	Experiment title: The study of phase changes in $HoBaFe_2O_5$ and in Ni_2MnGa using Differential EXAFS	**Experiment number**: HS-2945
Beamline:	**Date of experiment**: from: 14th Sept 2005 to: 19th Sept 2005	**Date of report**: 28th Feb 2006
Shifts:	**Local contact(s)**: S. Pascarelli	*Received at ESRF:*

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Report:

The aim of this experiment was to study the microscopic characteristics of thermally induced phase changes by use of Differential EXAFS (DiffEXAFS)[1] in samples of $HoBaFe_2O_5$[2][3] and Ni_2MnGa[4][5]. Although the technique of Thermal DiffEXAFS has been shown to work in proof of concept trials[6], no experiment to date has utilised the thermal resolution of the technique to study phase transitions. As such, our proposal aimed to perform the first Thermal DiffEXAFS measurements through a phase transition; probing the local changes in structure as a function of temperature changes of the order of 1K.

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. With the exception of the sample mount, the apparatus used was essentially the same as that previously reported[6].

The redesigned sample mount is shown schematically in Figure 1, and is discussed in detail in the report for experiment MI-803[7]. Accompanying the new sample mount was a new sample preparation technique, designed to minimise the mass of the sample in the beam, and thus improve its thermal response time. Samples, orignally in the form of 1μm powder, were to be created by using a diamond anvil cell to press a self-sustaining pellet 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. The measurement of the $HoBaFe_2O_5$ sample relied on the success of this technique, but unfortunately, despite numerous attempts to produce 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. Attempts were also made to produce a more standard Boron-Nitride based pellet, but again the sample was too inhomogenous under the beam. As a result, we had to abandon our attempt to measure the phase transition in $HoBaFe_2O_5$.

Fortunately, the Ni_2MnGa samples were in the form of polycrystalline foil (47μm thick), and as such could me mounted directly on to the sample mount without needing to be pressed into a pellet. The thermocouple required to measure the sample temperature was spot-welded directly onto the foil.

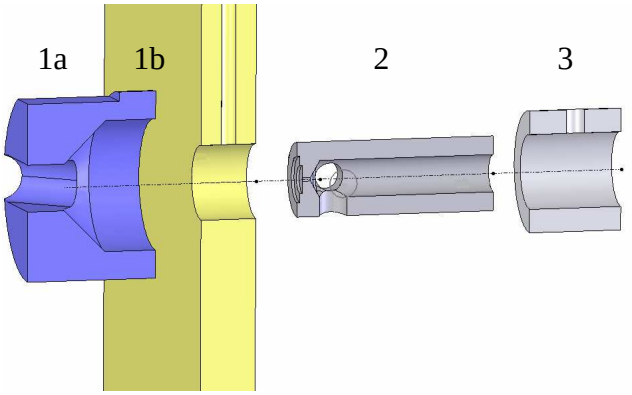

Figure 1a: Exploded view of the new sample mount. 1a and 1b: Sample sheath, 2: Sample holder, 3. Collar

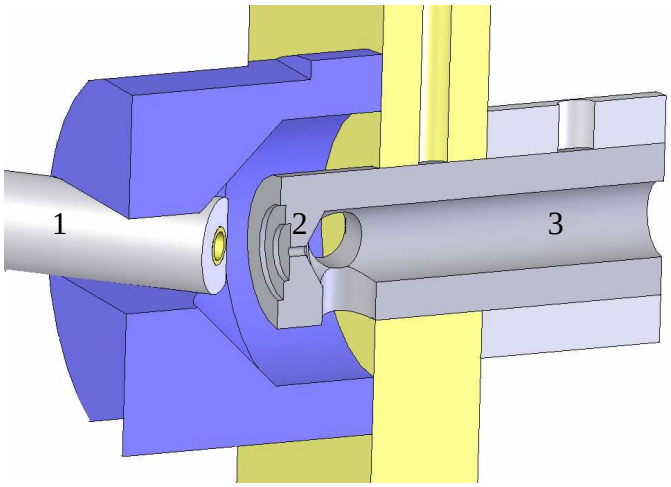

Figure 1b: Assembled view of the new sample mount with one of the two gas jets shown. 1: Gas jet, 2: Sample position, 3: Gas exit channel.

