	Experiment title: The atomic origins of Thermal Expansion as determined by Differential EXAFS	**Experiment number**: MI-803
Beamline:	**Date of experiment**: from: 7th Sept 2005 to: 12th Sept 2005	**Date of report**: 24th Feb 2006
Shifts:	**Local contact(s)**: S. Pascarelli	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

M. P. Ruffoni*, Dept. Physics, University of Warwick, Coventry, CV4 7AL, UK

R. F. Pettifer, Dept. Physics, University of Warwick, Coventry, CV4 7AL, UK

S. Pascarelli*, ESRF

A. Trapananti*, ESRF

O. Mathon, ESRF

Report:

The aim of this experiment was to further develop the measurement of small, thermally induced atomic displacements, by use of the new dichroic technique of Differential EXAFS (DiffEXAFS)[1][2]. Experiment MI-740, conducted previously on ID24 has proven the viability of such measurements[2]. Here we aimed to improve the technique by refining the sample preparation, implementing a new sample mounting arrangement, and by measuring thermal differential signals over smaller temperature changes with lower noise, and greater thermal stability. Our original proposal suggested repeating previous measurements taken on SrF_2[3], but for reasons described below, this was changed to repeating measurements taken on Fe foil.

New sample preparation and mounting techniques

The thermal modulation of a sample, necessary for measurement of thermal DiffEXAFS, was achieved by targetting jets of heated N_2 gas at the sample. These jets were generated using essentially the same apparatus as previously on ID24[2], and the reader is referred to the MI-740 report for more details. Important upgrades relating this experiment's aim of improving sample preparation and containment are however discussed here.

Despite some setbacks, we are able to report a large degree of success with respect to our proposed new sample preparation technique for Thermal DiffEXAFS[3], which was composed of two parts. The first aim was to redesign the sample mount to maximise the heat transfer across the gas-sample interface, and better thermally isolate the sample from the general hutch environment; and the second to reduce the sample size, improving its thermal response time.

The redesigned sample mount is shown schematically in Figure 1, and is constructed of three components. The first is the sample holder itself. This is a cylinder measuring 22mm long by 8mm diameter, into the end of which two 500μm deep recesses had been cut. The first, 5mm in diameter to accommodate a pellet produced by a 5mm die, and the second, 3mm in diameter to accommodate samples pressed into small gaskets. From the other end of the holder, a 4mm diameter hole was machined along the

length of the cylinder up to within 2mm of the sample position, where its diameter reduced to 500µm. This hole allows the unhindered passage of the beam through the sample. Just behind the sample, at the point where the hole narrows, three more holes, 3mm in diameter, were drilled at 90° angular intervals from the outside curved surface of the cylinder into the internal recess. These allow gas from the jets to pass around the reverse side of the sample and out along the line of the beam, which minimises the thermal gradient between the front and back of the sample; and isolates the sample from the enviroment, preventing oxidation, and thermal interference. The section of cylinder without one of these exit holes had two narrow channels cut into it, running the length of the holder, into which thermocouple wires could be glued.

The second component is a plastic sheath, fixed to a 6mm thick perspex sheet, into which a slot was machined to accommodate the gas jets. This sheath is slid over the jets to provide a contained environment for the gas-sample interaction. The sample is introduced to this enviroment via an 8mm hole in the perspex sheet, centred on the line of the beam. With this sheath in place, gas is forced to pass over the sample and out to atmosphere, either by passing between the two gas jets, or around through the exit channels cut into the sample holder.

The final component is a 10mm long collar, which is placed over the back of the sample holder such that it is flush with the end. This ensures that when the sample is pushed through the reverse of the sheath into the sample enviroment, it is reproduceably positioned exactly on the focal spot of the gas jets. All components of the new sample mount were made out of PEEK to prevent brittleness observed in most plastics, brought about by radiation damage.

