ESRF	**Experiment title:** Thermal Expansion as determined by Differential EXAFS	**Experiment number**: MI-740
Beamline: ID24	**Date of experiment**: from: 29th Nov 2004 to: 6th Dec 2004	**Date of report**: 17th Feb 2005
Shifts: 18	**Local contact(s)**: S. Pascarelli	*Received at ESRF:*

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Report:

The aim of this experiment was to measure the differential displacement of atoms resulting from strains induced by the modulation of temperature. Taking a first order Taylor expansion of the x-ray fine structure with respect to temperature, we obtain

$$\frac{d\chi}{dT}=\sum_j \frac{2k^2\sigma_{j0}^2}{T}\chi_j(k)+\alpha s_j kA(k)e^{-2\sigma_j^2k^2}\cos\left(s_jk+\phi\right) \tag{1}$$

where temperature changes affect the thermal disorder parameter σ^2, and the scattering path length s_j. From (1) it can be seen that contributions to the differential fine structure from thermal disorder, represented by the first term on the right hand side, will be in phase with the original EXAFS signal; varying only in amplitude. The second term, characterised by the linear thermal expansion coefficient α, will, by contrast, be in quadrature as shown by the changes to the phase component. The presence of k^2 and k factors respectively indicates that both effects become more pronounced further from the edge, with the disorder term dominating. Therefore, we expect to observe thermal expansion as an out of phase component to the original EXAFS in the lower extended region.

Thermal expansion coefficients are generally of the order of $10^{-5}K^{-1}$, which results in atomic displacements of the order of 1fm for a 1K change in temperature. For this experiment we selected samples of powdered SrF_2 and polycrystalline Fe foil, which have thermal expansion coefficients of $18.4x10^{-6}K^{-1}$ and $11.8x10^{-6}K^{-1}$ respectively. Additionally, they have high Debye temperatures of 420K and 470K respectively, reducing the effect of thermal disorder. Our original proposal for this experiment suggested the use of a Ge sample. Upon closer examination, it was determined that Ge was not suitable for investigation given a much lower thermal expansion coefficient, $6.4x10^{-6}K^{-1}$, and Debye temperature, 358K. Additionally, being a single crystal, Ge would have been incompatible with differential EXAFS measurements on ID24 as described below.

The thermal modulation necessary for the measurement of thermal expansion was obtained with a purpose built gas jet apparatus as shown schematically in Fig 1, and photographically in Fig 2.

