus tetragonal strain for 3 pressures. The increase of the gradient of the line, B_1, is important when the pressure is increased from ambient to 3.6 GPa. B_1 then stabilizes when the pressure is further increased to 8 GPa. The overall enhancement of B_1 largely compensates that of the elastic constants in this pressure range, leading to a larger magnetostriction at high pressure in agreement with experiment.

In conclusion, we have demonstrated the feasibility of an experiment that allows the measurement of the pressure

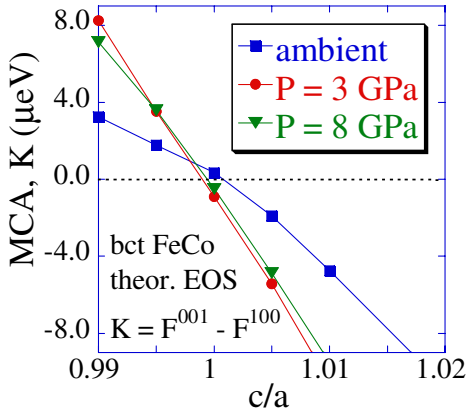

FIG. 3 (color online). The variation of the MCA energy with respect to distortions of the cubic lattice in FeCo. The gradient, B_1, of each line increases with pressure. The pressure values were determined from the theoretical equation of state (EOS).

evolution of tiny atomic displacements in complex and disordered systems. In principle, any reproducible distortion of the local structure induced by an external perturbation can be investigated with this method. As an example, we have studied the pressure evolution of magnetostrictive local atomic displacements in FeCo and compared our results with spin-polarized relativistic KKR-CPA calculations. We find that modern first principles approaches appear to be sufficient for the determination of the order of magnitude, the sign and mechanism of the tiny magnetostriction values observed in transition metals, and their evolution with pressure. Our combined experimental and theoretical approaches both lead to the conclusion that in FeCo magnetoelastic coupling favors enhancement of atomic displacements with decreasing volume, contrary to expectations based only on the commonly accepted ''stiffening'' of bonds with compression. Evidently the pressure-induced broadening of the d bands contributes to an enhancement of the distortion-induced band shifting and broadening, which is responsible for the positive magnetostriction constant λ_{100} in FeCo [7], and leads to an increase of B_1 with pressure. If a three dimensional compression of bulk FeCo obtained through the application of hydrostatic pressure enhances magnetostriction, then one could expect similar effects in thin epitaxially grown FeCo films where lattice mismatch plays a similar role as the application of pressure along two dimensions. Tetragonally distorted FeCo could, therefore, not only possess the desired properties for use in magnetic recording media [10], but could also have great potential for magnetostrictive applications. Investigating the effect of pressure on the magnetic behavior of $3d$ transition metals and their alloys is essential from both a fundamental and a technological point of view. In this respect, the combination of theory and experiment can help guide the search for the right elements and composition to synthesize materials with desired magnetostrictive properties. One can anticipate that these methods will be very useful in elucidating, for example, the atomic origin of the giant magnetostriction observed in rare-earth transition metal compounds.

We thank S. Pasternak (ID24) for the design of the experimental apparatus and for assistance with the high pressure equipment, M. C. Dominguez (ID24) for the development of software codes, W. Crichton and M. Mezouar (ID27) and J. Wright (ID11) for the x-ray diffraction measurements, and J. Chavanne and P. Van der Linden (ESRF) for providing the magnets and for assembling them. We are also very grateful to M. D. Cooke and M. R. J. Gibbs (Univ. of Sheffield, U.K.) for providing the samples. J. B. S. and S. O. acknowledge support from the EPSRC (U.K.) and the Centre for Scientific Computing at the Univ. of Warwick.

[1] E. R. Callen and H. B. Callen, Phys. Rev. **129** 578 (1963).
[2] R. J. Hemley and N. W. Ashcroft, Phys. Today **51**, No. 8, 26 (1998).
[3] R. M. Bozorth, *Ferromagnetism* (IEEE, Piscataway, NJ, 1993).
[4] M. Ekman, B. Sadigh, K. Einarsdotter, and P. Blaha, Phys. Rev. B **58**, 5296 (1998).
[5] G. Steinle-Neumann, L. Stixrude, and R. E. Cohen, Phys. Rev. B **60**, 791 (1999).
[6] R. F. Pettifer *et al.*, Nature (London) **435**, 78 (2005).
[7] R. Q. Wu *et al.*, J. Magn. Magn. Mater. **177**, 1216 (1998).
[8] S. Ostanin *et al.*, Phys. Rev. B **69**, 064425 (2004).
[9] S. S. A. Razee, J. B. Staunton, B. Ginatempo, F. J. Pinski, and E. Bruno, Phys. Rev. Lett. **82**, 5369 (1999).
[10] T. Burkert, L. Nordstrom, O. Eriksson, and O. Heinonen, Phys. Rev. Lett. **93**, 027203 (2004).
[11] F. Baudelet *et al.*, Phys. Rev. B **43**, 5857 (1991).
[12] O. Mathon *et al.*, J. Synchrotron Radiat. **11**, 423 (2004).
[13] S. Pascarelli *et al.*, J. Synchrotron Radiat. **13**, 351 (2006); M. P. Ruffoni *et al.*, in *X-Ray Absorption Fine Structure—XAFS13*, edited by B. Hedman and P. Pianetta, AIP Conf. Proc. No. 882 (AIP, New York, 2007), p. 838.
[14] E. Huang, W. A. Basset, and P. Tao, J. Geophys. Res. **92**, 8129 (1987).
[15] O. Mathon *et al.*, Phys. Rev. Lett. **93**, 255503 (2004).
[16] C. S. Yoo, H. Cynn, P. Soderlind, and V. Iota, Phys. Rev. Lett. **84**, 4132 (2000).
[17] V. Iota *et al.*, Appl. Phys. Lett. **90**, 042505 (2007).
[18] S. Pizzini *et al.*, Phys. Rev. B **50**, 3779 (1994).
[19] S. D. Jacobsen, J. Appl. Crystallogr. **40**, 26 (2007).
[20] R. A. Forman *et al.*, Science **176**, 284 (1972).
[21] G. Schutz *et al.*, Phys. Rev. Lett. **58**, 737 (1987).
[22] J. C. Labiche *et al.*, Rev. Sci. Instrum. **78**, 091301 (2007).
[23] F. M. Wang and R. Ingalls, Phys. Rev. B **57**, 5647 (1998).
[24] A. E. Clark, *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1980), Vol. 1, p. 539.
[25] S. Klotz and M. Braden, Phys. Rev. Lett. **85**, 3209 (2000); X. Sha and R. E. Cohen, Phys. Rev. B **74**, 214111 (2006).
[26] H. J. F. Jansen, Phys. Rev. B **59**, 4699 (1999).