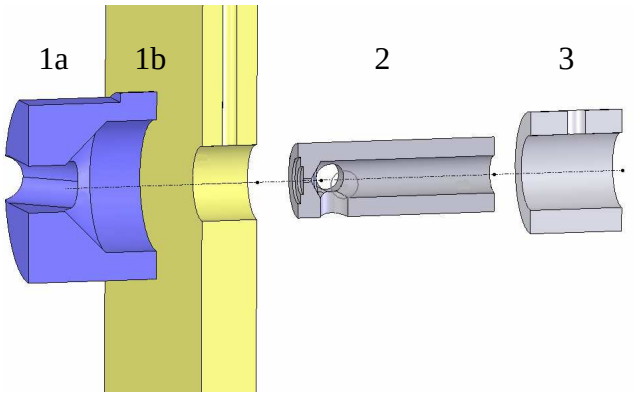

Figure 1a: Exploded view of the new sample mount. 1a and 1b: Sample sheath, 2: Sample holder, 3. Collar

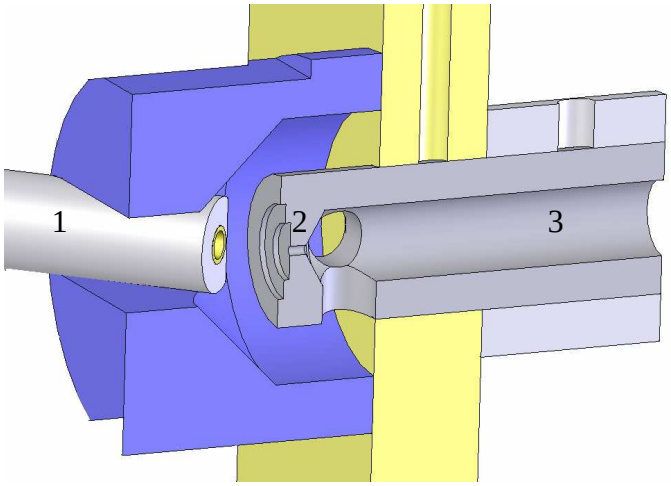

Figure 1b: Assembled view of the new sample mount with one of the two gas jets shown. 1: Gas jet, 2: Sample position, 3: Gas exit channel.

For the second part of the preparation, we proposed to minimise the sample mass by using a diamond anvil cell to press a self-sustaining pellet of sample into a 500µm hole in a copper gasket. A copper-constantan (T-type) thermocouple would be spot-welded to the gasket to provide a measure of the sample temperature. Unfortunately, despite numerous attempts to produce a such a sample, we failed to obtain a pellet of sufficient quality to be usable for DiffEXAFS measurements. Frequently a pellet could be produced that would appear acceptable under the microsope, but which was extremely inhomogenous when analysed in the beam. Some difficulty was also experienced in making the pellets self-sustaining and keeping them fixed in the gasket. As a result of these problems, we had to abandon this aspect of the experiment along with our proposal to repeat the powdered SrF_2 measurements taken in MI-740. We suspect that in future better results may be achieved either by mixing the sample with an x-ray transparent adhesive matrix, or by containing the pellet in the gasket between solid windows. Despite this setback we managed to spot-weld a thermocouple straight onto a 3mm diameter piece of polycrystaline Fe foil (7µm thick), and attach this to the sample holder. This still represented a significant reduction in sample size based on previous Fe foil measurements[2].

Measurements

A key assumption of DiffEXAFS is that all environmental parameters, apart from the one delibrately modulated, remain effectively constant between the two difference measurements (T+ and T- in this case). It is therefore necessary to check the DiffEXAFS baseline, obtained with no modulation of the control parameter, prior to taking any difference measurements. If all the required stability conditions have been met, this baseline should be flat, passing through zero, with only statistical noise present.

The acquisition of this flat baseline presented numerous problems through the first couple of days of beamtime. The black plot in Figure 2 shows an early attempt to acquire the baseline, and is undoubtedly not structureless. The region from about 7.10 to 7.35keV shows a that a fraction of the original EXAFS is still present in the difference spectum. Investigation revealed that this signal was only generated when switching of the gas jets was performed during the measurement. This led to the discovery that, when switching the gas jets, subtle changes in gas flow through apparatus, were causing pressure changes in the main N_2 supply

line in the hutch. This supply line was also coupled to ID24's 3rd mirror, which, as a result, caused small changes in N_2 concentration inside the mirror, and thus small changes in beam attenuation through the mirror. An order of magnitude calculation suggests a signal such as that in Figure 2 could be generated by a pressure change in the mirror of about 17mbar. Significantly, these fluctuations were perfectly in phase with the gas jet switching, and as such did not cancel upon calculation of the difference spectrum. Isolating the 3rd mirror by supplying its N_2 from a gas bottle eliminated the problem. Evidently extreme care should be taken in future DiffEXAFS experiments to ensure all beamline components are isolated from the sample modulation apparatus.