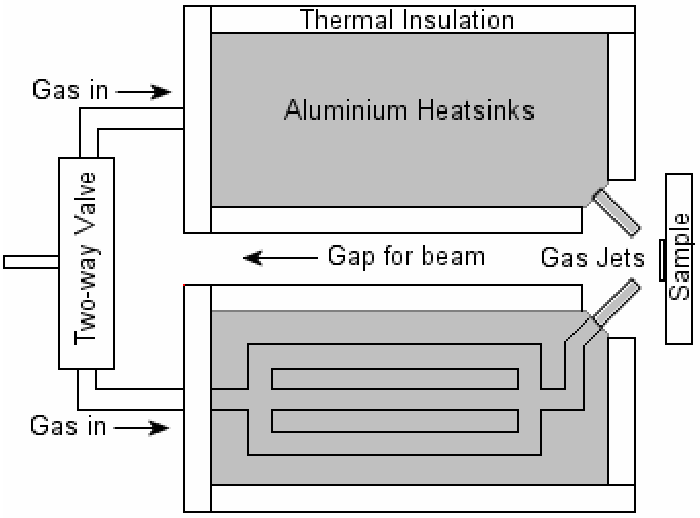

Fig 1: A Schematic representation of the gas jet apparatus

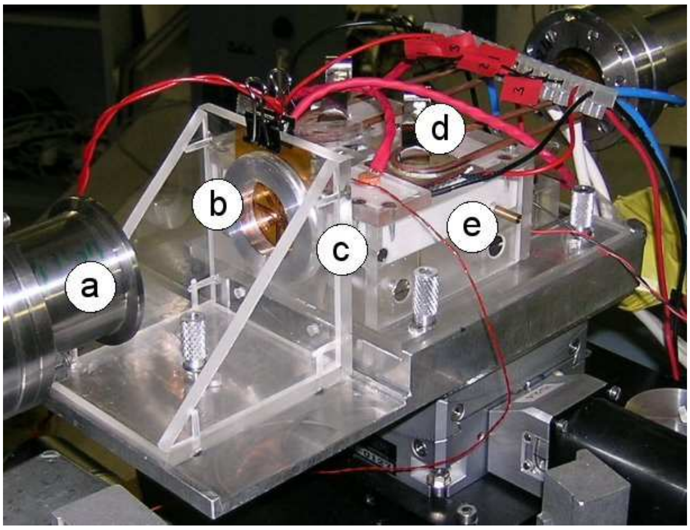

Fig 2: The actual gas jet mounted in the beam. a) beam in, b) thermopile with sample, c) gas jets behind here, d) heaters and sensors, e) heatsink.

Two jets of N_2 gas of differing temperature were targeting at samples, which were of a sufficiently low thermal mass to respond rapidly (of the order of a second or better) to the change in surrounding gas temperature. Performing the differential measurements on this time scale is necessary to minimize systematic drift problems inherent in any current synchrotron spectroscopy experiment. The most significant of these drifts, that of x-ray energy, was again addressed by selecting ID24, the dispersive x-ray spectrometer, due to its ability to capture an entire spectrum synchronously, with no moving parts.

The gas jets themselves were formed by passing ID24's N_2 mains supply line into a fast switching, two-way fluidic valve that directed the gas into one of two aluminium heatsinks 75 x 32 x 20 mm in size. Mounted on each heatsink was a water cooled 30 x 30 mm Peltier effect heater and a temperature sensor, both of which were connected to a PID temperature controller that allowed the heatsink temperatures to be set, monitored, and maintained throughout the experiment. Inside the heatsinks, the gas was split into three channels, passed along the length of the heatsink, and recombined to pass out of a needle on the opposite side. This arrangement ensured that the gas had sufficient time to reach thermal equilibrium with the heatsink before its exit.

The two needles were targeted at a single point 5mm in front of them, where the sample was placed. The samples were mounted at the centre of a 50mm diameter film of Kapton, upon which a radial array of eight copper-constantan thermocouples (connected in series) had previously been sputter deposited. Each thermocouple had one junction underneath the sample, to which it was thermally coupled by a thin film of silicone compound; and the other near the outer edge of the Kapton, where it was covered on both sides by aluminium rings; one 2mm thick and the other 5mm thick, each with an outer diameter of 50mm, and an inner diameter of 30mm. These rings acted as a large thermal mass, with a time constant significantly greater than that of the gas jet switching period, such that, for the duration of the experiment, the ring temperature remained at an equilibrium value defined by the ambient temperature in the hutch, and the average gas jet temperature. This provided a reference for the thermocouples, and was measured by a PT100 platinum-resistance thermometer mounted directly on the top of the 2mm thick ring. Therefore, ΔT at the sample can be determined by measuring the thermocouple temperature relative to the absolutely known ring temperature. A typical thermocouple response under gas jet switching is shown in Fig 3.