Measurements

Working initially at the Ni K edge in Ni_2MnGa, we are happy to announce that the experiment successfully detected the thermal differential signal in the vicinity of the Martensitic transition at $T_c \approx 51°C$. Starting at $T_{mean} = 18°C$ ($T_{mean} = \langle T+, T- \rangle$), where $T < T_c$ such that the sample is in its Martensite phase, and scanning up in temperature to $T_{mean} = 70°C$ revealed the series of signals shown in Figures 2 and 3. As $T \rightarrow T_c$ in Figure 2, the amplitude of the signal can clearly be seen to increase by in excess of an order of magnitude, whereas the structure itself remains unchanged. The unchanging structure shows that the Martensite phase persists. The amplitude increase however, indicates increasing thermal disorder in the system, which, based on previously published work, we believe may be due to phonon softening as the Martensite structure becomes unstable[8][9].

Interestingly, the signal at $T_{mean} = 18°C$ indicates onset effects from the transition are present despite being ~33°C away from T_c itself. This can be seen by comparing the DiffEXAFS signal with the orignal EXAFS. The theory of Thermal DiffEXAFS in the absence of a phase transition, predicts the differential structure will contain two components: one from thermal disorder, and one from thermal expansion. The thermal disorder component is in phase with the original EXAFS, and will dominate; with thermal expansion simply introducing a small phase shift. The structure in Figure 2 bears little resemblence to the original EXAFS as can be seen in Figure 4. Therefore the precondition that a phase transition is absent, can be regarded as invalid.

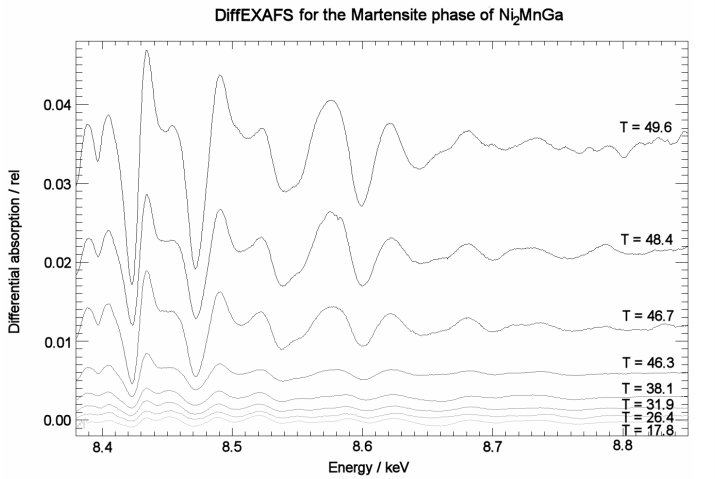

Figure 2: Thermal DiffEXAFS for the Martensite phase of Ni_2MnGa at the Ni K edge approaching the transition temperature, $T_c \approx 51°C$. Each plot has been translated vertically in order of temperature to aid visibility. Structure can be seen to increase significantly in amplitude as T_c is approached. Temperatures shown are mean of T+ and T- in °C ± 0.3K.