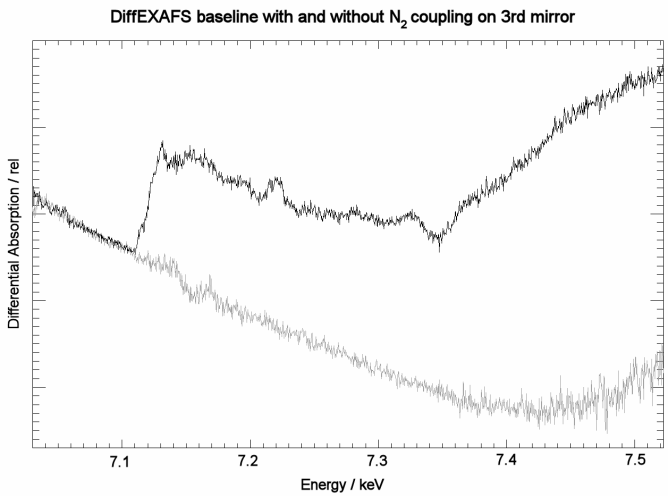

Fig 2: DiffEXAFS baselines ($\Delta T \approx 0K$) with varying 3rd mirror gas supply configurations. The black plot was acquired with the 3rd mirror coupled to the same N_2 line as the gas jets, and clearly shows that a residual fraction of the absorption spectrum is present after the subtraction of two, supposedly identical, spectra. The grey plot was acquired similarly, but with the 3rd mirror isolated; being supplied by a standalone N_2 gas bottle. The residual absorption has been eliminated, indicating the spurious differential signal was coming from changes in N_2 concentration in the 3rd mirror.

However, despite eliminating this structure, the baseline was still not flat; passing through zero. Figure 3 shows the baselines obtained for varying flow rates through the gas jets. At 3lpm, the baseline is significantly skewed; becoming flatter as the flow rate is reduced. This problem was eventually traced to the way in which gas was flowing through the new sample mount after passing over the sample itself. Figure 4a shows a horizontal cross-section through the mount, with the x-ray E-field in the plane of the paper. Gas flows through the mount along the path indicated. As it passes around the reverse side of the sample it flows across the beam, which importantly, is spatialy dispersed in the plane of the paper away from the sample position. Plotted on 4a is a finite element calculation of the gas density in the sample mount for an input flow rate of 2lpm. Behind the sample position, along the section marked D, a density gradient is present, which in turn means that each wavelength element of the dispersed beam is passing through a different concentration of gas; imposing a wavelength dependency on the beam intensity, which reverses when the gas jets are switched. Using Figure 4b, and assuming the beam is ~500μm wide at the centre of section D; an order of magnitude calculation for the differential signal due to the gas density gradient yields an amplitude of $\sim 10^{-3}$, as observed. This dependency was broken by blocking the lateral exits channels such that the gas could only flow vertically across the beam.

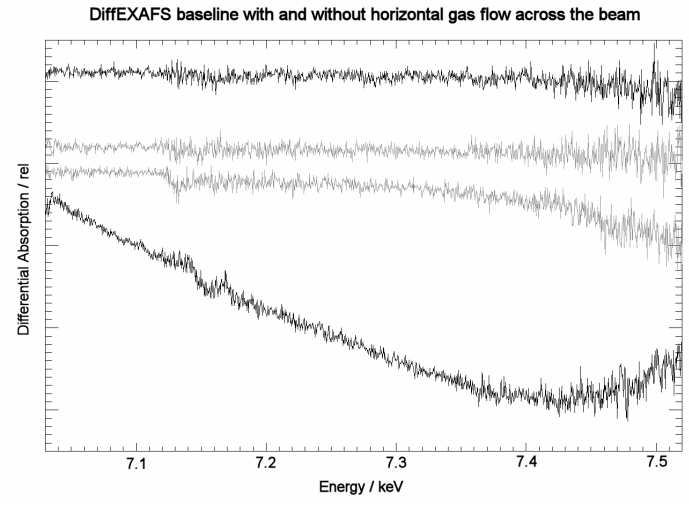

Fig 3: DiffEXAFS baselines ($\Delta T \approx 0K$) with varying gas flow rates and directions. The bottom three plots were acquired with gas flowing both horizontally and vertically across the beam, and show flows of 3.0, 1.6, and 0.8lpm respectively from bottom to top. The uppermost plot shows the baseline for gas flow of 3lpm, but with only vertical flow across the beam.