Our experiment was scheduled to begin on a Tuesday. Fortunately, we managed to set up most of the apparatus during machine time the day before, and therefore we began promptly when the beam came online. However, we encountered numerous problems, which prevented any useful data being collected until the early hours of Friday. The first of these problems was with the choice of sample. Tuesday was spent attempting to obtain differential measurements from a single crystal of SrF_2 at the Sr K edge, which proved impossible since the transmitted intensity persistently contained unforeseen glitches resulting from Borrmann transmission through

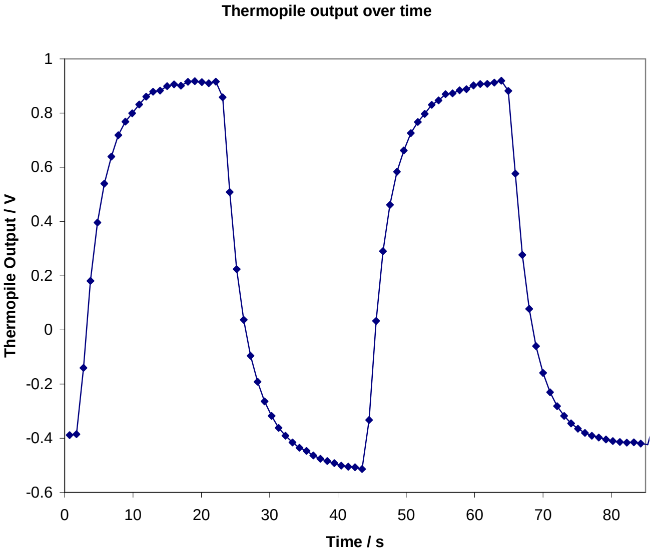

Fig 3: A typical thermopile response signal. Gas flow was set to 4lpm, and ΔT = 2.8±0.2K. Gas valve was switched every 20s

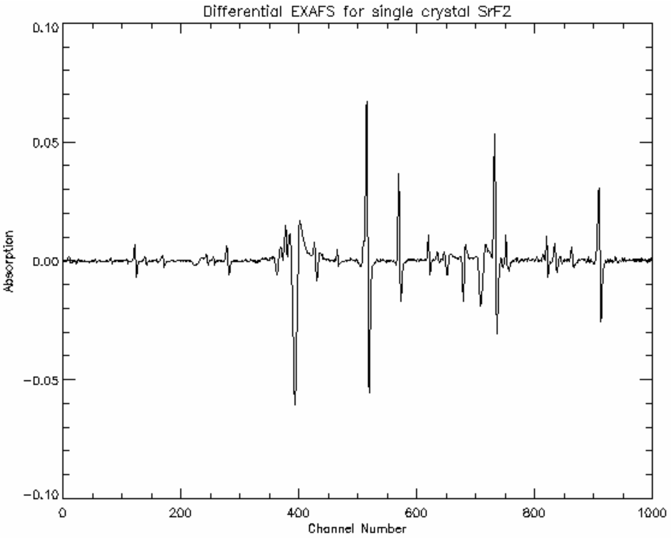

Fig 4: Differential EXAFS for single crystal SrF$_2$. The expected signal has been destroyed by Borrmann transmission glitches. Compare with Fig 5.

the crystal. These glitches moved significantly upon gas jet cycling and destroyed the differential signal as shown in Fig 4. From this we conclude that single crystal samples should be avoided where possible for differential EXAFS measurements, and more generally, that extreme care should be taken when using single crystal samples for x-ray transmission experiments on ID24. On Wednesday we produced a Boron-Nitride pellet containing 2.94mg SrF$_2$ so that $\Delta\mu x = 1$ at the Sr K edge. Some differential data was obtained, but was not useful since it was constantly corrupted by what we later found to be sample vibration under the influence of the gas jets; a problem that was undetectable prior to use of the beam. Wednesday and Thursday were spent investigating this problem, which was eventually solved by manufacturing and inserting a plastic plug into the 5mm thick aluminium ring around the sample to press on the Kapton film and stop it vibrating. At the same time, an additional temperature stability problem with ID24's water cooling system was addressed.

