

An Introduction to Differential EXAFS

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Abstract. Differential EXAFS (DiffEXAFS) is a novel technique for measuring atomic perturbations on a local scale that result from the modulation of a given sample property. Experiments conducted to date have revealed a sensitivity to such perturbations of the order of femtometres [1], two orders of magnitude more sensitive than is considered possible by conventional EXAFS techniques [2]. Here, the concept behind DiffEXAFS is described, and experimental factors required to detect such a signal discussed.

Keywords: Differential EXAFS, DiffEXAFS, Atomic Perturbations

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CONCEPT

Differential EXAFS (DiffEXAFS) is a novel technique for the study of small atomic perturbations, which was developed by Pettifer et al. over a period of years leading up to publication in May 2005 [1]. The technique employs the subtle changes in EXAFS signals induced by the modulation of a given sample property to measure changes in photoelectron scattering path length, and thus deduce any atomic displacements in the local area of the absorbing atom.

A Differential EXAFS spectrum is the difference between two conventional EXAFS spectra (designated + and -), taken with all sample properties kept constant, except for the unit modulation of some property of interest¹. This is very similar in principle to XMCD, except that instead of only studying magnetic effects in the near-edge region, DiffEXAFS examines the extended x-ray absorption structure for perturbations of the sample. For instance, dichroic signals can be produced by altering the angle between the linear polarisation vector and the sample magnetisation to give information about magnetostriction, or changes of temperature to give thermal effects. Given that strains contributing to these signals are small, it is possible to express them in terms of a first order Taylor expansion of the x-ray fine-structure function, χ , with respect to the modulated parameter.

$$\chi(k) = \sum_j A_j(k) \sin(ks_j + \phi_j(k)) \quad (1)$$

$$\Delta\chi = \sum_j A_j(k) k \cos(ks_j + \phi_j(k)) \Delta s_j \quad (2)$$

Strictly speaking, $A_j(k)$ and $\phi_j(k)$ are also path length, s_j , dependent, but changes in these parameters are negligible compared to Δs_j . In some situations though, additional factors are significantly dependent on the modulated parameter, such as the Debye-Waller factor when samples undergo temperature modulation. In this case, the differential fine-structure function becomes

$$\Delta\chi = \sum_j A_j(k) \left(k \cos(ks_j + \phi_j(k)) \Delta s_j - 2k^2 \sin(ks_j + \phi_j(k)) \Delta \sigma_j^2 \right) \quad (3)$$

This difference can be seen in Figure 1, where a typical Joule magnetostriction DiffEXAFS signal is plotted for a 90° rotation in sample magnetisation, and a typical thermal DiffEXAFS signal plotted for a 1K change in sample temperature; both at the Fe-K edge. The former spectrum is described by equation (2), and the latter by (3). Indeed, the Debye-Waller contributions to the thermal signal dominate, producing DiffEXAFS that is almost in phase with the original fine-structure, with thermal expansion only being detectable as a slight phase shift. Since the structure present in a DiffEXAFS spectrum is intimately linked to atomic perturbations, a different signal can be expected from the same absorption edge depending on which property is modulated, and how that affects the sample structure.

IMPLEMENTATION

The concept of DiffEXAFS is quite trivial. The reason it has not been demonstrated in practice until recently comes down to experimental limitations. Most structurally perturbative phenomena induce atomic displacements of the order of a few femtometres for unit modu-

¹ If non-unit modulation is employed, the spectrum is referred to as a Difference EXAFS spectrum, which must be normalised to unit modulation in order to extract information on structural changes.

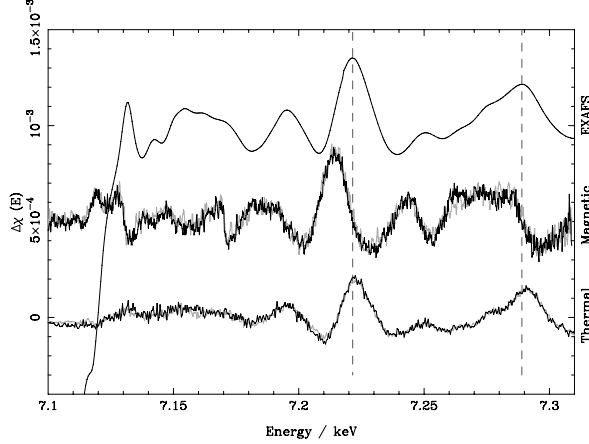


FIGURE 1. DiffEXAFS signals at the Fe-K edge for magnetisation modulation of FeCo and thermal modulation of Fe foil. EXAFS for the pure Fe sample is shown, which is virtually identical to the FeCo structure. As can be seen, the modulation of different sample properties results in very different signals. The magnetisation signal only contains one component through magnetostrictive strain, whereas the thermal signal contains components from expansion of the crystal lattice and changes to atomic vibrational amplitudes.

