EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Separating Overlapping Edges in EXAFS Spectra	**Experiment number**: CH1178
Beamline: ID 26	**Date of experiment**: from: 14th November 2001 to: 20th Nov 2001	**Date of report**: 20th December 2001
Shifts: 12	**Local contact(s)**: P.E. Petit	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

R.F. Pettifer *

Department of Physics,

University of Warwick

Coventry CV4 7AL UK

Report:

It was origionally anticipated to test this proposed advance in technique by studying a $Pr_{0.5}Sr_{0.5}MnO_3$ thin film as the Pr L and Mn K edges overlap. A film was produced for this purpose but in the time between writing the first application for beam-time and its arrival, the film suffered degradation via reactions with the air causing Pr to migrate out of the surface. Fortunately contingency samples were available and the one which we had time to study was a thin film Gd/Co multilayer. There were two samples consisting of 200Å Si-20(35Å Co 75Å Gd)-200Å Si and 200Å Si-20(35Å Co 5Å Si 75Å Gd) 200Å Si, and these were supplied by G. Kurlyandskaya . The main thrust of the proposal was to show that it is possible to separate overlapping x-ray absorption edges and indeed, the GdCo films served as perfect substitutes.

It was clear at the time of writing the proposal that since rare earth elements possess a number of emission lines which are closely spaced, that a moderate energy resolution detector, of a few eV, was required with good throughput, to enable excitation spectra to be accumulated in a reasonable time. Unfortunately, it is not possible to use a solid state detector for this purpose as its energy resolution is not adequate. The only other option is thus to use a wavelength dispersive x-ray spectrometer. On ID26, there is a high resolution wavelength dispersive secondary x-ray spectrometer capable of providing an energy resolution of approximately 1eV at energies of interest here (around 7KeV), and this can produce $K\alpha_1$ from a solid copper target at 20K counts per second (Petit private communication). Scaling this value to the thickness of film used here (thickness equivalent of 700Å) would produce about 200 counts per second which is too small to record excitation spectra in a reasonable time. However, it was fortunate that the ESRF had purchased, but not commissioned an Oxford

Instruments WDX spectrometer which was of the Johanasson design (Bent to 2R and ground to R, where R is the radius of the Rowlands circle) equipped with a number of crystals which were selectable on a turret. The crystals and detector moved to remain on the Rowlands circle, whilst the virtual source remained fixed This spectrometer is designed to be mounted on an electron microscope. There are two detectors of the proportional counter design. One is sealed (at the back) and the other is of the flow design (at the front and operates such that some radiation is trasmitted to the rear chamber). The sealed proportional detector is mainly of use in detecting hard radiation whilst the flow detector is of use in the soft energy range. The total detector gain is adjusted by software to exclude multiple orders from being recorded.

Unfortunately the intrinsic energy resolution of the proportional detector is paid for in terms of detector non-linearity. This was evaluated by recording an emission spectrum at two different excitation intensities. An analysis of this data showed that there was a typical dead time of about 5 microseconds and this limits the counting to below 40K counts per second where the corrections start to become substantial. Fig 1 demonstrates the non-linearity.

