Measuring Strain at the Atomic-scale with Differential X-ray Absorption Spectroscopy

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Outline

1) An introduction to Differential X-ray Absorption Spectroscopy

- What is it and how does it work?
- Proof-of-concept experiments on FeCo
- Studies into magneto-elastic coupling with applied pressure

2) Further Development for Quantitative Results

- DiffXAS data analysis procedures

3) Present Work

- A full example: The magnetostriction enhancement in Fe-Ga
- Giant magnetostriction in rare-earth transition metal alloys
- High anisotropy Fe-Pt for recording applications

Motivation for DiffXAS

Why develop a new technique for strain measurements?

At present

- Typical experiments measure strain on a macroscopic scale
- Theoretical models describe fundamental behaviour at an atomic level

Difficult to verify theoretical proposals from current experiments

To gain a greater insight into the origins of strain-inducing phenomena:

- Direct measurement of strain is needed at a local, atomic level
- Chemical selectivity is required to establish the behaviour of different atomic species

A potential candidate for such measurements is **X-Ray Absorption Spectroscopy (XAS)**

From XAS to DiffXAS

How the limitations of XAS required the development of DiffXAS?

Conventional XAS

- Can detect strain to typically ±1000ppm
- Strain from phenomena such as magnetostriction saturates at ~10ppm
- Noise is dominated by temporal beam drifts rather than photon counting

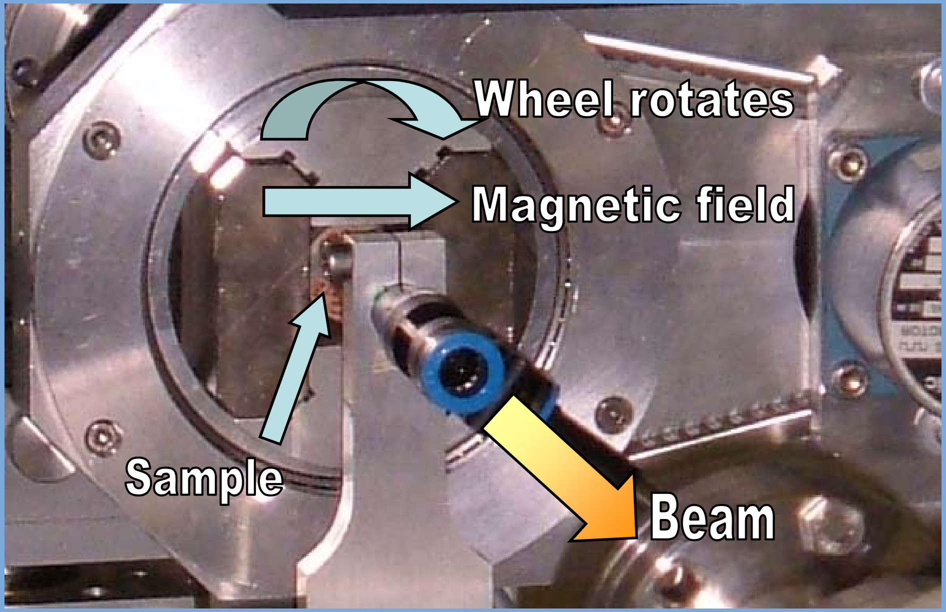
XAS lacks the sensitivity to detect the small strain from such phenomena

Differential XAS

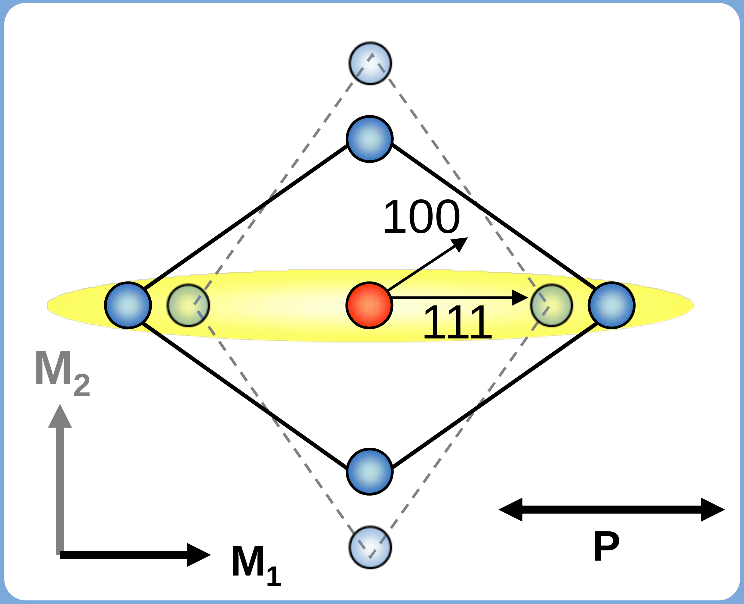
- Need fast acquisition (two spectra in a few seconds) & high stability
- Dispersive XAS set-up is ideal (polychromatic light & no moving parts)
- Can defeat temporal noise by taking two spectra under different strain conditions in a short space of time and looking at their difference
- Residual noise ~10^{-5}: **Femtometre resolution** in bond length changes

