102368 -1002

DL/SCI/TM38E

technical memorandum Daresbury Laboratory

DL/SCI/TM38E

X-RAY ABSORPTION SPECTROSCOPY

by

G.P. DIAKUN, G.N. GREAVES, S.S. HASNAIN and P.D. QUINN, Daresbury Laboratory

LENDING COPY

JANUARY, 1984

Science & Engineering Research Council

Daresbury Laboratory

Daresbury, Warrington WA4 4AD

CONTENTS

INTRODUCTION

This manual describes facilities for x-ray absorption spectroscopy at the SRS in the spectral range 0.3 - 3.2 Å or 40 - 4 KeV. It is divided into three main chapters. The first covers the station software (1.1 to 1.5), the second the station hardware (2.1 to 2.4) and the third is devoted to the analysis programmes.

In particular Chapter 1 describes loading the setting-up and data acquisition programmes (1.2) and transferring data from the experimental station to the mainframe (1.3). A command-by-command description of the software is then given - both for transmission as well as for fluorescence measurements (1.4 and 1.5). Chapter 2 covers the operation of the major items of equipment on the station: the order-sorting monochromator (2.1) the scintillation PMTs for fluorescence detection (2.2) and the Pt-coated toroidal mirror (2.3). Chapter 2 also includes broad guidelines for making both transmission and fluorescence EXAFS measurements (2.4). Finally, in Chapter 3 an introduction is provided to the data reduction and EXAFS analysis programmes available in the SRS Programme Library. The three principal programmes EXCALIB (3.1), EXBACK (3.2) and EXCURVE (3.3) are described.

A schematic of the EXAFS equipment is shown in figure 1. Unfocused or focused white x-rays from the beryllium window pass through monochromator vessels where they are defined in a vertical angle and horizontal aperture and monochromated. The EXAFS monochromator operates under rough vacuum pressure. Monochromated x-rays leave the exit slit vessel through a further beryllium window. EXAFS measurements are usually made in air either by monitoring

(a) transmission through the sample

or (b) fluorescence emitted from the sample.

The user can expect that the entrance and exit slits will be aligned with respect to the monochromator and that the Bragg angle of the monochromator will be approximately calibrated. Ion chambers will be in position and have suitable rare gas mixtures for the particular wavelength the monochromator has been left at. If fluorescence detectors are required help should be sought from the station master. Precise calibration of the monochromator is left to the user and requires the use of a metal foil whose K and L edges fall in the wavelength range of interest. Monochromatic beam can be detected using Polaroid film and a laser is provided to enable the sample to be aligned to the monochromated beam. Various cryostats and a furnace are available. If these or other enviromental stages are required the Station Master or Local Contact should be advised in advance of the scheduled beam time.

New users should be aware that x-ray beam lines at the SRS are multi-station ports and that there are two kinds of x-ray shutter. The port shutter, which controls the light to all the stations is under the control of the crew in the Main Control Room (MCR). Should this close for any reason the appropriate light will go out and the MCR should be contacted for it to be re-opened (telephone 560, 561 or 562). Persistent port shutter problems must be reported to the Beam Port Coordinator as soon as possible. The station shutter is under the control of the experimenter. Once the hutch is correctly interlocked the station shutter can be opened and closed as desired. See the instruction notice on the hutch for details of the hutch interlocking procedure. Station shutter problems should be reported to the Station Master.

The documentation that follows is designed to be reasonably comprehensive and will be updated as facilities at the SRS develop. If problems arise during data collection or analysis that are outside the scope of this manual, the Station Master or the Local Contact should be advised. In any event it is extremely important that all difficulties and problems encountered by users should be fully recorded in the station log-book at the time.

PEOPLE TO CONTACT FOR HELP

		Ext. No.	Bleep
S.S. Hasnain	(Station Master 7.1)	273	225
G.P. Diakun	(Deputy Station Master 7.1)	273	
G.P. Diakun	(Station Master 9.4)	273	
G.N. Greaves	(Deputy Station Master 9.4)	335	107
P.A. Ridley	CSE	405	105
E. Pantos	CSE, SRS Programme Library	275	
G. Mant	CSE	275	

		Ext. No.	Bleep
J. Sheldon	Mechanical Services (e.g. gas bottles, plumbing, rotary pumps)	557	173
User Support Team		560,561,562	

Beam Port Coordinators:

X-ray 7 G.P. Diakun (602124) (Deputy G.N. Greaves)

X-ray 8 S.S. Hasnain (93-710843) (Deputy J.S. Worgan)

Wiggler 9 G.N. Greaves (935-63194) (Deputy P.J. Duke)

CHAPTER 1 - STATION SOFTWARE

1.1 INITIAL CHECKS

1.1.1) Check the CAMAC power supply is switched on.

1.1.2) Check the disk drivers are switched on.

1.1.3) Programme status. Press 'carriage return'. If RT-11 is loaded the VDU will respond with the prompt '.', if CATEX is also loaded the prompt '+' will appear on the screen, if the EXAFS programme is loaded

INVALID COMMAND FOR HELP TYPE H

COMMAND?

will appear on the console.

1.2 LOADING THE VARIOUS PROGRAMMES

The EXAFS and system programmes are stored at the station on a Winchester Disk which also collects a permanent record of the experimental data collected. The loading procedure depends on the state the system is in. RT-11 responds with a '.' prompt, CATEX with a '+' prompt and the EXAFS programme with a 'COMMAND?' prompt. The loading procedure should therefore be taken up from the prompts shown on the screen when carriage return is pressed. The full procedure is necessary if the system crashes for some reason (e.g. power failure).

1.2.1) Using the keys on the VDU

Press BREAK

Enter 762000G

The system run light should now be illuminated, if the system does not load or the run light goes off repeat the sequence. If this fails seek advice.

1.2.2) When the system has been loaded the console will respond with:

RT11 FB(S) V04.00

DATE

TIME

.

When the RT-11 prompt '.' has appeared CATEX may be loaded by typing

CAT 'carriage return'

The system responds with:

******CATEX Version 2******

LAST MODIFICATION <date>

+

When the CATEX prompt '+' has appeared the data acquisition programme may be loaded by typing either

!RD SY:LOAD 'carriage return'

for transmission measurements or

!RD SY:LOAD2 'carriage return'

for fluorescence measurements.

If at any time during the running of the programme an unforeseen error occurs and the CATEX prompt appears the system should be reloaded with the above commands. Important: please report all errors in EXAFS7 logbook. When either programme has been loaded the console reponds with:

TABLE HEIGHT (MICRONS)=xxxx (e.g. 16000)

MONOCHROMATOR POSITION=xxxx (e.g. 24000)

The table height is the height of the optical bench (containing exit slits, ion chambers etc) that is offset from straight through beam. This offset is required because the white radiation when monochromatised is displaced by 2Dcosθ, where D is the separation between the two crystal surfaces of the monochromator and θ is the angle of the monochromator with respect to the incident beam, or the Bragg angle. The monochromator position is given in thousandths of a degree, the value 24000, therefore, is equivalent to 24 degrees. When moving the monochromator one step this is equal to a thousandth of a degree.