We are happy to announce that on Friday we observed the first differential thermal expansion signal, which was accumulated over a 10 minute scan for a temperature difference of 1.4±0.2K in SrF$_2$. The measurement was repeated with phasing of the gas jets switched, and the observed signal inverted as expected. The measurements were also repeated for a temperature difference of 2.8±0.2K, upon which the signal can be seen to increase in

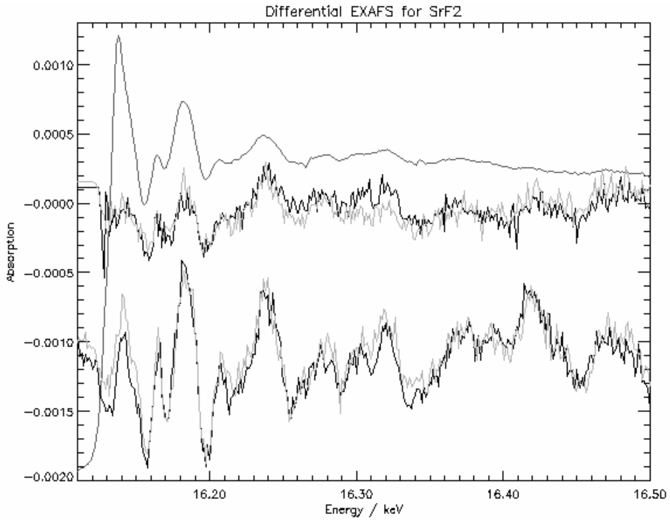

Fig 5: Differential EXAFS for powdered SrF$_2$. The top set is for ΔT = 1.4±0.2K, and the lower set for ΔT = 2.8±0.2K. The original EXAFS is at the very top. Gas flow was set to 5lpm. The grey lines are the gas jet phase shifted signals inverted.

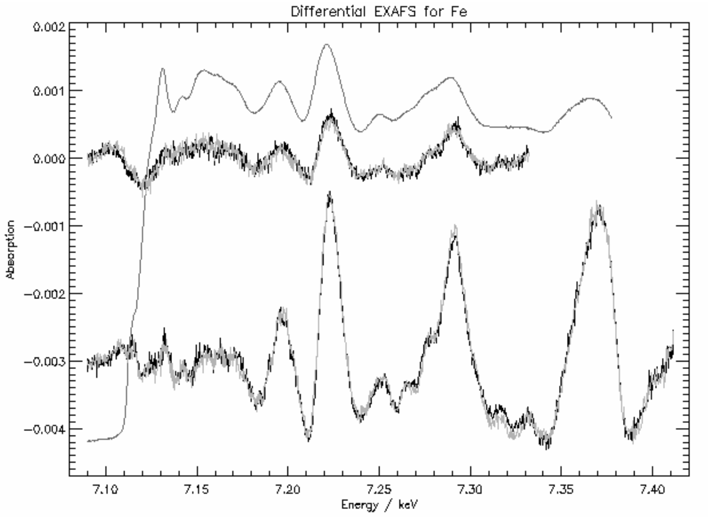

Fig 6: Differential EXAFS for polycrystalline Fe. The top set is for ΔT = 1.4±0.2K, and the lower set for ΔT = 2.8±0.2K. Gas flow was set to 5lpm. The grey lines are the gas jet phase shifted signals inverted.

amplitude as expected. Fig 5 shows this data. The signal noise remains of the order of $4x10^{-5}$ except at high energies where few photons were present. However, a problem is clearly present with the temperature calibration. We expect the fine structure amplitude to vary linearly with temperature as seen in (1). From Fig 5, the amplitude change is a factor of 4 whereas the temperature measurements would suggest a factor of two. This needs to be investigated. The corresponding signal was also observed in Fe, again for a 10 minute scan at a temperature difference of 1.4±0.2K. As before, inversion occurred upon gas jet phase switching, and the signal amplitude increased when the temperature difference was increased to 2.8±0.2K as seen in Fig 6. The quadrature component of the SrF_2 data with respect to the fine structure is difficult to see with the naked eye, but is much more pronounced in the Fe data.