Differential XAS (DiffXAS)

Giving XAS the precision to detect magnetostriction



The DiffXAS apparatus *in situ* on beamline ID24 (ESRF)



A schematic representation of DiffXAS

A DiffXAS spectrum is the difference between two XAS spectra, taken under different conditions in a short space of time.

Temporal noise from the beam is eliminated, and so XAS precision increased

Proof-of-Concept

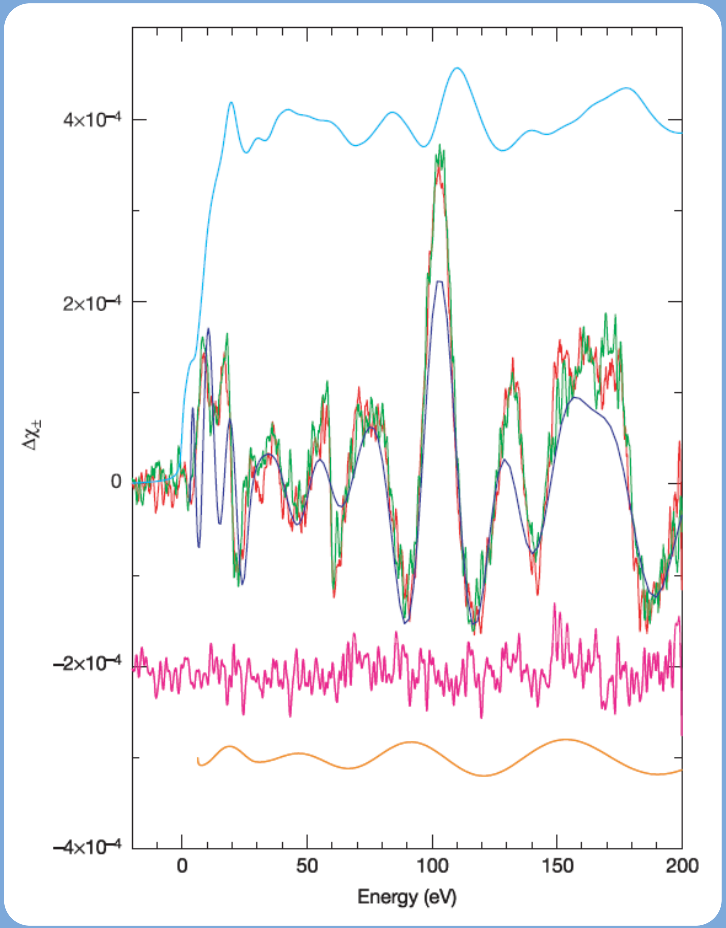
Early DiffXAS experiments on ID24 – Magnetostriction of FeCo

The Task

- Detect atomic magnetostriction of FeCo
- λ_{100} ~ 210ppm and λ_{111} ~ 60ppm

Results

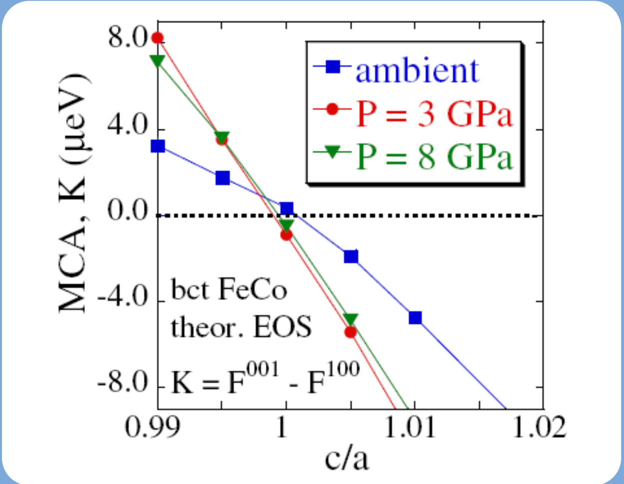
- DiffXAS signals detected (red and green)
- Experiment matched theory simulations
- Noise permitted detection of 1fm motion

