Thermal Differential EXAFS

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Outline

- An introduction to Differential EXAFS
- Thermal modulation of sample materials
- Proof of concept – Thermal expansion measurements
- Data analysis procedure
- Future work – Probing phase transitions with single Kelvin resolution

What is Differential EXAFS?

A Differential EXAFS spectrum is the difference between two conventional EXAFS spectra, taken with all environmental parameters kept constant except for *unit modulation* of some parameter of interest, such as temperature.

As a result, the signal contains information relating to structural *strain* that occurred due the change in chosen parameter.

First used to measure magnetostriction in FeCo (**R.F. Pettifer et al., Nature 435, 78**)

Potential problems:

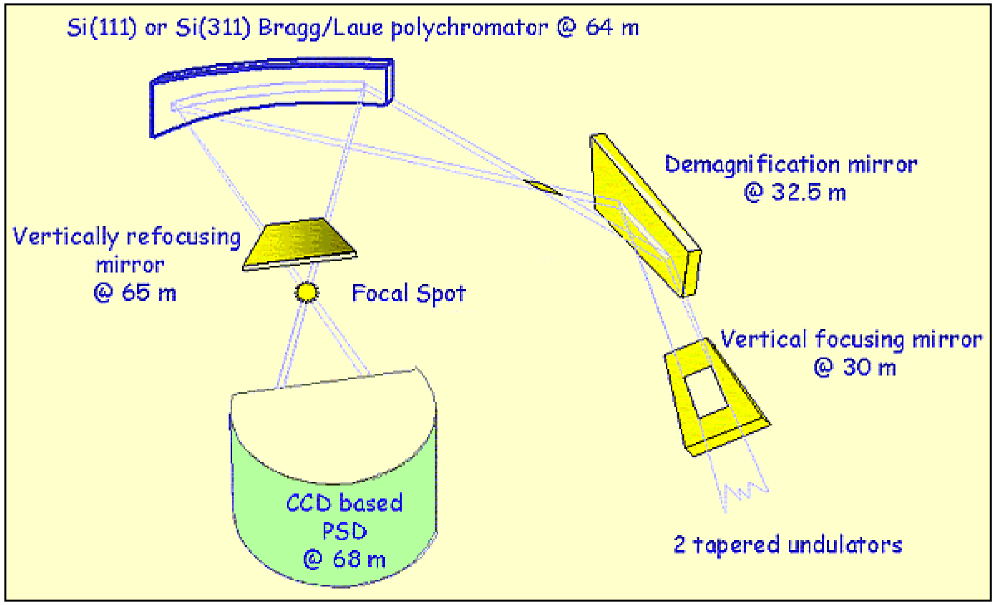
- Energy drift of the beam generating spurious signals
- Spatial drift of the beam causing measurement of different parts of sample
- Statistical noise preventing resolution of structural changes, typically ~10^{-5}Å

Solutions:

- Acquire both spectra in minimal time; of the order of a few seconds or less
- Use a high intensity 3^{rd} generation source in conjunction with a sensitive detector
- Average signal over many pairs of measurements
  (**O. Mathon et al., J. Synchrotron Rad. 11, 423**)