A list of commands also appears on the console. For the programme LOAD these are:

TYPE L LIST SCAN PARAMETERS

C CHANGE SCAN PARAMETERS

E MOVE SLITS, TABLE, EXPERIMENT AND MIRROR

P MONOCHROMATOR POSITION

M MOVE MONOCHROMATOR

S START DATA COLLECTION

I FOR INFORMATION ON K AND L(3) EDGES

R READ ION CHAMBERS

T HAVE TABLE SYNCHRONISED WITH MONOCHROMATOR

V TABLE HEIGHT

O MOVE COARSE MOTOR

D % HARMONIC REJECTION FOR DC

H HELP

COMMAND?

For the programme LOAD2 these are:

TYPE L LIST SCAN PARAMETERS

C CHANGE SCAN PARAMETERS

E MOVE SLITS, TABLE, EXPERIMENT AND MIRROR

P MONOCHROMATOR POSITION

M MOVE MONOCHROMATOR

S START DATA COLLECTION

I FOR INFORMATION ON K AND L(3) EDGES

R READ ION CHAMBERS

T HAVE TABLE SYNCHRONISED WITH MONOCHROMATOR

V TABLE HEIGHT

O MOVE COARSE MOTOR

D % HARMONIC REJECTION FOR DC

H HELP

A TO SET UP FLUORESCENCE DETECTORS

COMMAND?

These commands enable a user to set up his experimental parameters prior to data collection. They allow adjustments to be made to the slits, optical bench, mirror and the Bragg angle of the monochromator. They enable the counts in the reference and signal ion chambers to be read and the energy window of the fluorescence detectors to be set. They also provide the facility for the user to set up spectral regions for a scan. The commands are described in detail in the next section.

1.2.3) Important: ensure that the Station Master has updated the system with your current grant number.

1.3 TRANSFERRING DATA TO THE MAINFRAME

Once a spectrum is complete, data can be transferred from the experimental station to the SRS mainframe. This is useful as it enables initial data to be analysed as the experiments progress. In order to transfer the data type 'F' to finish session in the scanning programme. The command appears in the transfer to the scanning programme by first using command 'S'. Then type

!AB ' carriage return'

The console will respond with the prompt '.' which means the user is in RT77.

Once in RT11, load DQ and SL, viz

.LOAD DQ

.LOAD SL

CATEX should then be loaded by typing

CAT 'carriage return'

The VDU will respond with

******CATEX Version 2******

LAST MODIFICATION <data>

+

As soon as the CATEX prompt '+' has appeared type

!RS SY:CATSTR

A prompt '+' will appear when the subroutine has been loaded, then enter

!RD SY:TPILE

This loads the programme which allows data to be transferred to the NAS7000. The CATEX prompt '+' is displayed on the VDU after the programme has been read in. In order to obtain a list of the files on the data disk so that the user can choose which to transfer, type

!DI

and the directory of the data disk is then printed on the VDU.

To start the programme type

1ST

and then reply to the questions as they appear. When files have been transferred unload DQ and SL, viz

+IAB

.UNLOAD DQ

.UNLOAD SL

Then load CATEX and read the LOAD programme as described above in section 1.2.

How to Re-initialise a Floppy Disk

If for any reason Floppy Disks are used for data collection these are re-usable. In order to re-initialise a Floppy Disk transfer to RT-11. To enter RT-11 from CATEX (which has the prompt '+') type

IAB

The VDU will respond with the prompt '.'. To wipe the disk clean type

INI/BA FD1: 'carriage return'

The system will ask if you are sure and the reply is

Y 'carriage return'

The system will then clean the disk and check if any bad blocks are dpresent. If this is so do not re-use the disk to collect data. Also do not type 'INI/BA FD0:' to re-initialise as this will wipe the system disk clean. To get back to CATEX after re-initialising type

CAT 'carriage return'

1.4 RUNNING PROCEDURE FOR TRANSMISSION MEASUREMENTS

A transmission measurement involves placing the sample between the two ion chambers and scanning the monochromator through the x-ray absorption edge of one of the elements present. Figure 2 shows the transmission spectrum of Ni foil. The specimen should be of appropriate thickness (2.4.2) and the ion chambers should be filled with rare gas mixtures to suit the spectral wavelength range chosen (2.4.8). Details of K and L edges - wave-

lengths, energies, monochromator Bragg angles and suggested spectral ranges are provided in the INFORMATION command 'I' described below.

With the programme LOAD installed, typing 'H' displays the commands necessary for setting up a transmission EXAFS spectrum.

TYPE L LIST SCAN PARAMETERS
C CHANGE SCAN PARAMETERS
E MOVE SLITS, TABLE, EXPERIMENT AND MIRROR
P MONOCHROMATOR POSITION
M MOVE MONOCHROMATOR
S START DATA COLLECTION
I FOR INFORMATION ON K AND L(3) EDGES
R READ ION CHAMBERS
T HAVE TABLE SYNCHRONISED WITH MONOCHROMATOR
V TABLE HEIGHT
O MOVE COARSE MOTOR
D % HARMONIC REJECTION FOR DC
H HELP
COMMAND?

The user may enter any of the commands available by typing the appropriate letter (no 'carriage return necessary). If a letter is typed which is not on the list of commands the programme responds with:

INVALID COMMAND FOR HELP TYPE H

COMMAND?

COMMANDS

1.4.1) L - LIST SCAN PARAMETERS

This lists the number of scans and regions (for each scan) previously entered into the programme and these may be changed using command 'C'. The contents of each region are also displayed on the VDU, for example:

```
SCANS 1          REGIONS 2
REGION 1
START 14100          TIME 100000
INCR      10         REF 8000000
END   13000          SIG    80000
REGION 2
START 13000          TIME 100000
```

INCR 2 REF 8000000

END 12000 SIG 100000

COMMAND?

These scan parametere are for a single scan of two regions starting at 14.1 degrees and ending at 12.0 degrees. The number of steps the monochromator moves before a reading is taken is determined by incr (short for increment). Time is measured in milliseconds and the values for the reference and signal are counts from the ion chambers. The usual mode of setting up the regions is to give large values for time and reference so that the counting is limited on signal, i.e. once the number for the signal is reached the accumulation of counts for references and time are stopped simultaneously and a reading taken, the monochromator then moves to the next angle. In this way the reference counts are inversely proportional to the sample transmission. Command 'R' can be used to choose appropriate values for time, reference and signal.