We are happy to announce that upon the elimination of these problems, we sucessfully observed the anticipated thermal expansion signal. Figure 5 shows the DiffEXAFS spectra obtained for temperature differences, ΔT, of 3.2±0.2, 2.4±0.2, 1.7±0.2, and 0.2±0.2K close to room temperature. Each spectrum was obtained by averaging 600 pairs of T+, T- measurements to reduce statistical noise. The total acquisition time for one pair was approximately 2 seconds; this period being dominated by a 1.5 second interval between measurements to allow the sample to equilibriate at a new temperature after gas jet switching. It can be shown that the presence of this interval did not violate our environmental stability requirements, since when each measurement was repeated with the starting gas jet phase reversed, an essentially perfect mirror image of the spectrum about $\Delta\chi = 0$ was produced, showing that the signal was thermal in origin. These phase reversed spectra have been inverted about $\Delta\chi = 0$, and plotted on Figure 5. Additionally, the absence of a sharp peak at the edge, where the EXAFS derivative is greatest, is testament to beam energy stability of better than 0.01eV as required.

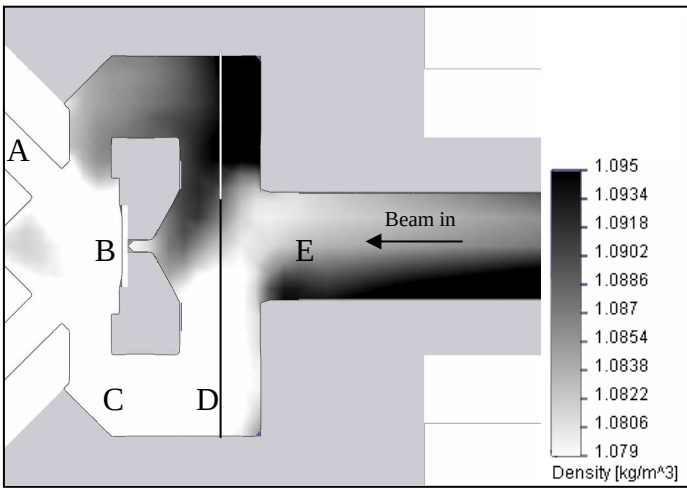

Figure 4a: A gas density profile through the lateral gas exit channels of the sample mount. Gas enters the sample mount at A and interacts with the sample at B. Gas then exits through C, flows horizontally across the beam along the section marked at D before passing out of the reverse of the mount along E.

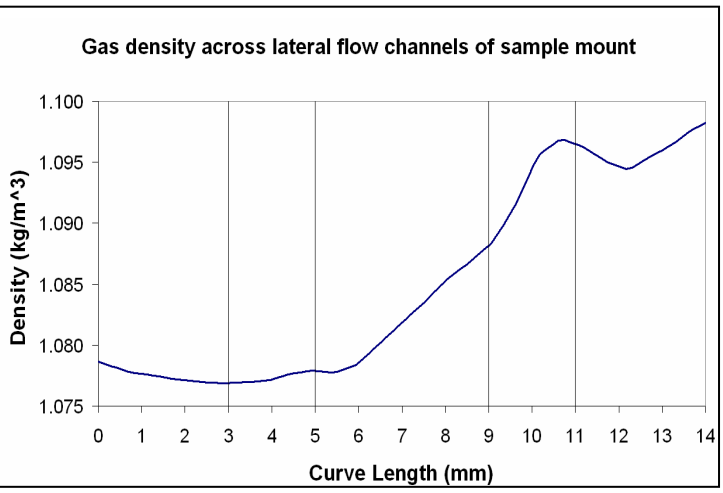

Figure 4b: Gas density plotted from bottom to top along cross-section D of 4a. The exit holes are located between 3 and 5mm, and 9 and 11mm as indicated by the vertical lines. The beam passes along the central section between 5 and 9mm. Across this region, gas density changes by approximately 1%.

These 1.5s temperature equilibration intervals are a significant improvement on measurements taken in MI-740, where approximately 7s were needed for equilibrium to be reached between gas and sample temperature. This therefore indicates the new sample mount along with a smaller sample has indeed achieved its goal of increasing heat flow across the gas-sample interface, and reducing the sample response time. Along with the use of 2/3 filling mode as opposed to 16-bunch for MI-740, this interval reduction accounts for a significant reduction in observed noise. Previously a noise level of 5×10^{-5} was achieved, whereas Figure 5 indicates noise of 2×10^{-5} for these mesurements.