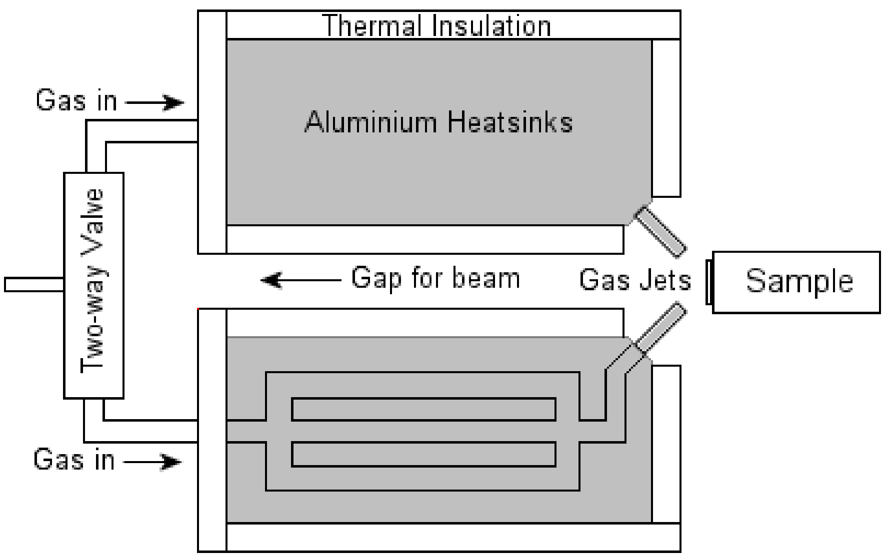
ID24 for Differential EXAFS

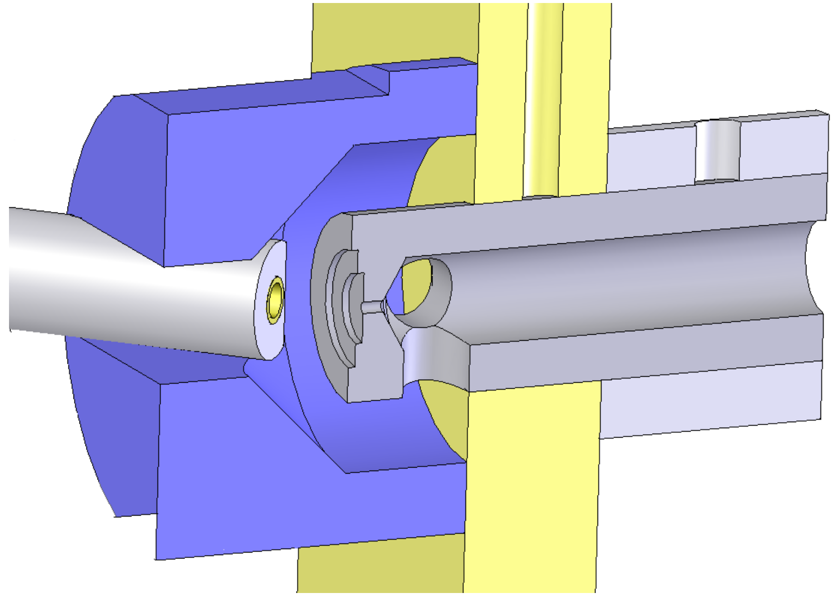
- All Differential EXAFS experiments performed to date have been conducted on ID24, the Dispersive XAS beamline of the ESRF.
- Mounted on a high-intensity 3rd generation undulator source.
- Entire spectrum is obtained simultaneously in around 200ms, minimising drift.
- Has no moving parts, which improves beam stability.
- Tight focal spot size allows use of samples with tiny thermal mass.