1.4.2) C - CHANGE SCAN PARAMETERS

Typing this letter allows a user to change the number of scans and regions he wishes to have from those already inputed into the programme. The parameters for each region can also be changed. The VDU responds with:

TYPE P CHANGE PARAMETERS

R CHANGE REGION

E EXIT

By typing 'P' the console prompts the user for the number of scans he wishes to run repetitively, the maximum number allowed is 100. If a value greater than this is entered the programme will use the default of 100. If the user does not wish to alter the number already present then 'carriage return' is pressed. The user is then asked to input the number of regions he requires for a scan, the maximum number allowed is 10. If a value greater than this is inputed the programme assumes the default of 10. After the value has been entered the user is taken back to the above three commands.

Typing 'R' causes the user to be prompted for a region number. If he enters a value larger than the regions specified, the programme responds with:

INVALID REGION

?

By entering an appropriate region number the console displays:

B START OF REGION

I INCREMENT

F END OF REGION

T CHANGE TIME

R REF.I.C.

S SIG.I.C.

N NEW REGION

E EXIT

B, I and F are used for entering the start, increment and end of a region in a spectrum in millidegrees. The start of the region should have a larger number than the end of a region. T, R and S are used as limits on time (milliseconds), reference ion chamber (in counts) and signal ion chamber (in counts) respectively. The maximum allowed time is 100,000, and for reference and signal ion chamber the maximum counts are 8,300,000. When a user exits from these sub-commands the programme returns to the main commands. An example is given below of a three region scan for the copper edge of a copper foil using a Si(111) monochromator.

REGION 1

START 13400 TIME 100000

INCR 20 REF 8000000

END 12740 SIG 500000

REGION 2

START 12740 TIME 100000

INCR 1 REF 8000000

END 12490 SIG 100000

REGION 3

START 12490 TIME 100000

INCR 3 REF 8000000

END 11800 SIG 100000

The first region has a coarse increment and finishes about 20 steps before the start of the copper edge, the second region encompasses the edge and near edge structure, and has the finest increment. The final region covers the EXAFS oscillations and extends to about 800 eV above the edge. Because the sample absorbs in regione 2 and 3 the number of counts entered for the signal is lower than for region 1. This takes into account the decrease in x-rays entering the signal ion chamber above the absorption edge so that the counting time for each point remains roughly the same for all regions. As the EXAFS oscillations are broader then the near edge structure the increment in region 2 is smaller than in region 3.

1.4.3) E - MOVE SLITS, TABLE, EXPERIMENT AND MIRRORS

Typing this letter the console responds with:

A MOVE ENTRANCE SLIT VERTICALLY
B MOVE ENTRANCE SLIT HORIZONTALLY
C MOVE EXIT SLIT VERTICALLY
D MOVE EXIT SLIT HORIZONTALLY
F MOVE FRONT OF TABLE
G MOVE BACK OF TABLE
H MOVE FRONT OF EXPERIMENT
I MOVE BACK OF EXPERIMENT
J MOVE FRONT OF MIRROR
K MOVE BACK OF MIRROR
E EXIT

This command allows the user to perform the following adjustments:

1) Open and close the slits before and after the monochromator by entering a positive or negative number (A-D).

2) Raise and lower the optical bench to compensate for any change in position of monochromatic beam (F-G). When the table is moved its new height is displayed in microns. The number is calibrated with respect to the white radiation passing through the entrance and exit slits with no deviation encountered. A positive value for the table height means the optical bench is displaced upwards as compared to the straight through beam. The front and back of the table can be moved independently to facilitate levelling of the equipment. The value for the table height is taken from the front of the table, so remember to move the back of the table to retain the bench in a horizontal position.

3) Raise and lower the whole of the experimental assembly in the EXAFS hutch to compensate for the reflected beam off the mirror when placed in the synchrotron radiation (H-I). This adjustment should not be made without permission of the station master.

4) The mirror to be moved in and out of the x-ray beam and also variation in the glancing angle of the mirror (section 2.3). This adjustment should not be made without permission of the station master.

1.4.4) P - MONOCHROMATOR POSITION

This informs the user of the present position of the monochromator and allows him to recalibrate if required, if not 'carriage return' is pressed. Calibration can not be made by driving the monochromator to the 'turning point' of the absorption edge of the element and entering the angle tabulated in command 'I'.

1.4.5) M - MOVE MONOCHROMATOR

This command enables the monochromator to be increased or decreased in Bragg angle by a desired number of steps (1 step is 1 millidegree). The maximum number of steps the monochromator may have at any one time is 30000, if a value greater than 30000 is entered the console informs the user of the maximum permissible steps he is allowed and prompts for a new value to be typed. When the monochromator has finished moving the VDU responds with its new angle and also the table height.

If the wrong direction is entered by mistake do not interrupt until the movement has been completed and re-enter in the opposite direction with double the number of steps to correct. Zero steps is not allowed, the console will prompt the user for a new value.

1.4.6) I - FOR INFORMATION ON K AND L(3) EDGES

When 'I' is inputed the programme prompts the user for the particular edge he is interested in:

ENTER 1 FOR K EDGE 2 FOR L(3) EDGE

After the appropriate value is entered the console responds with:

ENTER ELEMENT

All that is required is for the chemical symbol of the element concerned to be entered. Should the chemical symbol have only one letter the user should type this letter followed by a blank then 'carriage return', if it has two letters no space is required just 'carriage return'. The programme reponds with information on the edge in terms of where it occurs (in energy (KeV), wavelength (Å) and monochromator position for Si(220) and Si(111) crystals. Sample scan ranges of 300 eV before the edge and 600 eV after the edge expressed as monochromator steps are also given.

1.4.7) R - READ ION CHAMBERS

With this command a user may read the counts in the ion chambers for a fixed time during the setting up procedure. The default value for time is 1000 milliseconds and this may be altered by the user. The reference and signal counts both have default values of 1,000,000 which are fixed. This system is useful for setting up the reference and signal limits in the scan parameters. With the shutters closed the user is also able to obtain dark current (amplifier off-set) readings.

1.4.8) T - HAVE TABLE SYNCHRONISED WITH MONOCHROMATOR

Because the separation between the two crystals is fixed (D) the output beam from the monochromator moves relative to the entrance beam as θ is scanned, the displacement is given by 2Dcosθ. The 'T' option allows the user to track the output beam with the exit slits and optical bench. The user is prompted to input the crystal separation (millimeters) and the amount of beam movement permissible before the table is moved to correct for it (microns). The programme responds by converting the beam movement into steps for the stepper motors on the optical bench.

WHAT SEPARATION BETWEEN CRYSTAL SURFACES (MM) <VALUE>

Input new value 'carriage return'

AMOUNT OF BEAM MOVEMENT (MICRONS) BEFORE TABLE MOVED <VALUE>

Input new value 'carriage return'

STEP=?

If a user does not wish to track the beam then zero should be entered for both separation of crystal surfaces and amount of beam movement. The separation of the crystal surfaces of the two crystal order-sorting monochromator is 15 mm and the separation for the Si(111) channel cut (D-shaped) is 4 mm for other crystals, ask the station master. A reasonable step size

for the synchronised motion is 1-5 microns.