We are also able to rectify the DiffEXAFS amplitude issue raised previously[2]. The differential fine structure function predicts a linear variation in signal amplitude with respect to the size of ΔT. Doubling ΔT should double the amplitude. However, in MI-740, signals from temperature changes of 2.8±0.2K and 1.4±0.2K produced an amplitude difference of a factor of 4. We can now conclude this this was due to temperature stability problems our control apparatus. Having upgraded this apparatus, we can confirm from our present results that the predicted linear amplitude relation prevails, as shown in Figure 6.

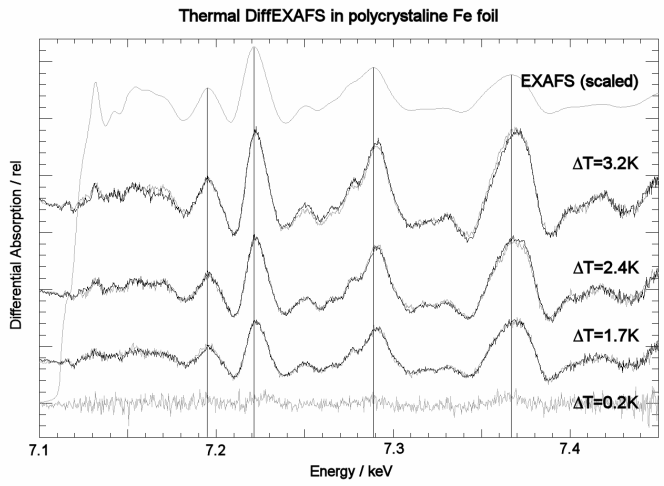

Figure 5: Thermal DiffEXAFS in polycrystaline iron foil. Thermal disorder dominates being as the signal is largely in phase with the original EXAFS. However, by comparing the peak positions between the EXAFS and difference spectra, a phase shift is also seen. This shift is negligable near the edge but increases with k as anticipated, and is testament to the successful detection of thermal expansion. Inverted gas jet phase reversed spectra are also shown (grey under difference spectra). Error in ΔT is ±0.2K.

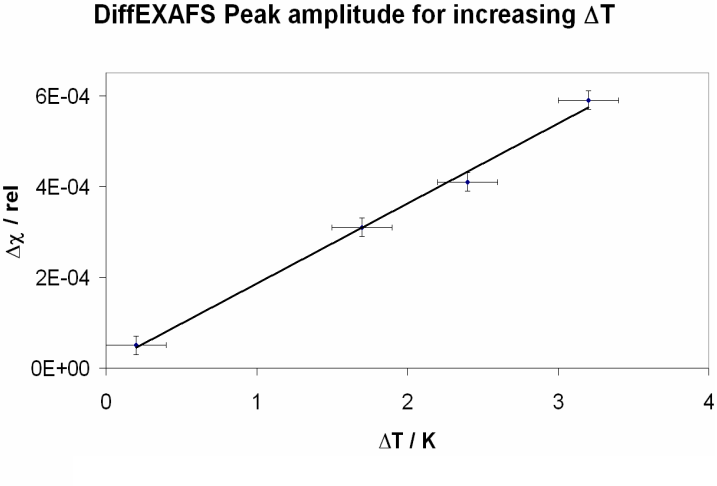

Figure 6: Taking the DiffEXAFS peak from Fig 5 at E = 7.37keV, and mapping its amplitude reveals it scales linearly with ΔT as predicted from the differential fine structure function.

This experiment has therefore successfully achieved it's primary aims. Thermal DiffEXAFS data have been taken with an accuracy not achieved previously. Upgrades made to our thermal modulation apparatus have reduced the equilibriation period required between dichroic measurements, and thus reduced signal noise introduced from temporal drifts in storage ring and beamline components. Improvements made to our control systems have allowed us to resolve issues raised previously regarding the scaling of the differential fine structure with respect to changes in temperature difference. However, further work should be undertaken in the future to reduce the sample mass beyond what has been achieved here. With the small beam spot size on ID24, samples of just a few tens of microns in size should be measureable given some suitable preparation technique. The thermal response time of such a sample would allow rapid temperature modulation, which in turn would reduce signal noise, opening the possiblity of mesuring thermally induced atomic displacements on a sub-Kelvin scale. This would, for example, be of particular interest in the study of thermal phase transitions. Further efforts should also be made to improve temperature stability in the gas jets, which at ±0.2K, currently constitutes our largest experimental uncertainty.

References

[1] Pettifer et al., Nature **435** (2005) 78-81
[2] Ruffoni et al., ESRF experimental reports, MI-740 (2004)
[3] Ruffoni et al., ESRF experimental proposals, MI-803 (2005)