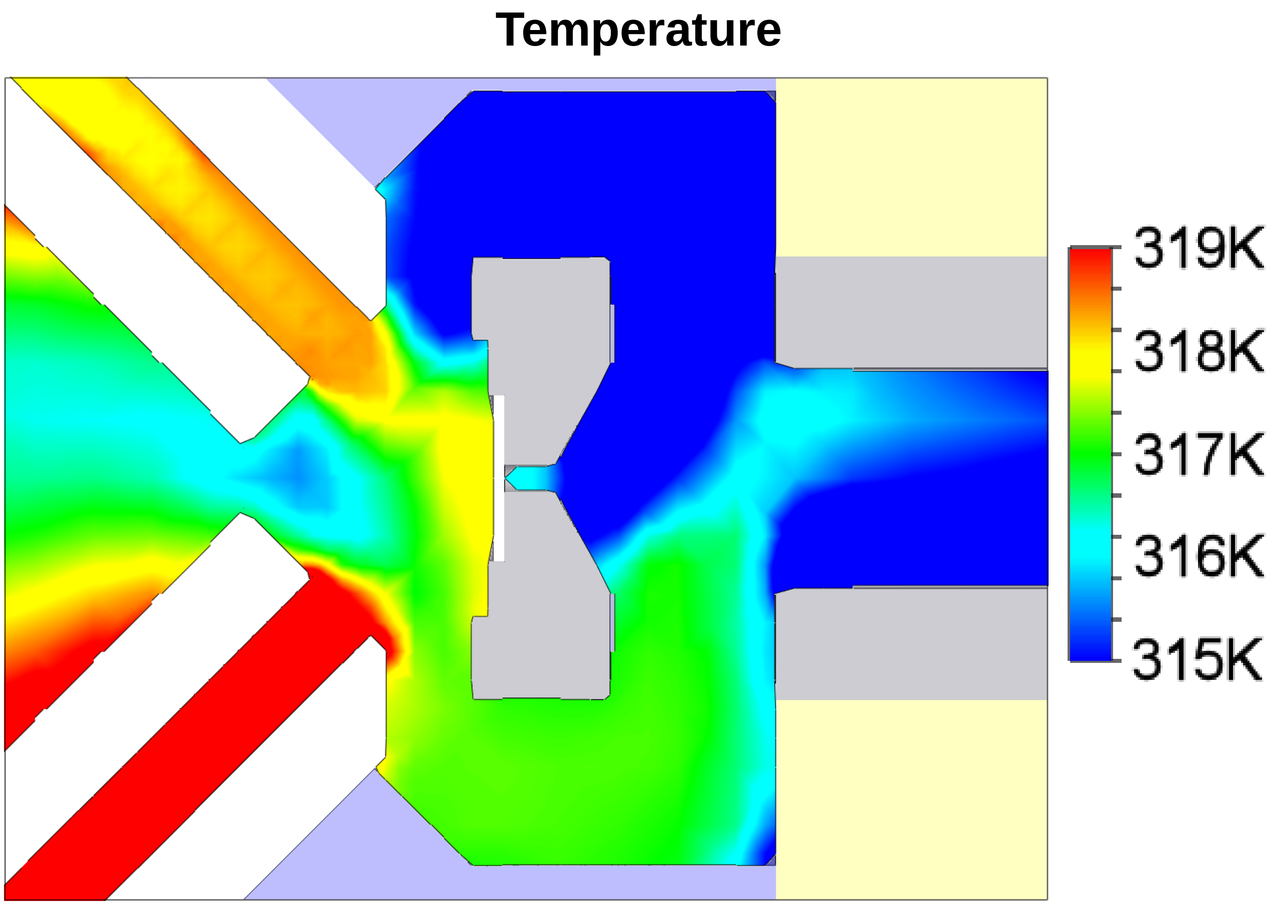
Thermal modulation apparatus

- Thermal modulation apparatus must alternately heat and cool the sample material between XAS measurements at T+ and T-.
- The heating/cooling must be quick. Ideally less than 1 second.
- Temperature at T+ and T- must be both stable and reproducible.
- Solution is to use two jets of heated gas, switched by a fluidic valve.





Thermal modulation apparatus



- Gas is heated as it traverses the heatsink
- Heated jet of gas strikes sample
- Gas passing around the rear of the sample provides secondary heating

Thermal Differential EXAFS

$$\chi(k,T)=\sum_j A_j(k)e^{-2\sigma_j^2(T)k^2}\sin\left(s_j(T)k+\phi_j(k)\right)$$

Neglect weak path length dependence of A and ϕ, making them T independent.