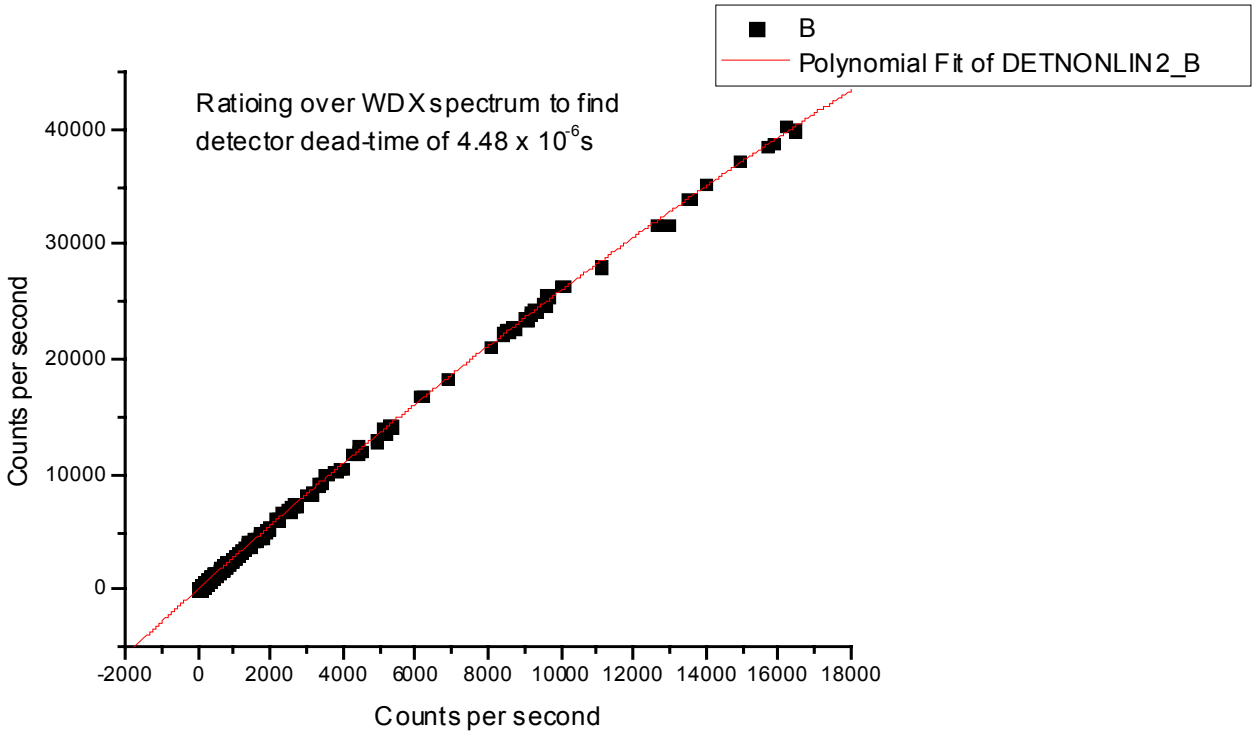

Fig. 1. A plot of the count-rate for a portion of the emission spectrum against count-rate for the same region but with a different intensity. An analysis gives a dead-time typical of the proportional detector operating under these conditions.

The emission spectrum appropriate for this study is shown below, which shows a number of lines closely spaced. If the same spectrum were to be taken with a solid state detector then none of the lines shown would be resolved. In particular, note the proximity of the Gd $L\beta_6$ to the Co $K\alpha_{1,2}$ lines. From the splitting of the Kα lines and also by recording the Rayleigh scattered radiation the full width at half maximum of the instrument function of the WDX operating with 200μm slits is 10eV at these energies. The resolution can be improved to 8eV, but with the inevitable loss of intensity, at at the Cu Kα lines, but this is probably at the limit set by vertical divergence and crystal penetration abberations.

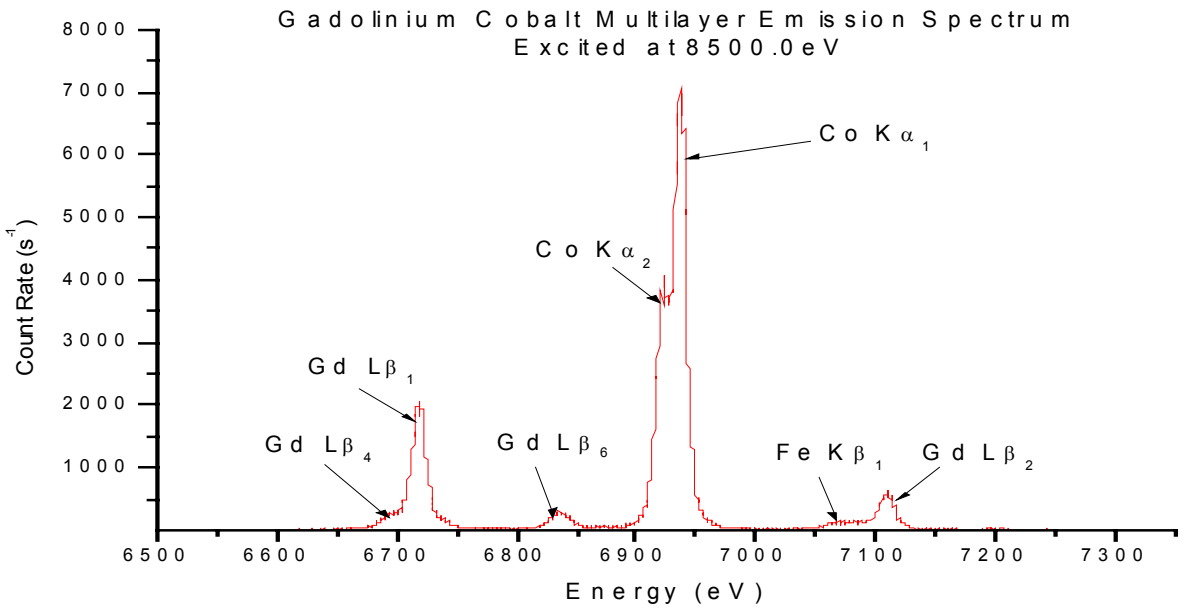

Fig. 2 The emission spectrum of the GdCo multilayer specimen excited by incident radiation of 8500.0eV, which is just above the GdL_1 edge. The coaseness of the plot is created by inclusion of the figure into a word document.

Having recorded the emission spectrum, the excitation spectrum (set the WDX to the peak of the $K\alpha_1$ emission and record its intensity as a function of the primary energy from ID26), suitably normalised to the incident energy as recorded by a transmission photodiode. This is shown in Fig. 3.