1.4.9) V - TABLE HEIGHT

This command informs the user of the present height of the optical bench with respect to the straight through beam and may be recalibrated if required. If the monochromator angle is calibrated, the table height is given by 2Dcosθ, where D is the separation of the crystal surfaces.

1.4.10) O - MOVE COARSE MOTOR

This command should only be used when a double crystal monochromator is being operated. It allows a stepper motor to turn which alters the angle of the first crystal with respect to the second crystal. This varies the intensity of monochromatic light leaving the monochromator and with it the degree of harmonic contamination. Fine control is effected with the solenoid drive which can be operated manually (see '2.1 SETTING UP AND OPERATION OF ORDER SORTING MONOCHROMATOR').

1.4.11) D - % HARMONIC REJECTION FOR D.C. (Double Crystal)

This command should only be used if the double crystal monochromator is installed. It allows a user to carry out a scan with approximately the same harmonic rejection throughout. This is done by a servo linkage between the output of the reference ion chamber (I(O)) and the angle of the first crystal of the monochromator. Before using this command the peak height for I(O) at the beginning and end of the scan should be noted. These can be obtained using the coarse motor (command 'O') in conjunction with the solenoid manual drive control (see '2.1 SETTING UP AND OPERATION OF ORDER SORTING MONOCHROMATOR').

When 'D' is typed the console inquires the percentage of I(O) desired for the scan. This is directly related to the degree of harmonic rejection. For Si(220) on EXAFS station 7.1

Scanning around the 3 A region the % of I(O) should be 40%

Scanning around the 2 A region the % of I(O) should be 50%

Scanning around the 1 A region the % of I(O) should be 75%

The above values are meant as rough guidelines for the SRS ring operating at 2 GeV. If the storge ring is running at a lower energy these may be increased. However values of greater than 85% I(O) should not be used as the monochromator servo mechanism will have difficulty holding a level so close to the rocking curve peak during the scan. As an example fig.3 shows the effects of harmonic contamination on an absorption spectrum (in this case V foil).

After entering the % of I(O) required the programme prompts the user for the rocking curve peak height of I(O) at the start of the scan, followed by the rocking curve peak height at the end of the scan range. When these values have been entered the programme returns to the list of main commands. Also the user will observe a value displayed on the servo reference on the right-hand DVM of the EXAFS servo panel. This displays the I(O) value which will act as the servo reference at the start of the scan. In order to limit the solenoid current, the monochromator should be detuned by using the coarse motor motion (command 'O'). The output of the reference ion chamber displayed on the left-hand DVM on the 'EXAFS CURRENT MONITOR' panel should be adjusted as close as possible to the servo reference value shown above. The servo current is displayed on the left-hand DVM of the EXAFS servo panel (see '2.1 SETTING UP AND OPERATION OF ORDER SORTING MONOCHROMATOR').

1.4.12) S - START DATA COLLECTION

This allows a user to start collecting an EXAFS spectrum with the data stored on the winchester disk. However <u>before</u> issuing this command:

1) Check that the position of the monochromator is greater or equal to the start of the first region otherwise the scan will automatically abort.
2) Ensure the end of one region does not overlap with the start of the following region (they may, however, have the same value).
3) Check the start of a region is always greater than the end of the same region.

Issuing the command 'S' causes the parameters to be saved on the winchester disk and the setting up programme is then replaced by the scanning programme. This procedure takes approximately 5 seconds to perform, so wait till the console responds with the following commands before pressing any keys on the VDU.


```
TYPE S START DATA COLLECTION
     C CHANGE SETTING UP PROCEDURE
     F FINISH SESSION
```

When the letter 'S' is typed the console responds with

```
EVERYTHING OK Y/N
```

If the user is satisfied he is then prompted for an expansion factor for the y-axis of the scan which is to be plotted on the session VDU.

```
EXPANSION FOR Y AXIS 3.0 LARGER INTEGER SMALLER EXPANSION
?
```

For a metal foil the value entered is typically between 15 to 40 and for a dilute sample 1 to 3. This is a cosmetic to the display and does not affect the data collected. After the scaling factor has been entered the console displays

```
STARTING RUN NUMBER R******
NUMBER OF BLOCKS ALLOCATED TO THE DATA FILE = ****
ENTER TITLE
ENTER CONDITION
ENTER COMMENT
```

After the title has been entered (maximum of 40 characters) the user is prompted for conditions 1 to 3 (up to 8 characters may be entered for each condition), and is then prompted for comments (up to 40 characters). To exit from this sequence press 'carriage return'.

The dataset produced on the winchester disk will have its run number with the letter 'R' before it and will have the title R****.DAT on the disk. The dataset will contain the standard SRS header before the data, e.g.:-

```
&SRS
SRSRUN=1677,SRSDAT=820421,SRSTIM=171441
SRSSTN='EXP1',SRSPRJ='SR1234',SRSEXP='GLASSES'
SRSTLE='*****'
CONDITION 1='*****'
COMMENT='*****'
&END
```

SRSRUN, SRSDAT and SRSTIM informs the user of the run number of his data, the year, month and day when the data was collected and the time at which data collection started. SRSSTN is the station where the experiment was performed. SRSPRJ and SRSEXP are respectively the project number and the type of system under investigation. After this header the title with any conditions and comments are printed followed by the data.

If you wish to abort during a scan, type 'A' followed by 'carriage return'.

The data collected so far will be saved on winchester disk and at the end of the file the user will be informed that the scan was aborted.

During a multiple scan, after entering the relevent details for the initial scan, the user is not required to input the same information for subsequent scans. At the end of a scan, or multiple scans, the user has the option to compare the last three datasets collected to be plotted on the session screen.

Typing 'C' causes the setting up programme to replace the scanning programme, the user can then make alterations to his input parameters using command 'C'.

Typing 'F' removes the compiled programme, however the last input parameters the user used are saved on winchester disk. To re-load the programme after letter 'F' has been typed, input

!RD SY:LOAD

(see '1.2 LOADING THE VARIOUS PROGRAMMES').

1.5 RUNNING PROCEDURE FOR FLUORESCENCE MEASUREMENTS

In order to make a fluorescence measurement the sample should be placed behind the reference ion chamber, inclined at 45 degrees with respect to the monochromatic beam and surrounded by an array of scintillation detectors. A photograph of the detector arrangement used for fluorescence measurements is shown in fig.4. An x-ray excitation spectrum is obtained by scanning the monochromator through the absorption edge of the dilute component. The specimen should be of appropriate thickness (2.4.2). The fluorescence detector should be arranged (with filtere if necessary) to optimise the fluorescence to scatter (see section 2.2). Fluorecence spectra

for a selection of concentrations of $CuSO_4$ are presented in fig.5.