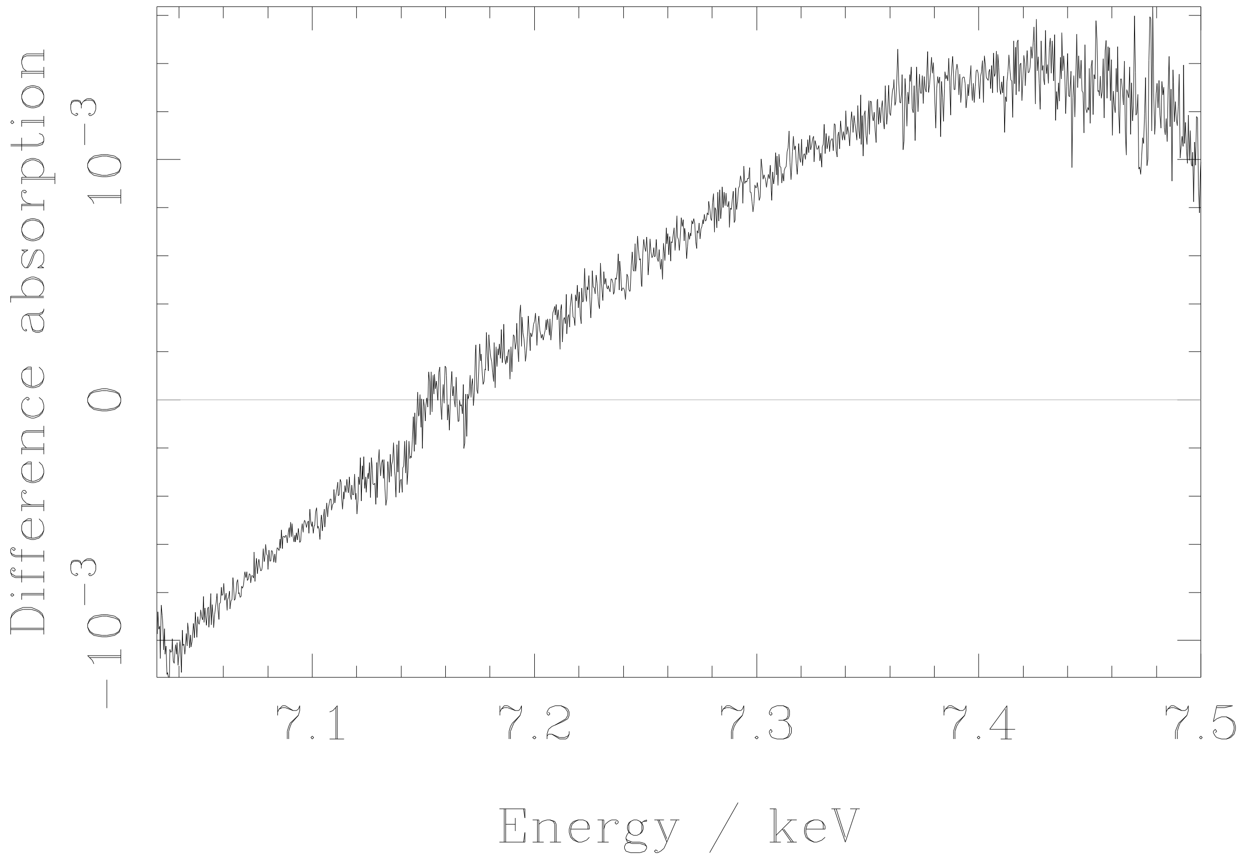
Take a first order Taylor expansion with respect to temperature

$$\frac{\partial\chi(k,T)}{\partial T}=\sum_j\left(\alpha s_j k A_j(k)e^{-2\sigma_j^2(T)k^2}\cos\left(s_j(T)k+\phi_j(k)\right)\right.$$
$$\left.-2k^2\frac{\partial\sigma_j^2}{\partial T}A_j(k)e^{-2\sigma_j^2(T)k^2}\sin\left(s_j(T)k+\phi_j(k)\right)\right)$$

Key Features

- The Differential signal contains both a Thermal Expansion and Disorder term.
- Thermal Disorder contributions are in phase with the original EXAFS signal.
- Thermal Expansion contributions are in quadrature with the original EXAFS signal.
- Given $\alpha \ll \partial\sigma_j^2/\partial T$, signal will be largely in phase with χ, but slightly phase shifted.