Additionally, considerable difficulty was experienced whilst attempting to calibrate the SrF_2 data at the Sr K-edge. This was due to the mismatch in instrument properties between ID24 and BM29, from which a reference spectrum of known calibration was recorded. To solve this problem, a number of characteristic instrument functions were convolved with the BM29 data so as to match its resolution to that of ID24. Firstly, since BM29 uses a twin bounce monochromator and ID24 a single bounce polychromator, the Darwin reflectivity curves of each instrument will differ, with more x-ray transmission at undesired energies on ID24 . This can be accounted for by convolving the BM29 spectrum with a lorentzian so as to lowers its resolution to match that of ID24. The optimum width of this lorentzian was found to be 3.4eV. Once applied, the residual difference was asymmetric; an artefact indicative of x-ray penetration into the Si of ID24's polychromator, and one which is corrected by convolving the data with a function that is zero in $-\infty \leq E \leq 0$ and an exponential decay in $0 < E \leq \infty$. The optimum width of this exponential was found to be 1.2eV. The result of these corrections is shown in Fig 7.

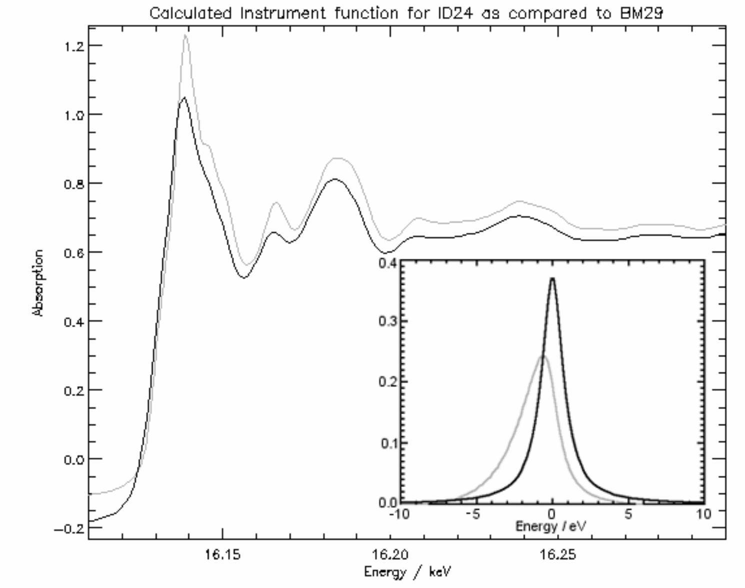

Fig 7: Instrument function corrections to match BM29 data to that from ID24. The black line in main graph shows the calculated absorption spectrum of ID24 resulting from convolutions to the corresponding BM29 spectrum (grey). The insert shows the convolution function (grey line), which results from combining a lorentzian of width 3.4eV (black line) with a function that is zero in $-\infty \leq E \leq 0$ and an exponential decay of width 1.2eV in $0 < E \leq \infty$.

This experiment has therefore successfully achieved its aim, and for the first time, proven the concept of measuring thermal expansion by differential EXAFS. However, refinements are still needed in the future to improve the technique. Firstly, it is clear from Fig 3 that the thermocouples respond to changes in gas temperature relatively slowly; a direct consequence of heat needing to pass through the sample and a layer of grease before being detected. The sample itself changes in temperature much quicker, and therefore, the x-ray time constant, as seen in the fine structure, is considerably shorter. More work needs to be done to quantify this x-ray time constant, and in doing so improve the accuracy of temperature measurements. Secondly, more work should be done with different forms of sample preparation. The present experiment used relatively large (and thus thermally massive) pellets and foils compared to what can be achieved by other methods. In the future we intend to investigate the behaviour of much smaller samples prepared in a copper gasket, as for high pressure experiments. Finally, and most importantly, now that this technique has been shown to work in practice, it would be significant to investigate the differential EXAFS of phase changes in materials by fine temperature sampling through the transition itself; an approach to the study of phase changes that has not been possible until now.