Having loaded the LOAD2 programme typing 'H' displays the commands necessary for setting up a fluorescence EXAFS spectrum

```
TYPE L LIST SCAN PARAMETERS
     C CHANGE SCAN PARAMETERS
     E MOVE SLITS, TABLE, EXPERIMENT AND MIRROR
     P MONOCHROMATOR POSITION
     M MOVE MONOCHROMATOR
     S START DATA COLLECTION
     I FOR INFORMATION ON K AND L(3) EDGES
     R READ ION CHAMBERS
     T HAVE TABLE SYNCHRONISED WITH MONOCHROMATOR
     V TABLE HEIGHT
     O MOVE COARSE MOTOR
     D % HARMONIC REJECTION FOR DC
     H HELP
     A TO SET UP THE FLUORESCENCE DETECTORS
     COMMAND?
```

The majority of these commands are identical to those described previously for transmission measurements (1.4). The user may enter any of the commands by typing the appropriate letter - without a carriage return. If a letter is typed which is not included in the list above the programme responds with:

```
INVALID COMMAND FOR HELP TYPE H
COMMAND?
```

COMMANDS

1.5.1) A - TO SET UP FLUORESCENCE DETECTORS

The idea of this small routine is to allow a user to set up the detectors individually and then to match them with each other. Also it allows a user to choose his MCA window for data collection. Note that at the start of each day the detectors should be checked individually to ensure they have not drifted or broken down. Below more detailed information is given about the routine.

Typing 'A' removes the main programme from memory and also stores any changes on the winchester disk. The programme asks the user

'DO YOU WISH TO RETURN TO MAIN PROGRAMME'

If 'N' is typed the VDU responds with

'TIME'

The console waits for a value to be inputed. (Important a value of 50 = 1 second).

After counting for the time specified the programme asks

'DO YOU WISH TO COMPARE SPECTRA' Y/N

If the answer is 'Y' the terminal displays

'J=x'

x can be 1 or 2. This corresponds to a memory allocation for displaying two spectra on the Hytec TV screen which allows you to set up the detectors to match one another. For instance using memory 1 for the correctly adjusted detector, the other detectors can be matched to this via memory 2.

If the reply is 'N' the spectrum is placed in memory 1 (J=1) and is displayed on the Hytec TV screen with a line of dots at regular intervals half way up the screen. These dots are spaced at every 10th channel of the MCA so allowing the user to choose the window for his data collection. Section 2.2 for further de- tails. The programme then returns return to the start

'DO YOU WISH TO RETURN TO MAIN PROGRAMME'

Exit by typing 'Y'.

1.5.2) R - READ ION CHAMBERS

This command is very similar to that in the transmission menu except for the addition of two more options. When 'R' is typed at the console the VDU displays

TIME 1000

?

This allows the user to count ion chamber and fluorescence detectors for 1 second (1000 milliseconds) or enter an alteration time if desired.

The programme continues by asking the user

'OVER WHICH CHANNELS DO YOU WISH TO INTEGRATE'

These channels correspond to the multichannel analyser described above (see also 2.2).

'START=xxx'

?

The programme prints the starting chennel already in memory which can be altered by inputting a new value and then proceeds to print

END=xxx

and this value may also be changed by typing in a new number. The programme then counts for the time specified at the beginning and displays the readings from both ion chambers and also the total number of counts from the multichannel analyser over the window specified.

2.1 SETTING UP AND OPERATION OF ORDER SORTING MONOCHROMATOR

Harmonic rejection is achieved with the two crystal monochromator by off-setting the first crystal out of parallel with respect to the second by a desired amount and employing a simple servo system to hold it there as the scan proceeds. Two mechanisms are provided to do this - a coarse adjustment and a fine adjustment. A schematic describing the mechanism of the order sorting monochromator is shown in fig.6. For details of the monochromator and the principles of x-ray harmonic rejection see 'An Order Sorting Monochromator for Synchrotron Radiation ' G.N. Greaves, G.P. Diakun, P.D. Quinn, M. Hart and D.P. Siddons, Nucl. Instrum. Meth. 208, (1983) 335-339 (DL/SCI/P340E).

2.1.1) COARSE ADJUSTMENT

The first crystal is mounted on a spring loaded lever which is moved up and down with a small stepper motor. The motor is driven by computer software by typing 'O' from the list of commands in the setting up programme and then entering the desired number of steps you wish to move the motor. The coarse adjustment is used to set the monochromator near the rocking curve peak or the required offset position from the peak. One step is approximately 0.9 arc seconds movement. Allow for two or three steps backlash when changing the motor direction. A negative number of steps decreases θ for the first crystal.

2.1.2) FINE ADJUSTMENT

A small ferrite attached to the bottom of the first crystal is attracted or repelled by a solenoid fixed to the monochromator frame. Very fine adjustment of the crystal angle can therefore be achieved simply by varying the solenoid current. A 20 mA change in solenoid current is appproximately equivalent to 1 step of the coarse adjust motor. The fine adjustment is controlled from the solenoid drive module located in the NIM BIN. The layout of the NIM module is shown in fig.7.

2.1.3) SOLENOID DRIVER

A double width NIM module is provided for driving the solenoid. With manual control selected a front panel potentiometer allows the solenoid

current to be set at any value within the range plus or minus 500 mA. The current is displayed on the left-hand DVM of the solenoid control panel. The output in millivolts equals the solenoid current in milliamps (see fig.7)

With the servo control selected, the module compares the reading from the I(O) ion chamber amplifier with a reference displayed on the right-hand DVM of the solenoid control panel (see fig.7). It adjusts the solenoid current automatically to keep the two equal. The servo reference can be set internally by a ten turn potentiometer (switch to 'INT' on the solenoid driver module) or externally by a DAC from the setting-up and scanning programmes (switch to 'EXT' on the solenoid driver module). The monochromator must first be preset sufficiently near the required set point with the coarse motor because the range of the solenoid is limited, particularly at long wavelengths. If for any reason the I(O) ion chamber reading moves out of range of the solenoid, the current will reach the 500 mA limit and the module will break the circuit. The reset button must be operated before the solenoid is used again. This is located at the bottom of the driver module. The servo mechanism operates on the 'negative side' of the rocking curve. This is defined as the side where a positive signal from the driver module increases the amount of light leaving the monochromator and hence the output of the I(O) ion chamber. The driver module will not control on the 'positive side' of the rocking curve. To locate the 'negative side' drive through the rocking curve using the coarse adjustment in a succession of negative steps. If the servo reference is set to match the I(O) output the servo can be switched on and the mechanism will control with only a few mA of current flowing through the solenoid. If this is not the case the solenoid current can be reduced by operating the coarse adjustment with the servo still switched on. A negative movement with command 'O' will drive the solenoid current less negative and vice versa.

2.1.4) SETTING THE MONOCHROMATOR FOR A SCAN AT 'CONSTANT I(O)'

Use the following procedures:

1) Move the monochromator to the start of the scan (command 'M') and peak the I(O) chamber reading as far as possible with the coarse adjust motor (command 'O').

2) Peak the I(O) chamber reading precisely with the solenoid driver on manual control of the driver module - NOTE THIS READING.