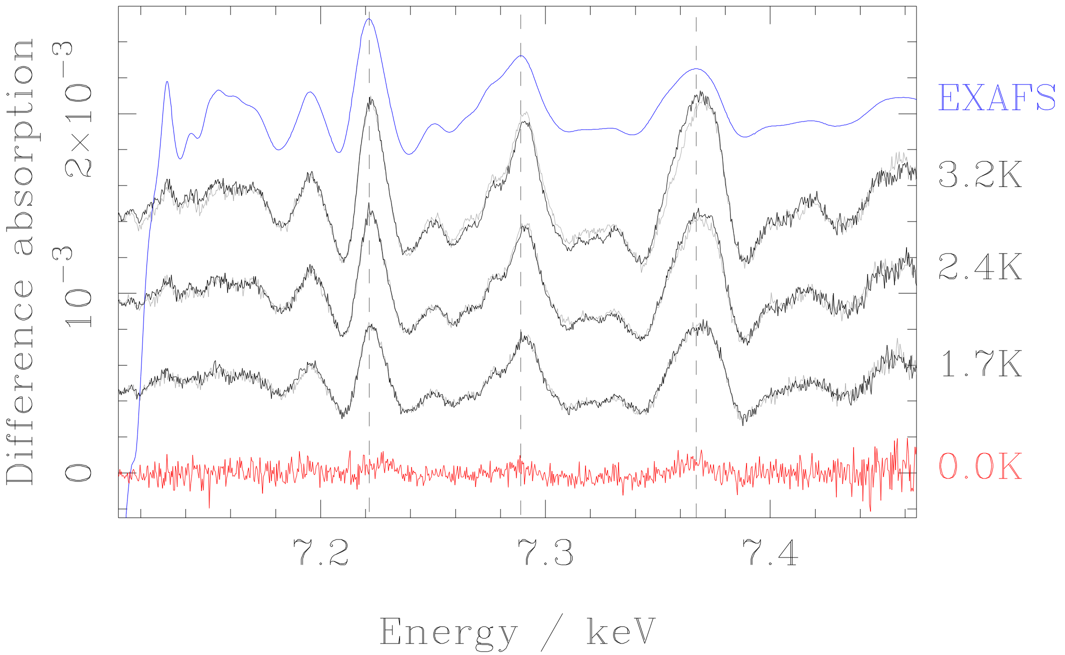
Tuning the apparatus

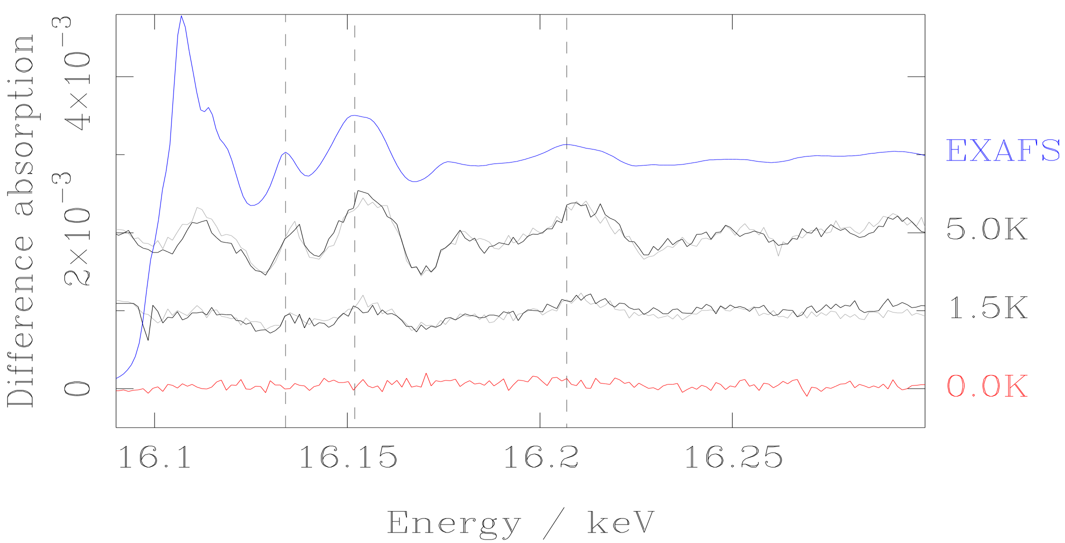


- Must obtain a flat DiffEXAFS baseline, passing through $\Delta\chi$ = 0, for ΔT = 0K.
- Pressure gradients within sample mount generated grey signal.
- 4 days of beamtime were needed to produce a flat baseline!