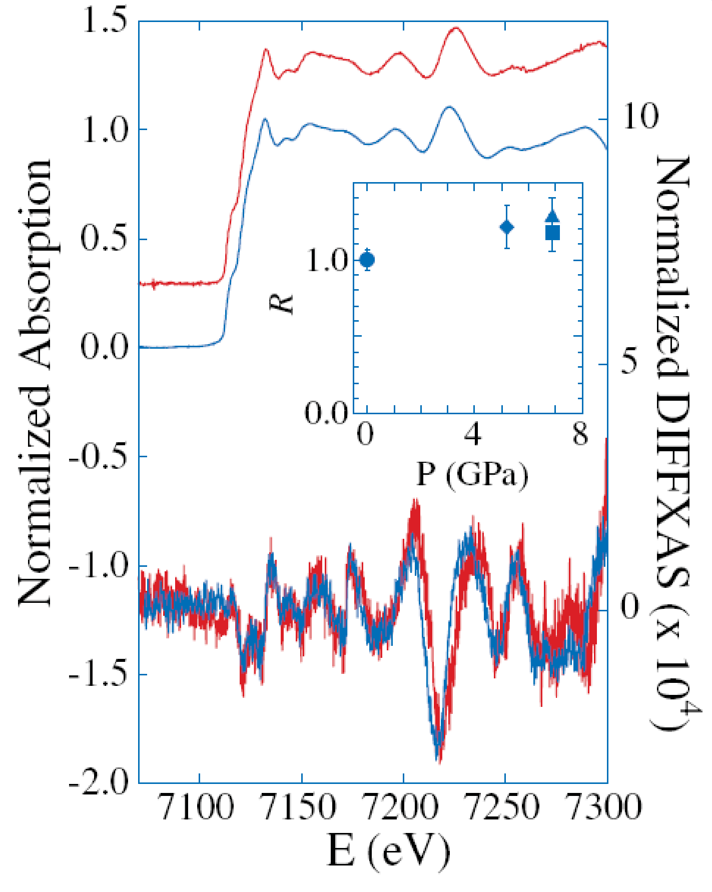


R. F. Pettifer, O. Mathon, S. Pascarelli, M.D. Cooke, M.R.J. Gibbs, **Nature 435**, 78 (2005)

Further FeCo Studies

Using pressure to investigate magneto-elastic coupling





Magnetostriction **increases** with pressure

S. Pascarelli, M. P. Ruffoni, A. Trapananti, et al., **Phys. Rev. Lett. 99**, 237204 (2007)

Quantitative DiffXAS

Developing data analysis and fitting techniques

Magnetostrictive DiffXAS:

$$\Delta\chi_j(k) = A_j(k)\cos(s_j k + \phi_j(k))\, k\Delta s_j$$

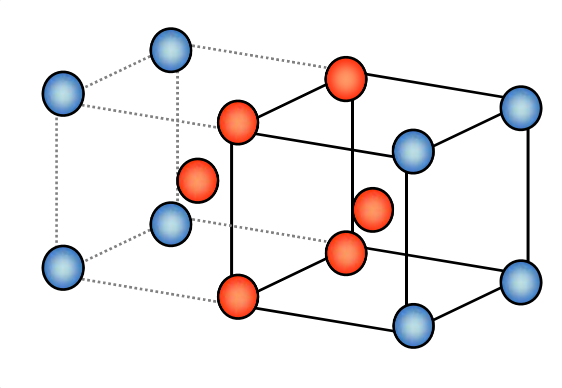
- Scattering amplitude & phase calculated from *ab initio* theory
- Absolute structural parameters found from a conventional XAS fit
- Magnetostrictive strain found from fitting the filtered DiffXAS signal

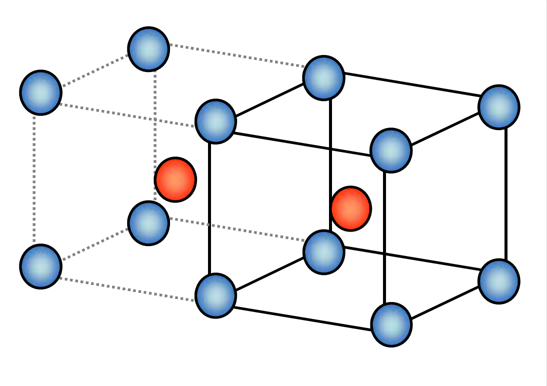
The DiffXAS is in quadrature with the XAS and its amplitude scales with the size of the magnetostriction through Δs_j

Enhanced Magnetostriction in Fe-Ga

Why does the addition of Ga to Fe increase its magnetostriction?