3) Calculate the I(O) chamber reading for the required offset, and set the servo reference to this value using the ten turn potentiometer with the reference switch set to 'INT'.

4) Zero the solenoid current, but leave the manual control selected.

5) Use the coarse adjust motor to bring the I(O) chamber reading as near as possible to the required set point. If the monochromator has only been exposed to beam for a short period leave for two or three minutes at this point and then re-adjust with the coarse motor. Use negative steps to come down the rocking curve to the set point (see section 2.1.3 above).

6) Switch the control module from manual to servo. The I(O) chamber reading should now move to within 1% of the reference value and the solenoid current should be close to zero. Small changes may be made to the reference value with the servo on. The solenoid current will alter to accommodate the change. If the solenoid current is too large (positive or negative), reduce this by operating the coarse adjustment, the servo remaining on (see section 2.1.3 above).

7) On some long EXAFS scans the drift in solenoid current from the start to finish may be large. The procedure in earlier paragraphs is designed to start the scan with the solenoid current near zero. If it is known that a large positive drift in I(O) will occur over the scan, then the coarse motor should be adjusted to produce a negative solenoid current (say, -100 to -150 mA), at the start of the scan. This increases the effective range of the solenoid over the scan.

2.1.5) SETTING THE MONOCHROMATOR FOR A SCAN WITH 'CONSTANT' HARMONIC REJECTION

1) Move monochromator to the start of the scan (command 'M') and peak the I(O) chamber as far as possible with the coarse adjust motor (command 'O').

2) Peak the I(O) chamber reading precisely with the solenoid driver on manual control in the NIM BIN - NOTE THIS READING.

3) Move the monochromator to the end of the scan and peak the I(O) chamber as far as possible with the coarse adjust motor.

4) Peak the I(O) chamber reading precisely with the solenoid on manual control - NOTE THIS READING.

5) Move the monochromator back to the start of the scan. Remember to take the backlash out of the monochromator motor. This is achieved by adding 50 more than is required to reach the start position, and then move down 50 steps to the beginning of the scan.

6) Exit from moving the monochromator, this will return you to the menu of main commands. Type 'D' to set the percentage harmonic rejection for double crystal monochromator and reply to the inquiries (explanation of this command is dealt with in section 1.4.11 above). When all the prompts have been answered the programme returns to the main list of commands - then you should switch to the external reference.

7) Use the coarse adjust motor to bring the I(O) chamber as near as possible to the required set point which is now displayed on the servo reference. If the monochromator has only just been exposed to white radiation do not carry out any movement of the first crystal until the system has equilibrated. This will take approximately three minutes. Make sure when you sit at the set point on the rocking curve it is the negative side (see section 2.1.3 above).

8) Switch the control module from manual to servo. The I(O) chamber reading should now move to within 1% of the reference value. At each new monochromator position the reference value will be recalculated. This is obtained by linear interpolation between the start and end values of I(O) inputed in command 'D'. The method allows for a more constant harmonic rejection to be achieved. This is particularly important at short or long wavelengths where the intensity of the SRS changes rapidly with wavelength.

2.2 SETTING UP AND OPERATING OF FLUORECENCE DETECTORS

At present five scintillation detectors are used, four look at the front face of the sample with the remaining looking at the back face. More detectors can be accommodated if the station is used with the mirror, as the reflected beam facilitates more space around the sample. Detectors are arranged on the 18 cm sphere and an optimum geometrical arrangement is described in DL/SCI/P380E.

The fluorescence detectors are connected to a summing amplifier which is connected to a fast multiple channel analyser (MCA). The MCA spectrum is integrated between start channel and end channel, for a particular excitation energy (Bragg angle or monochromator position). The start and end channels are defined using command 'R' (1.5.2). The integrated counts are printed in the sixth column on the console. The excitation spectrum is plotted (as MCA counts/reference counts) on the sension, simultaneously with the absorption spectrum.

2.2.1) SETTING UP PROCEDURE

1) Check the individual gains of each photomultiplier tube (PMT) one tube at a time by disconnecting others from the summing amplifier.

2) Display the MCA spectrum on the Hytec VDU by using command 'A' (1.5.1).

3) If the gain of a scintillator + PMT needs adjustment, this can be achieved by trimming the HT using the potentiometer provided for the individual detector on the common power supply.

4) Check the harmonic content by observing that the MCA spectrum is symmetric. If a broad shoulder exists on high energy side (higher channel number), harmonic rejection is not sufficient. This can be increased using command 'D' (1.4.11).

5) The summed signal from all the detectors should be less than 500,000 counts/sec. This limit is defined by the detectors and amplifying electronics. Ensure that the MCA does not overflow for the counting time as defined in the scan parameters (see section 1.5). This can be rectified by changing the lower and upper level discriminator setsetings. The changes required are <u>extremely small</u>, so care should be taken [if in doubt contact S.S. Hasnain or P.D. Quinn].

6) Define the common limits for integration using command 'R' (1.5.2). These should encompass the bulk of the MCA apectrum, removing any low energy pile up and any high counts due to scatter or incomplete harmonic rejection.

7) If detectors can not be matched in this way contact S.S. Hasnain or P.D. Quinn.

2.2.2) CHOICE OF DETECTOR FILTERS

Fluorescence radiation is accompanied by scattered radiation (excitation wavelength) for all the detectors. The scattered contribution is small (and not worth worrying about) for the in-plane 90 degree detector [see DL/SCI/P380E], for all other detectors it is preferable that a filter is used with the collimator which is provided. Filters are essential if the metal concentration is less than 20 milli Molar.

Material for a filter is chosen such that scattered radiation is preferentially absorbed compared to the fluorescence signal. For all 3d metals for instance, filter made from the (Z-1) element is optimum, while for higher Z atoms filters made from (Z-1) or (Z-2) are most appropriate. Table 1 illustrates the principle clearly, for five examples, with Z=23 to 48, the filter material is chosen such that its K absorption edge is at a higher energy than the energy of sample fluorecence. Thus for 23<=Z<=36 filter material can be made from (Z-1) atom, for 37<=Z<=47 material can be from either (Z-1) or (Z-2) while for higher Z>=48, a choice can be made from (Z-1), (Z-2) or (Z-3). The optimum thickness of the filter depends on a number of factors including the concentration of the sample, matrix (the bulk of the sample), the size of the beam, the energy of the x-ray beam etc. As a guideline, the thickness should be chosen such that the scattered intensity (as measured before the edge) is reduced by a factor of ten but the fluorescence signal (i.e. the difference of above edge Sc+Sf and pre-edge Sc, as defined in DL/SCI/P380E) is not reduced to less than 50%. A typical thickness range might be 5-15 µm.