Thermal Expansion measurements

- To prove Thermal Differential EXAFS works in practice, thermal expansion measurements were made on samples of α-Fe and SrF_2
- Signals are averaged over 600 pairs of acquisitions for a range of temperature differences.
- Disorder term dominates given signals are largely in phase with EXAFS.
- DiffEXAFS peaks are phase shifted, indicating detection of the thermal expansion component.

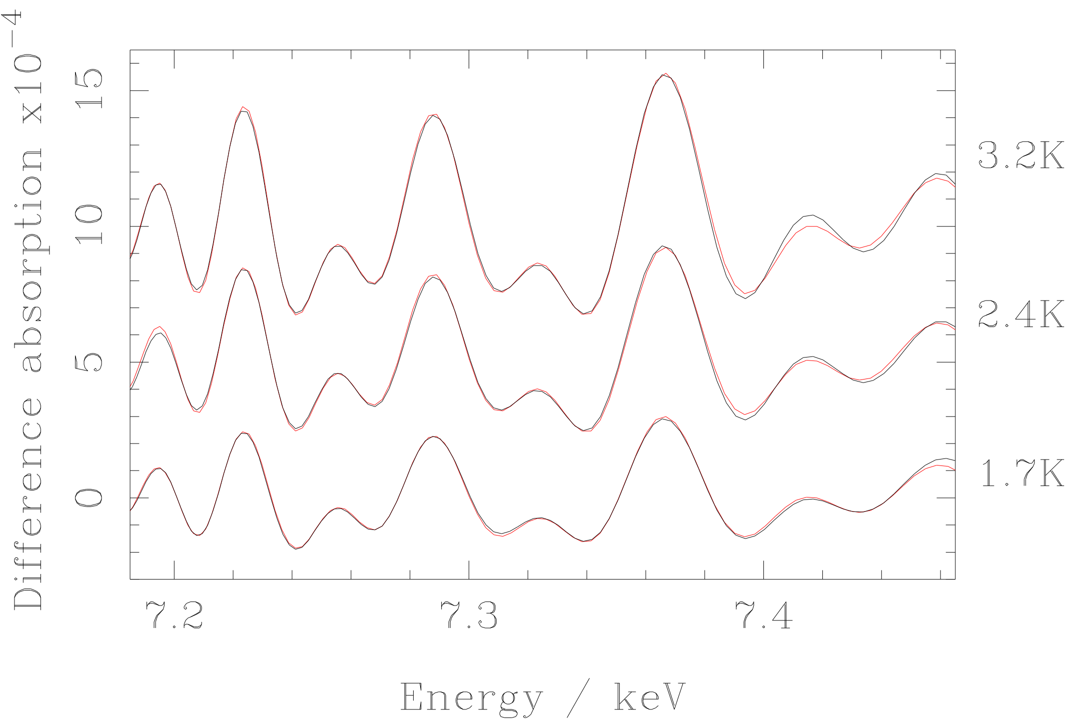




Thermal Expansion measurements

To obtain the thermal expansion coefficient:

1. Define a reference from which to measure thermally induced displacements
2. Fit the differential fine-structure function to each differential signal to establish α and the $\partial\sigma_j^2/\partial T$
3. α for Fe is 11.8 x $10^{-6}K^{-1}$