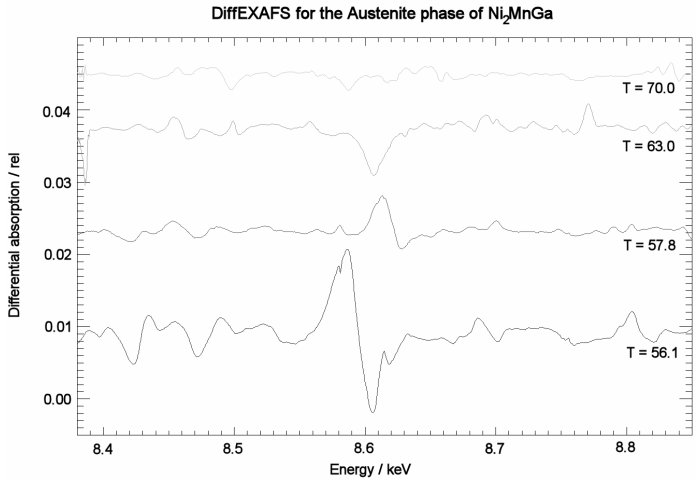

Figure 3: Thermal DiffEXAFS for the Austenite phase of Ni_2MnGa at the Ni K edge receeding from the transition temperature, $T_c \approx 51°C$. Each plot has been translated vertically in order of temperature to aid visibility. The structure is significantly different from the Martensite phase, although some similar feature exist persist, such as those between $8.38 \leq E \leq 8.55keV$. The structure appears to evolve with increasing temperature. Temperatures shown are mean of T+ and T- in °C ± 0.3K.

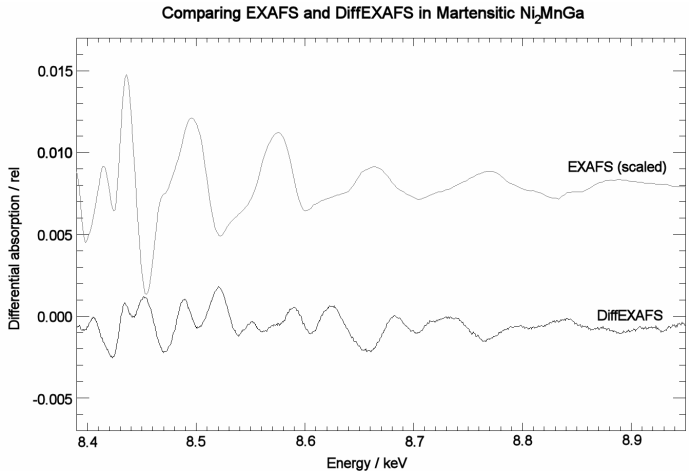

Figure 4: A comparision between EXAFS and DiffEXAFS signals in the Martensite phase of Ni_2MnGa at T = 18°C. In the absence of a phase transition, the DiffEXAFS signal should have essentially the same structure as the original EXAFS due to the domination of thermal disorder over the other, smaller, thermal expansion component. The clear differences in structure between the two spectra indicate that the DiffEXAFS is detecting some early component of the phase transition, despite $T_c \approx 51°C$.

Beyond T_c, the DiffEXAFS changes dramatically as seen in Figure 3; clearly indicating the sample has transformed into its Austenite phase. Some features bear resemblence to their Martensitic counterparts such as those between $8.38 \leq E \leq 8.55$keV, but the remainder of the spectrum does not. Indeed, the structure in this region is either not entirely stable, or is heavily influenced by the thermal modulation from the gas jets; being as it appears to evolve as T increases. Preliminary analysis for this region shows an anomalously large Debye-Waller factors for the second, fourth, and sixth shell Ni-Ni scattering paths, which must be investigated further. Indeed, work in analysing this signal is ongoing, and results will be published in due course.

Additional data were also taken to investigate the presence or otherwise of hysteresis in the transition. The Martensitic transition in Ni_2MnGa is first-order and diffusionless, and therefore hysteretic effects are expected to be negligable. This was corroborated by our results, as no hysteresis whatsoever was observed on the scale of measurements steps of the order of 1K.

Once data were acquired at the Ni K edge, we proceeded to spend the remaining beamtime studying the Ga K edge. Figures 5 and 6 show the DiffEXAFS signals obtained for the Martensite and Austenite phases respectively. As with the Ni data, changes in structure can be observed beyond T_c, but in this case, are more subtle; appearing to evolve much more slowly as T increases. These data, although not as finely sampled in T, should complement analysis of the structural changes in conjunction with the Ni data.