Table 1 K-edge

Z	Element	E scatter (eV) or EXAFS range	E fluo (eV)	Possible filter	Absorption edge for filter (eV)
48	Cd	26720 - 27300	22300	Ag	25560
				Pd	24357
				Rh	23260
42	Mo	20000 - 20800	17400	Nb	18990
				Zr	18000
30	Zn	9600 - 10200	8600	Cu	8980
25	Mn	5640 - 7200	5900	Cr	5990
23	V	5450 - 6000	4940	Ti	4965

2.3 OPERATION WITH TOROIDAL MIRROR

2.3.1) DESCRIPTION

A cylindrical mirror is available to enhance the intensity and brightness of the monochromatic beam at the sample. The wavelength range is limited in this mode to wavelengths >=1.1 Å i.e. Zn is the heaviest element for which this mode is useful in K-edge meaurements while Ta is the heaviest element for L-edge measurements.

The mirror is Pt-coated quartz, 58 cm long, 5 cm wide designed for a glancing angle of 7 mrad with F1=11.5 M and F2=5.8 M. Ray tracing programme and experimental evaluation show that when the mirror is bent in the vertical plane it is able to intercept 3 mrad of horizontal aperture and all of the vertical aperture (0.2 mrad). Note that without the mirror 0.7 mrad of horizontal radiation (12 mm) is used, a limit imposed by the present monochromator crystal. If full vertical aperture is used the energy resolution is degraded simply as if the slit at the monochromator had been increased to 3 mm. Slits are provided in front of the mirror to define the vertical and horizontal acceptance of the mirror, resolution compatible with EXAFS and XANES can be easily be achieved. It is recommended that XANES and EXAFS are recorded separately with different mirror acceptance.

The gain in intensity at higher energies is small particularly for a resolution compatible with XANES but this improves as the energy is lowered, e.g. for Cu XANES where 2 eV resolution is required, intensity gain is approximately 2, while for Fe the gain is >4 and for Ca the gain is >6 - all compared to an unfocused 12 mm beam. For EXAFS applications, these gains in intensity can further be increased by roughly a factor of two.

The image produced by the mirror is close to 2:1 demagnification of the source at the sample position i.e. 3 mrad horizontal and full vertical beam is condensed into a spot at 17.3 M from the source of less than 6 × 0.5 mm resulting in a brightness increase of approximately 60 over the unfocused beam. This is of course an important improvement particularly for dilute and/or small specimens if intensity can be traded for energy resolution.

2.3.2) ADJUSTMENT

Installation of the mirror in the beam is fairly involved - particularly its optimisation for energy resolution and intensity gain. Adjustments to the mirror are therefore only to be done by the in-house group. Users requiring the mirror should let the laboratory know well in advance so that mirror installation can be properly scheduled. Horizontal and vertical slits at the mirror are provided with manual adjustments which are available to the user.

Finally the mirror is separated from the monochromator by a beryllium window in order that it operates under high vacuum conditions. The pressure in the mirror vessel is metred at the station and should normally be less than 10^{-7} torr. If this is not the case the port 7 will normally close and cannot be re-opened until the high vacuum recovers. This may occur when the mirror is first placed in the beam. If this happens the station master and the beam port coordinator should be called.

2.4 GUIDELINES FOR EXAFS MEASUREMENTS

Facilities have been described for measuring x-ray absorption in transmission and fluorescence geometry. The following information is designed to help newcomers make the best use of their beam time.

2.4.1) MODEL COMPOUNDS

The comparative nature of the EXAFS technique necessitates the use of model compounda. These should be chosen, if possible to be similar to the local chemistry anticipated for the unknown system. They can generally be chosen from the three main groupings of metallic, covalent and ionic lattices. Model compounds enable the fitting parameters in EXAFS analysis, notably the phaseshifts, to be reliably chosen (see section 3.3). Make sure the model compound structures are known with precision. This is not always true of crystalline systems. If a change in coordination number is expected for instance, choose model compounds that exhibit the two extreme local structures. The valence state of a transition metal can often be deduced from the location of a transition metal can often be deduced from the location of the absorption edge, in which case the chemical shifts from a range of model compounds of known valence state should be measured. In the case of dilute systems model compounds of similar dilution should be used wherever possible.

2.4.2) SAMPLE THICKNESS

When carrying out transmission measurements the sample should have an absorbance u*t of about 1-2 at just above the absoprtion edge, where u is the absorption coefficient of the material and t is the thickness of the sample (typical sample thickness for transmission EXAFS might be 5-10 μm). When preparing the sample, make sure it is of uniform thickness. If the sample has too high an absorption make it thinner or dilute it with boron nitride or solvent. If the sample is in the form of a powder grind the two materials - specimen and dilutant - together to a fine homogeneous powder. Liquid samples can be contained in cells but ensure the region intercepted by the beam is free of bubbles. For fluorescence measurements the optimum sample thickness depends on the atomic weight of the host material. For aqueous solutions a u*t of around 0.5 is useful for concentrations >2 m Molar and Z<30. For concentrations of 0.5 m Molar and less a thickness of 1.5-2 u*t is required. Typically for FLEXAFS samples might be several millimetres of thickness.

2.4.3) SAMPLE AREA

The unfocused monochromatic beam dimensions are approximately 1 mm × 12 mm. Specimens measuring 5 mm × 20 mm will require only a little alignment. For slightly smaller samples the beam dimensions can be reduced

but at the expense of x-ray intensity. For extremely small specimens a focused beam should be used (see section 2.3). This measures approximately 0.5 mm × 6 mm and offers a gain in x-ray intensity at longer wavelengths that can be traded for a smaller beam size still.

From the sample thickness and area the quality of material required can be judged. This is always less than 1 gm and may be as little as a few mgm.

2.4.4) SAMPLE ALIGNMENT

A badly aligned sample can result in:

1) reduced signal in the final ion chamber because of the beam catching the sample jig;
2) saw-tooth spectrum where the exit beam moves periodically on and off the sample as the table height is altered;
3) increased signal in the final ion chamber because part of the beam is missing the sample altogether - this will result in a diminished absorption edge.

Aligning the sample can be carried out by placing a polaroid at the sample stage and marking its position in the stand. Open the shutter for approximately two seconds. Remove the polaroid and develop it. Replace the developed photograph in its original position at the sample stage. Remove the signal ion chamber. Switch on the laser and align the spot onto the centre of the beam on the photograph. Once this has been accomplished remove the polaroid and check that both ion chambers are at the correct height. Finally, align the sample with the laser.

2.4.5) MOVING TO A NEW EDGE

When moving the monochromator through 10 degrees or more (command 'M'), the monochromator should bemoved in stages of 5000 steps. If the table is synchronised to the movement of the beam it will move in sympathy. However, this movement is not precise over the whole monochromator range of 0 to 90 degrees. It should therefore be checked periodically by moving the table up and down (sub commands 'P' and 'G' of main command 'E') and noting if there is any change in the values of the ion chambers - a 200 step movement should be sufficient. If there is, move the table in the direction where I(O) or I(T) increases until the change disappears. Remember that in moving to longer wavelengths the sample will become more opaque and I(T) may go to zero if the sample is left in place. Slit heights should be typically set at half a millimetre for 1 Å and two millimetres for 3 Å.