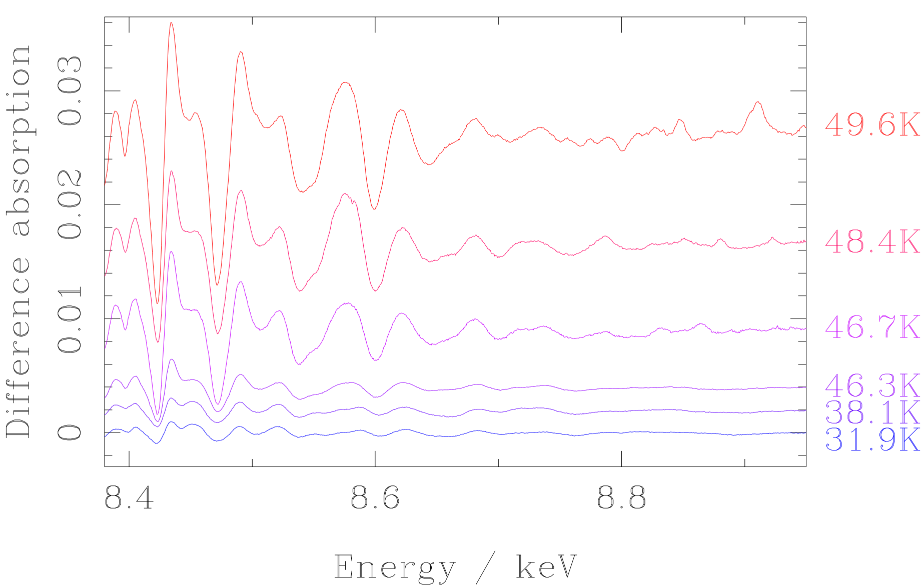
$\partial\sigma_j^2/\partial T$	ΔT = 1.7K	ΔT = 2.4K	ΔT = 3.2K
SS1	1.13±0.04	1.08±0.02	1.08±0.01
SS2	0.88 ±0.08	0.91±0.05	0.91±0.04
SS3	0±300	2.1±0.1	1.72±0.08
SS4	2.6±0.4	3.4±0.3	2.7± 0.2
α	**12±1**	**12.1±0.8**	**11.8±0.6**

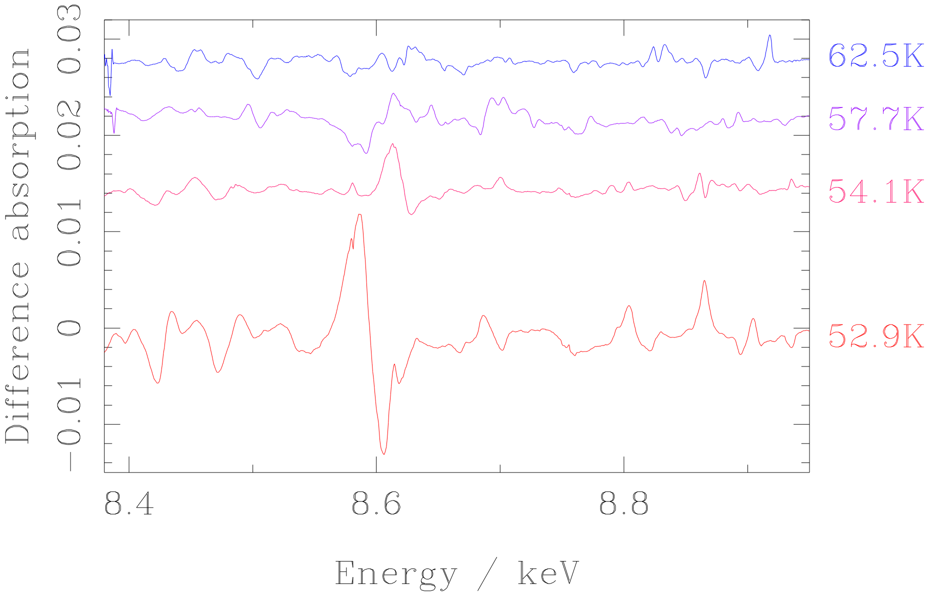
Units of $\partial\sigma_j^2/\partial T$ are $\times10^{-4}$ Å^2 and α is $\times10^{-6}K^{-1}$

Future Work – Phase Transitions

Thermal expansion measurements have shown Thermal Differential EXAFS works in practice.

But the true power of the technique lies in studies of disordered or amorphous systems or of non-linear phenomena such as *phase transitions*.





With temperature steps of ~1K, it is possible to measure structural changes over many points through the transition region itself rather than just above and below it.