lation of a sample property, giving strains of the order of 10^{-5} .

Conventional EXAFS typically only has sensitivity to strains of the order of 10^{-3} depending on circumstances [2], so in order to resolve a difference signal, sample modulation must be a hundred times larger, inducing displacements of the order of 0.1pm. DiffEXAFS however, offers direct sensitivity to displacements of the order of femtometres.

Such sensitivity is achieved due to the method by which DiffEXAFS spectra are acquired, and the beam conditions over that time. Three main problems must be overcome. Firstly, statistical noise in $\Delta\chi$ in each spectrum must be low - no more than about 10^{-5} for femtometre resolution, which suggests the use of a high-intensity 3rd generation synchrotron source such as an undulator beam.

The next problem is that of beam energy stability. If the energy of photons passing through the sample changes between the + and - measurements, spurious signals can be generated from the resulting shift in fine-structure. Assuming the noise limit in $\Delta\chi$ is 10^{-5} , the edge energy would need to be stable to at least 0.1meV for any drift signal be indistinguishable from the noise.

The third and final problem is that of spatial beam stability. Unless the sample material under study is perfectly homogenous, subtle changes in thickness could generate a difference in x-ray absorption if the beam were to move between the + and - measurements. Beam drift must therefore be minimised, or the beam spot size in-

creased such that any drift changes the illuminated section of sample by only a tiny fraction.

Given that both energy and spatial stability of a beam are time-dependent, measurements of the sample at the + and - modulation states must be made in as short a space of time as possible; with both complete spectra acquired in a period of a couple of seconds or less. The solution therefore, is to use a Dispersive XAS (D-XAS) beamline. To date, all DiffEXAFS experiments have been conducted on ID24 of the ESRF [3], which has the added advantage of being mounted on a twin undulator source, providing x-ray intensities of the order of 10^{13} photons/sec to minimise statistical noise.

A complete spectrum can be acquired and output in about 200ms, which ideally, with rapid sample modulation apparatus, allows two spectra to be obtained under different sample conditions in less than a second; the limiting factor being how quickly the sample responds to the modulation stimulus. However, whilst such quick measurements minimise time-dependent beam drifts, exposure times of the order of 100ms are not capable of providing statistical noise in $\Delta\chi$ of 10^{-5} as required in one pair of +/- measurements.

It is therefore necessary to average the DiffEXAFS signal over many pairs of measurements - typically around a thousand, giving a total acquisition time for a single DiffEXAFS spectrum of anything from thirty minutes to two hours depending on the speed of sample modulation. Averaging over such a period requires the consideration of additional factors, most notably the decay of beam intensity as electrons are lost from the storage ring. This, and other linear and exponential drift effects, may be accounted for by taking XAS transmission measurements in the following sequence as described by Mathon et al. for XMCD signals [4]

$$I^{0+}, I^{1-}, I^{2+}, I^{3-}, \dots, I^{2n-2+}, I^{2n-1-}, I^{2n+} \quad (4)$$

and then calculating the DiffEXAFS signal from the following algorithm.

$$\Delta\chi = \frac{1}{2n} \ln \left(\frac{I^{0+} (I^{2+})^2 \dots (I^{2n-2+})^2 I^{2n+}}{(I^{1-})^2 (I^{3-})^2 \dots (I^{2n-1-})^2} \right) \quad (5)$$

DIFFEXAFS VS. CONVENTIONAL EXAFS

DiffEXAFS can be compared to conventional EXAFS by taking the example of, say, thermal expansion, where typical strains are of the order of 10^{-5}K^{-1} . Conventional EXAFS would require sample modulation of around 100K between measurements for any variation in fine-structure to be measurable. DiffEXAFS however, could resolve changes with a modulation of just 1K, allowing

structural changes in the same 100K region to be probed in considerably greater resolution. The resulting measurement then yields not just the net structural change over the whole region, but precise incremental perturbations as a function of temperature.