Theory Proposals:


Ga clusters in the material


<001> Ga-Ga pair defects

Does the magnetostriction arise directly from clusters of Ga in the material?

Does Ga simply mediate the magnetostriction of Fe from Ga-Ga pair defects?

S. Pascarelli, M. P. Ruffoni, R. Sato Turtelli, et al., **Phys. Rev. B 77**, 184406 (2008)

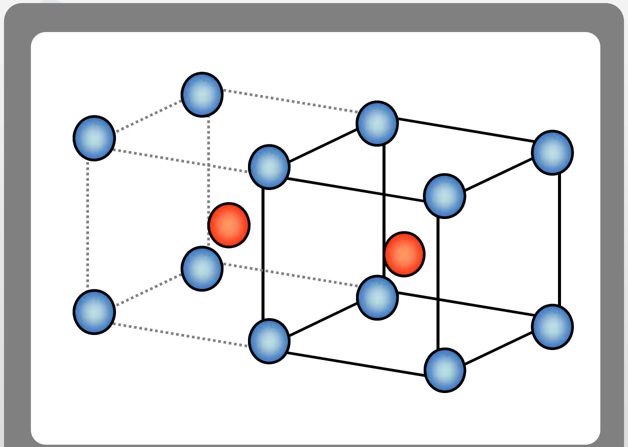
Enhanced Magnetostriction in Fe-Ga

Why does the addition of Ga to Fe increase its magnetostriction?

Theory Proposals:

Conventional XAS found no clusters of Gallium

But this is only the static structure. What about the magnetostriction?



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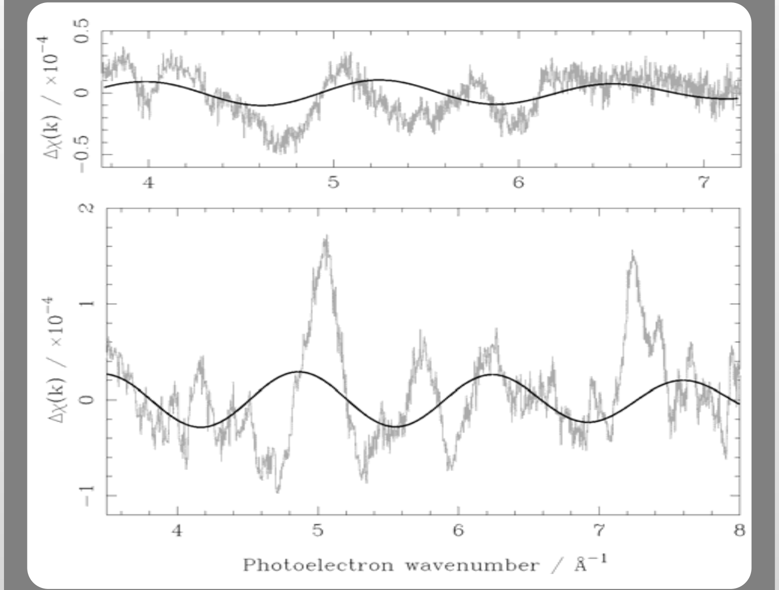
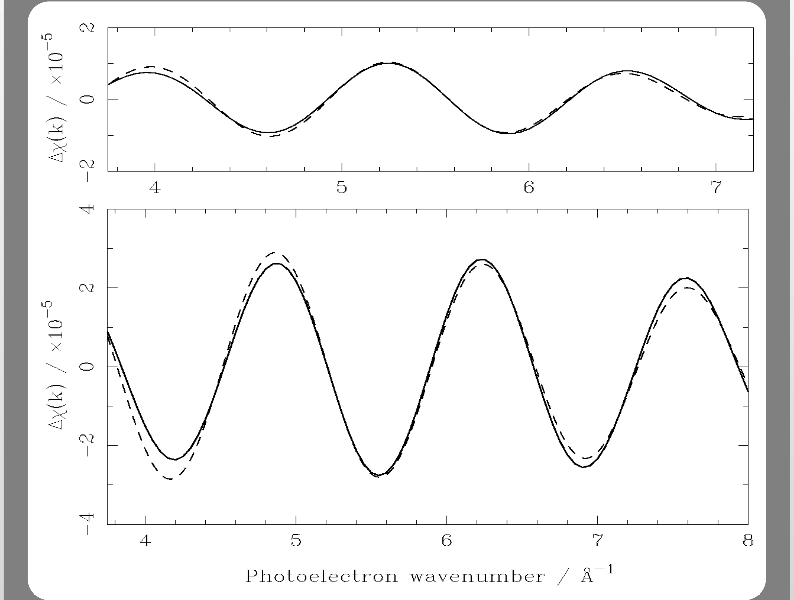
S. Pascarelli, M. P. Ruffoni, R. Sato Turtelli, et al., **Phys. Rev. B 77**, 184406 (2008)