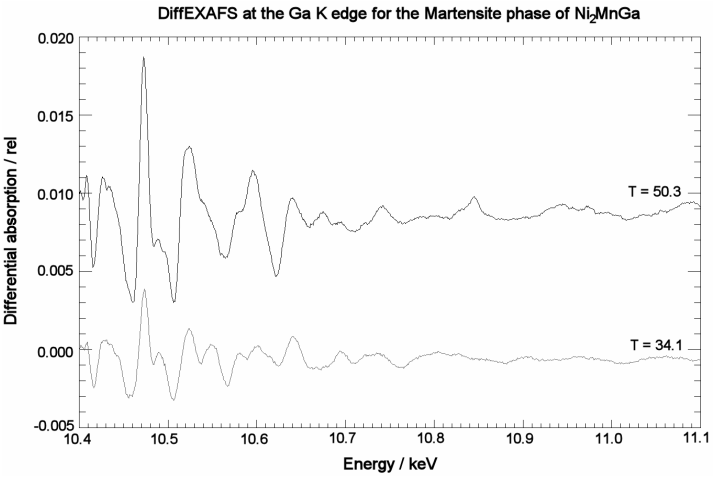

Figure 5: Thermal DiffEXAFS for the Martensite phase of Ni_2MnGa at the Ga K edge approaching the transition temperature, $T_c \approx 51°C$. Each plot has been translated vertically in order of temperature to aid visibility. Again, the structure can be seen to increase in amplitude as T_c is approached. Temperatures shown are mean of T+ and T- in °C ± 0.3K.

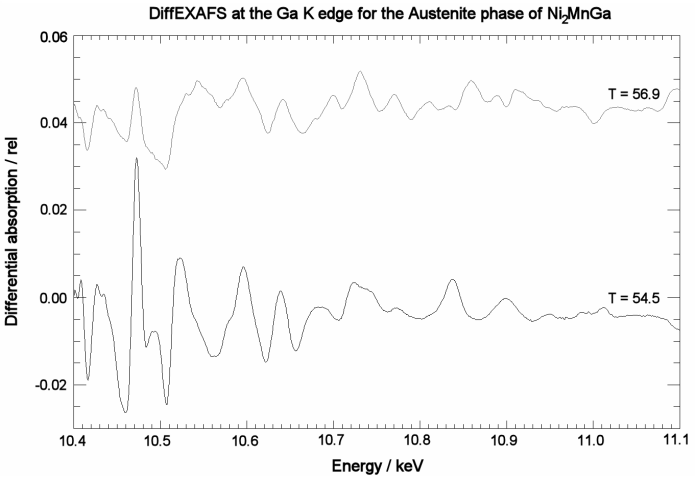

Figure 6: Thermal DiffEXAFS for the Austenite phase of Ni_2MnGa at the Ga K edge receeding from the transition temperature, $T_c \approx 51°C$. Each plot has been translated vertically in order of temperature to aid visibility. The structure is different from the Martensite phase, although the severity of the changes are not as great as at the Ni K edge. Temperatures shown are mean of T+ and T- in °C ± 0.3K.

This experiment has therefore successfully achieved it's primary aim. The sensitivity of Thermal DiffEXAFS to atomic displacements over temperature changes of the order of 1K has, for the first time, been utilised to take data through a phase transition. Despite problems pertaining to the measurement of $HoBaFe_2O_5$, the Martensitic transition (first-order, diffusionless) in Ni_2MnGa has been detected in data taken at both the Ni K and Ga K edges. However, further work should be undertaken in the future to improve the quality of data. Firstly, additional work should be done in improving sample preparation. The Ni_2MnGa foil used here was 47μm thick giving an edge jump of ~4 at the Ni K edge; presenting problems with data acquisition. Clearly a thinner sample is required with $\Delta\mu x \sim 1$. This will also allow data to be acquired at the Mn K edge; the measurement of which should be undertaken in order to obtain a complete set of structural information from all atomic sites in the sample. Further improvements

should also be made in the temperature modulation apparatus. Presently, errors in T+ and T- are ±0.2K, giving an error in T_{mean} of ±0.3K. Reducing these will allow greater accuracy in setting not just the relative temperature difference ΔT, but also the absolute temperatures T+ and T-, which is vital the closer they approach T_c. Furthermore, if ΔT could be reduced in conjuction with increased accuracy, say to the order of 0.1K, finer sampling close to T_c could reveal more useful data regarding the transition itself.

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