It is true that such parameter resolution may not be required in all situations, particularly where phenomena inducing structural changes are either linear or vary only weakly as a function of the modulated sample property. However, many phenomena do not conform to these restraints; most notably non-linear phenomena such as phase transitions. In these situations the ability to detect atomic displacements over small changes in sample parameters is an absolute necessity. Indeed, this is where we believe the full power of DiffEXAFS is exploited.

Whilst conventional EXAFS will be able to detect net perturbations across some such discontinuity, and describe the sample structure in the stable region either side, it is generally not possible to look at how the sample responds approaching and receding from the transition - to say whether there are any onset features, or whether any particular structural instabilities become evident close to the primary transition itself. Even if a given transition were to induce perturbations large enough to be probed in a number of individual steps with conventional EXAFS, DiffEXAFS will always still offer around two orders of magnitude greater sensitivity and thus potentially a hundred times more sampling points across the transition region. No other XAFS technique offers this potential.

FUTURE APPLICATIONS

DiffEXAFS is not limited to the study of any particular set of materials or to the study of any given type of phenomenon. In principle it may be used to examine any situation where the modulation of a sample property results in some small degree of atomic perturbation on a local scale.

Initial data from [1] demonstrated the measurement of magnetostriction by DiffEXAFS, which should be of great interest to those wishing to examine the atomic origins of this and other -striction type phenomena. Work is also currently being undertaken to study the more complicated case of samples undergoing temperature modulation.

However, the real interest will be in one of two areas. Firstly, in the study of non-linear phenomena as already described. Then in the examination of disordered or amorphous systems, where techniques such as diffraction fail, and where macroscopic measurements of sample properties may not necessarily scale down to the locally observed atomic perturbations due to the presence of intermediate scale deformations, such as the relief of

microscopic strain by sample defects.

At present, factors limiting the resolution of atomic perturbations are all experimental in origin, and relate to the stability or otherwise of beam components, noise in measured spectra, and to the accuracy and precision with which the sample can be modulated.

CCD detectors used in experiments to date have achieved statistical noise in $\Delta\chi$ of about 10^{-5} , determined by a 14-bit quantisation limit on read-out. A more sensitive detector (i.e. one with a greater number of bits) should be capable of 10^{-6} based on the flux available from a typical 3rd generation undulator, enabling investigation of displacements on a 0.1fm scale. This would further test beam stability. To prevent corruption of a signal on this scale, energy stability would be required to 0.01meV between +/- measurements; suggesting improvements to beamline components, a reduction in time between +/- measurements, or a combination of the two. The effects of spatial drift must also be reduced, which is most easily achieved by increasing the beam spot size, currently about $(10 \times 10)\mu m$, to about $(30 \times 30)\mu m$.

However, the area where the greatest advances can be made, is in the modulation of the sample. Apparatus constructed to date has only focused on sample magnetisation and temperature. New designs will allow the study of different phenomena via the modulation of different sample properties. Developments to these and existing designs, capable of modulating the sample at, say, extremes of temperature or pressure, would further expand the technique. And improvements to the stability of the sample at measurement, and the reproducibility of modulation between + and - states, will allow signals to be detected from ever smaller changes to the sample; particularly useful where large atomic displacements occur from tiny changes in sample parameters, as is the case at phase-transitions.

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REFERENCES

1. R. F. Pettifer, O. Mathon, S. Pascarelli, M. D. Cooke, and M. R. J. Gibbs, *Nature* **435**, 78–81 (2005).
2. G. Dalba, P. Fornasini, R. Grisenti, and J. Purans, *Phys. Rev. Lett.* **82**, 4240–4243 (1999).
3. S. Pascarelli, O. Mathon, M. Muñoz, T. Mairs, and J. Susni, *J. Synchrotron Rad.* **Accepted** (2006).
4. P. Mathon, F. Baudelet, I. J.-P. S. Pasternak, A. Polian, and S. Pascarelli, *J. Synchrotron Rad.* **11**, 423–427 (2004).