DiffXAS Measurements and Analysis

How do Ga-Ga pair defects enhance the magnetostriction of Fe?



DiffXAS: Fe (top) and Ga (bottom)



Theory fit to first two shells

DiffXAS measured in a polycrystalline foil of $Fe_{81}Ga_{19}$ where macroscopic $\lambda_{100} \sim 400$ppm

Ab initio theory fitted to the DiffXAS contribution from the first two coordination shells

The Atomic Magnetostriction of $Fe_{81}Ga_{19}$

With experimental confirmation of theory

From the point-of-view of the Fe site:

1) The magnetostriction is only about two times greater than pure Fe

From the point-of-view of the Ga site:

1) XAS sees one [100] type Ga–Ga pair that provides a “B2-like” defect.
2) DiffXAS sees negligible strain in the Ga–Ga bond → Ga–Ga not fitted.
3) The enhanced magnetostriction comes from Fe–Ga bonds in the vicinity of Ga–Ga pairs.

M. P. Ruffoni, S. Pascarelli, R. Grössinger, et al., **Phys. Rev. Lett. 101**, 147202 (2008)

	1st shell	2nd shell
Fe environment	5 Fe–Fe 3 Fe–Ga	5 Fe–Fe 1 Fe–Ga
Ga environment	8 Fe–Ga	5 Fe–Ga 1 Ga–Ga

The Disordered A2 structure found from XAS

	$(3/2)\lambda_{100}$	$(3/2)\lambda_{111}$
Fe env.	(40±10)ppm	(−32±5)ppm
Ga env.	(390±40)ppm	(−10±20)ppm

The magnetostriction coefficients around each site

Work in Progress

Giant magnetostriction in rare-earth transition metal alloys

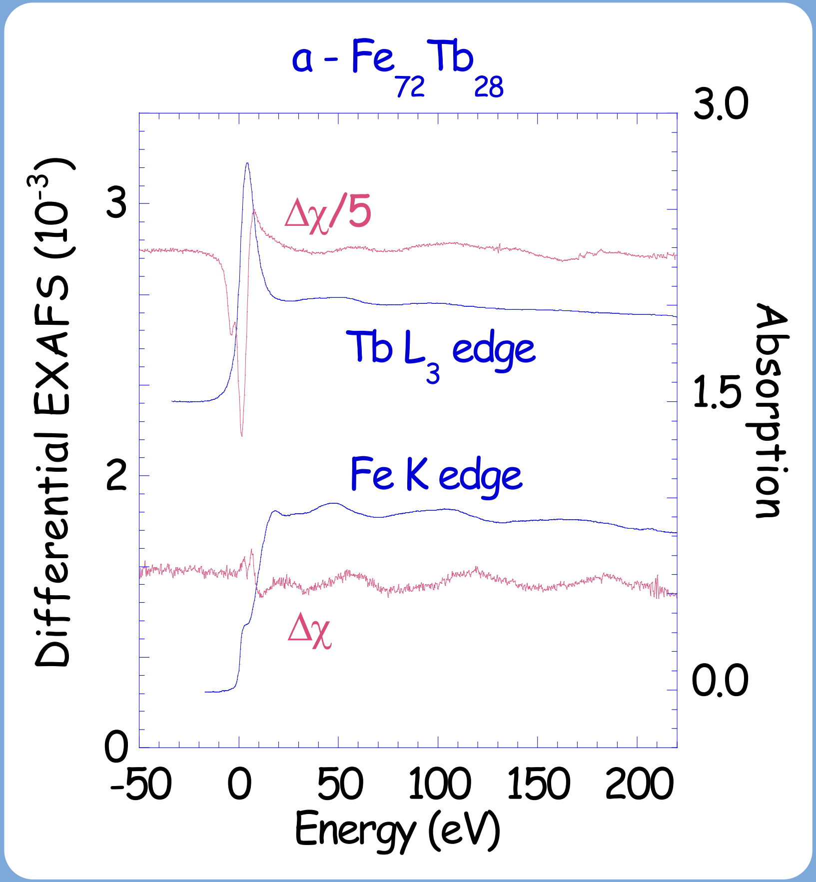
Amorphous Laves-phase samples of Fe_2Tb, Fe_2Dy, and Terfenol-D