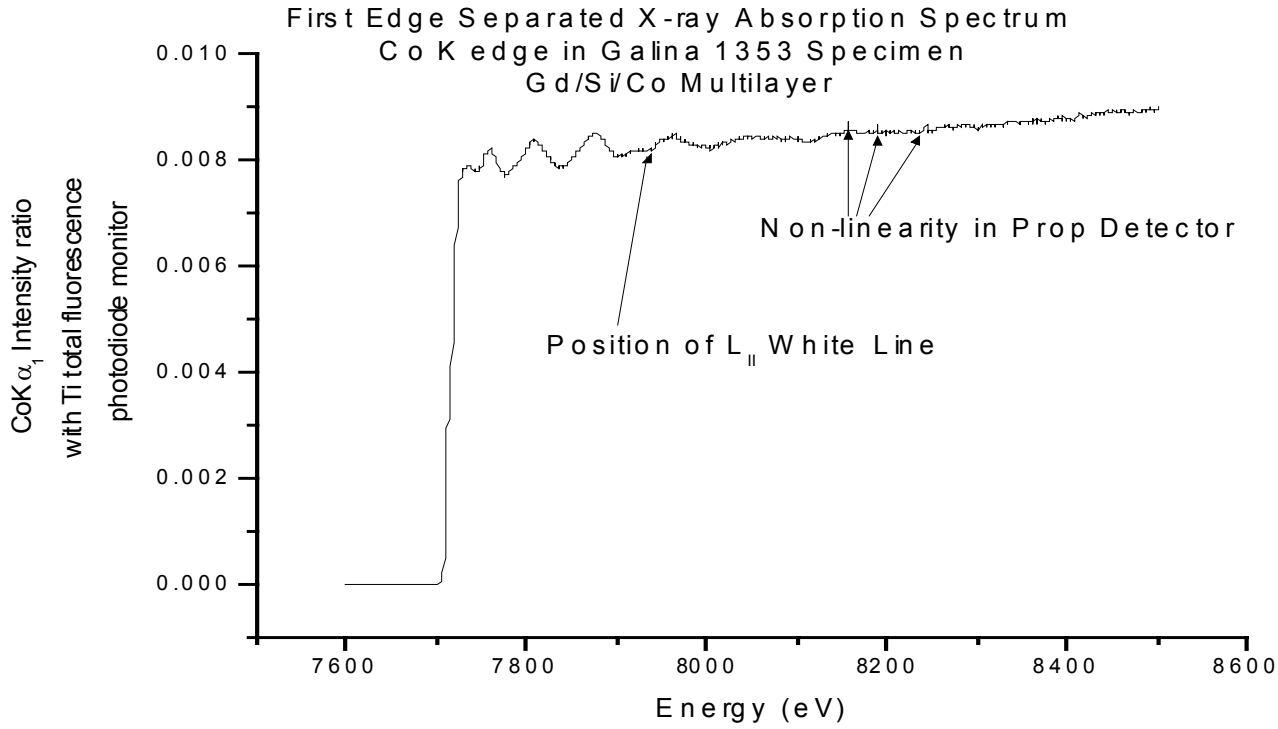

Fig 3. The excitation spectrum of the Gd/Co film taken from the Co $K\alpha_1$ line. The angle of incidence was 5.5^o.

Several features can be deduced from this spectrum, which has not been corrected for detector nonlinearity. Firstly there are a collection of positive spikes in the spectrum caused by non-linearity of the detector and these are marked as such. Secondly, it can be noticed that the self-absorption effects are very small, but under close inspection they can be observed at the position marked with an arrow. The same spectrum was then recorded at an angle of incidence of 45^{o}, which roughly doubled the self absorption effect at the Gd L_1 edge. Using the $L\beta_1$ line the excitation spectrum of the Gd L_2 edge was recorded which will permit a complete self absorption correction. We feel that we now have sufficient data for a publication which we believe will be the first demonstration of edge separation in x-ray absorption spectroscopy.

A visual examination of the data shows that the Co layer is disordered and it is probably not possible to discern the phase of Co present. A detailed analysis will reveal the extent of the disorder.

There are several peripheral points to be noted. The first is that the yield of good spectra is at the moment small, only about 30% of the spectra not suffering from measurement artefacts. These artefacts consist of additional inconsistent structure above the absorption edge at the few percent level. The origin of this structure is not at present known, and needs to be investigated before stating that the recording of excitation spectra with the WDX can be considered routine. Secondly, the sample was located in a vacuum box to permit cooling, but this also allowed soft x-ray spectra to be recorded. Only a brief examination of this prospect was investigated, and it revealed that usable count-rates from the Co $L\alpha_1$ could be obtained.

The following persons took part in this investigation, apart from the author of this report and they were T. Neisius, who worked on an in-house investigation earlier in the year and P-E. Petit who took part in the measurements reported here. The whole effort could not have been so sucessful without the excellent help from J. Morse and C. Cohen from the detector group. In addition, the WDX was expertly interfaced via the SPEC software by L. Claustre. The mounting and vacuum concepts were realised by the efforts of G. Blattmann and Y. Dabin of the drawing office. The author would like to express his thanks to the ESRF for the facilities to realise this project.