Large XMLD signal at Tb L_3 edge but EXAFS region not reliable

DiffEXAFS seen at Fe K edge:

- Strain in Fe-Fe bonds: 250±50 ppm
- Strain in Fe-Tb bonds: 380±100 ppm

See poster by Pascarelli et al.

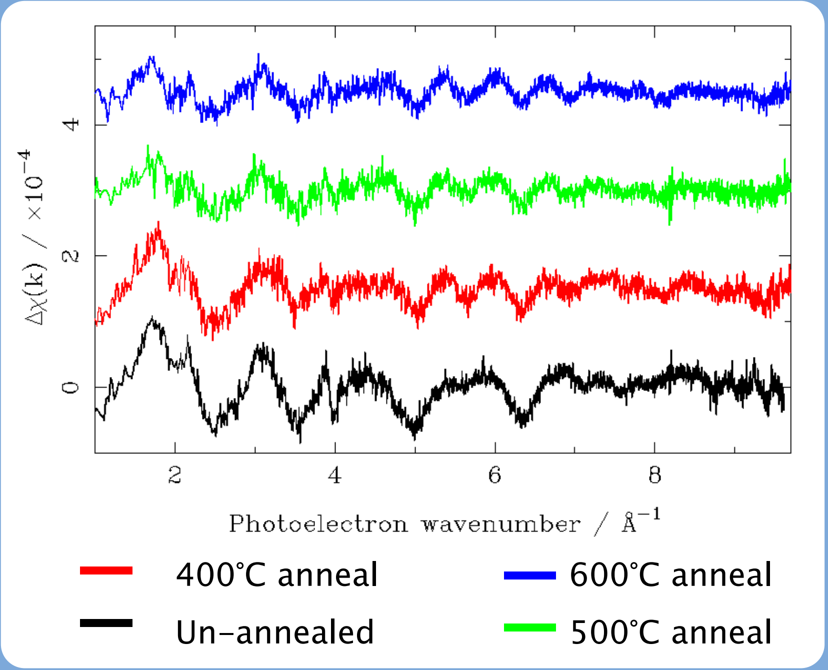


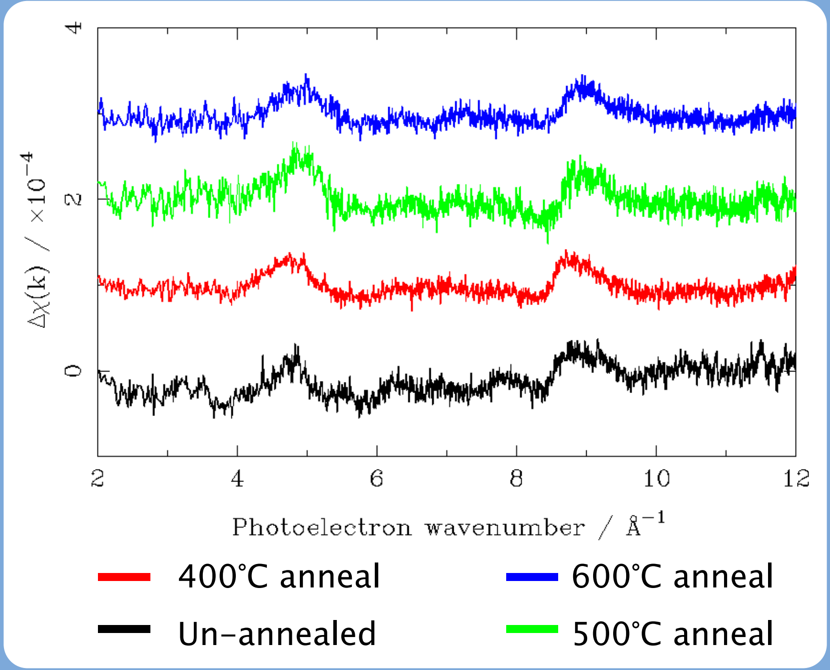
Work in Progress

High anisotropy Fe-Pt for recording applications

Fe–Pt undergoes a transition from a lowly–anisotropic cubic phase to highly–anisotropic tetragonal upon annealing.

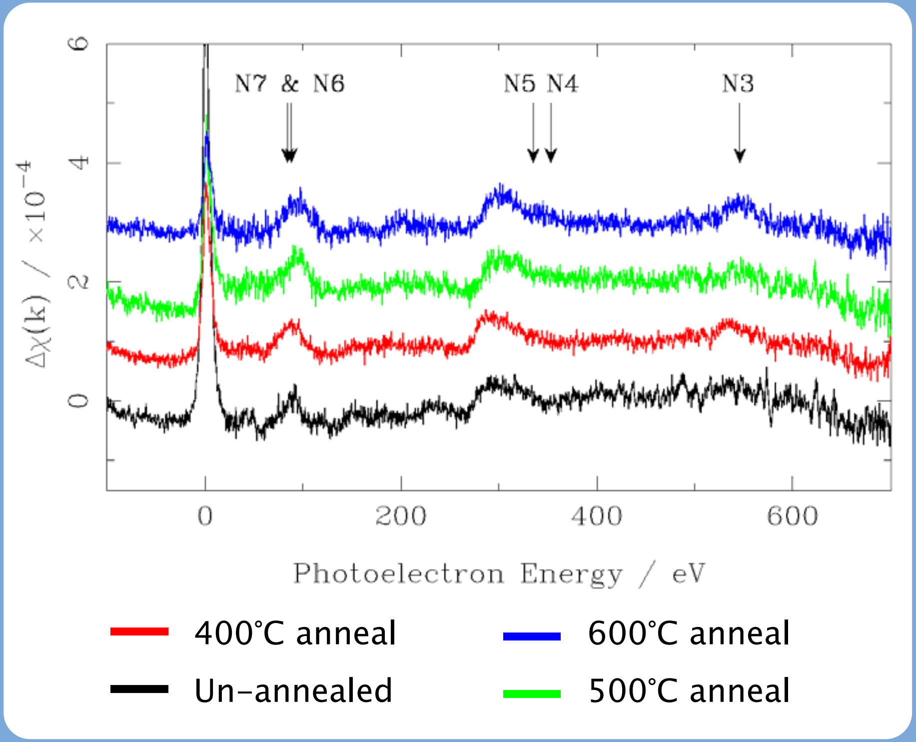
How does this affect the intrinsic magnetostriction of the material?





Work in Progress

Detection of double electron excitations in Pt



At the Pt L_3-edge, the DiffXAS shows components not consistent with normal EXAFS.

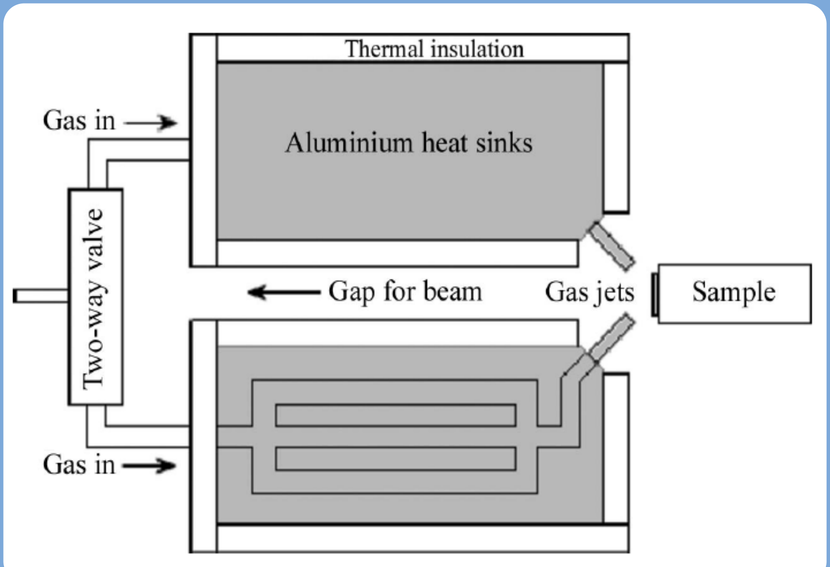
These components arise from double electron excitations.

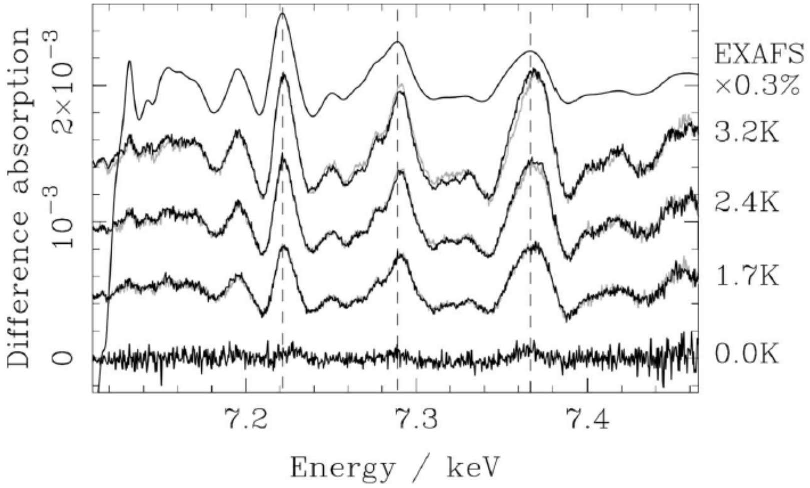
Other Applications

Atomic strain measurements beyond magnetostriction

DiffXAS may be taken from the modulation of any type of atomic strain

E.g. electrostrictive, piezoelectric, elastic, or **Thermal DiffXAS**





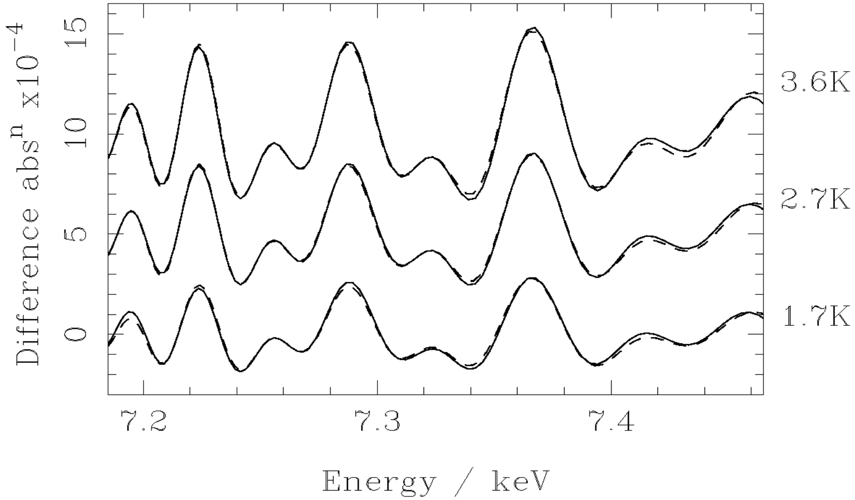
M.P. Ruffoni, R. F. Pettifer, S. Pascarelli, et al., **J. Synchrotron Rad. 14**, 421 (2007)

The Thermal Expansion of α-Fe

Quantifying thermal strain through sample temperature modulation

Thermal DiffXAS Function:

$$\Delta\chi_j(k) = A_j(k)\,[\cos(s_jk + \phi_j(k))\,k\Delta s_j - 2\sin(s_jk + \phi_j(k))\,k^2\Delta\sigma_j^2]$$



Analysis is essentially the same as for magnetostriction except Δχ has a second term since σ varies with temperature.

Literature gives $\alpha = 11.6 \times 10^{-6}\mathrm{K}^{-1}$

DiffXAS gives:

$\alpha = 11.1 \pm 0.9 \times 10^{-6}\mathrm{K}^{-1}$ for $\Delta T = 1.7\mathrm{K}$

$\alpha = 12.1 \pm 0.6 \times 10^{-6}\mathrm{K}^{-1}$ for $\Delta T = 2.4\mathrm{K}$

$\alpha = 11.5 \pm 0.5 \times 10^{-6}\mathrm{K}^{-1}$ for $\Delta T = 3.2\mathrm{K}$

Closing Remarks

Our thanks to:

S. Pasternak and F. Perrin for technical assistance on ID24

For more information:

The DiffXAS technique:	R. F. Pettifer et al., **Nature 435**, pp. 78 (2005)
Applications to date:	M. P. Ruffoni et al., **Phys. Rev. Lett. 101**, pp. 147202 (2008)
	S. Pascarelli et al., **Phys. Rev. Lett. 99**, pp. 237204 (2007)
	S. Pascarelli et al., **Phys. Rev. B 77**, pp. 184406 (2008)
	M. P. Ruffoni et al., **J. Synchrotron Rad. 14**, pp. 421 (2007)

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