2.4.6) ENTRANCE AND EXIT SLITS

The height of the entrance slits define the energy resolution of the monochromator, dE/E. This is given by

$$\frac{dE}{E} = \cot \sigma \frac{S}{P}$$

where σ is the Bragg angle, S is the entrance slit height and P the source to monochromator distances. For the various EXAFS stations the values of P are 7.1 (16 m), 7.4 (55 m) and 9.4 (20 m). Typically at 7.1 S should be set to around 0.5 mm for 1 Å work, 1 mm for 2 Å work and 2 mm for 3 Å work. Values of S for other stations can be found by scaling by P.

Exit slits are designed to pick up any scatter from the entrance slits that has traversed the monochromator. Except for particularly exacting experiments, exit slits should be left several millimetres wider than the entrance slits. If they are set closer than this they may catch the exit beam and some of the symptoms of poor sample alignment will be experienced.

2.4.7) AMPLIFIER GAINS

Typical settings for Keithley amplifiers are in the range of 10^8 to 10^{10} for both reference and signal ion chambers. They do not need to have the same gains, but the same rise time should be used of 300 milliseconds and there should be zero suppression. Saturation on any particular range setting results in a flat output of approximately 11 volts. Should this occur the gain should be reduced or the x-ray intensity attenuated.

2.4.8) ION CHAMBER SETTINGS

The Ortec power supply which provides the HT for the ion chambers should be set at 300 V. Before running a scan make sure you have readings from both ion chambers without any beam (use command 'R'). Usual dark current readings are between 500-2000 counts in one second. If no counts or too many counts are registered, use the zero adjust on the front of the Keithley which can be altered using a small screwdriver.

2.4.9) CHOICE OF FLUORESCENCE FILTERS

A variety of filters are available for covering the PMTs of the fluorescence detector array. These are mainly 3d metal foils (see section 2.2.2). Other filters should be provided by the user following the rules laid out in DL/SCI/P380E.

A typical HT setting for the fluorescence PMTs is about 1.5 KV. Before beginning a set of measurements at a particular absorption edge each PMT should be checked in turn as described in 2.2.1.

2.4.10) THE DON'TS

1) Don't run spectra with the monochromator and slit vessels let up to air.

2) Don't empty the ion chambers prior to filling without first switching off the HT.

3) Don't switch on the PMT HT directly without first ramping from zero. (Be gentle).

4) Don't drive the coarse motor of the order-sorting monochromator more than 20 steps without taking a record subsequent alignment can be tedious.

5) Don't alter the height of the front of the experiment (commands 'E' and 'F') without altering the height of the back of the experiment (commands 'E' and 'G').

CHAPTER 3 - DATA REDUCTION AND ANALYSIS

The following description provides a guide through the EXAFS data reduction and analysis programmes. A number of programmes exist in the SRS Programme Library and here we briefly describe three of them, namely:

EXCALIB:- starting from the experimental data file, this produces normalised spectra of absorption/fluorescence versus electron energy in eV and Hartrees.

EXBACK:- takes absorption from EXCALIB and produces normalised EXAFS spectra and Fourier transforms.

EXCURVE:- curved wave and Fourier transform analysis programmes.

All three programmes are interactive on TSO and the user should be in a region equal to 650 K and using a Tektronix or Tektronix compatible terminal. The description provided is only meant as an introduction to their use - full documentation exists in the SRS Programme Library. For details from TSO, type

SRS HELP

To obtain hard copy documentation for these programmes type

RECORD

followed by

SRS EXCALIB/EXBACK/EXCURVE

Wait for details to be completed on the VDU, then type

EXIT

For fuller details on EXCURVE type

EXCURVE PRINT.

3.1 EXCALIB

This interactive programme reads the data as produced by the data acquisition programme and reduces it to an x-ray absorption spectrum like that shown in fig.2 or the spectra shown in fig.5. The programme is executable from a registered SRS ID by typing:

EXCALIB 'carriage return'

(In the following descriptions the programme responses are preceeded by an asterisk.)

* TEKTRONIX TERMINAL? Y	This programme can also be executed from a normal VDU in which case type N.
* ENTER DS NAME 'EXP1.Rxxxx.DATA'	
* REF. OFFSET? 150	This is the dark current reading of the ion chamber amplifier.
* TRAN. OFFSET? 250	
* GAIN RATIO? 1	This is the ratio of I(t)/I(0) amplifier gains.
* PLOT SPECTRUM? N	A response of Y is also possible here.
* READ EXAFS SPECTRA.? N	If more than one scan of a sample is to be averaged type Y, in which case the DS name for the subsequent scan will be requested.
* READ INST. FUNCTION? N	If answer Y the DS of the instrument function will be asked for. This is the spectrum obtained without the sample in place.
* MONOCHROMATOR TYPE, SI(111) (0), SI(220) (1), GE(111) (2) ? 0	

>>> CORRECTED SPECTRUM

* PLOT SPECTRUM ?
  Y

* DEGLITCH
  Y

Deglitching enables instrumental artifacts to be removed and replaced by straight lines or curves.

* KEEP OUTPUT SPECTRUM ?
  Y

* ENTER DATA SET NAME
  Rxxxx.DATA

* RESTART ?
  N

READY

3.2 EXBACK

This interactive programme is available for removing background from either absorption or fluorescence excitation spectra. An absorption spectra as recorded may look like the example of the Ge K-edge shown in fig.8.

Pre-edge background (1) is subtracted by defining a polynomial (of up to order 3) by choosing two points, N1 and N2, in the pre-edge region. A post-edge background (2) is subtracted by defining a polynomial (of up to order 4) by choosing two points, N3 and N4. The choice of N3 is quite critical and in most cases a point chosen along the rising part of the first EXAFS peak gives a satisfactory background correction. The normalised EXAFS spectrum from fig.8 is shown in fig.9.

The programme can be executed at a Tektronix (or equivalent) terminal by typing

EXBACK SJ R42624A 'carriage return'

(using an SRS ID of SJ and a data set R4624A.DATA purely as an example).

You then proceed as follows:

* ENTER NUMBER OF DATA RECORDS TO BE SKIPPED
  2

* ENTER COLUMN NUMBER FOR ABSCISSA VALUES
  1

If the absorption spectrum was produced from EXCALIB, column 1 is energy in eV.

* ENTER COLUMN NUMBER FOR ORDINATE VALUES
  2

* ENTER POINT FREQUENCY
  2

This is the plotting frequency; all the points are saved in the background subtracted data. If there are more than 1024 points, use a point frequency >2.

* ENTER WEIGHTING FACTOR 0, 1, 2, 3
  0

* ENTER INPUT ENERGY FLAG, 1 FOR eV,
  2 FOR HARTREES

at this stage the spectrum is plotted.

* SELECT EZERO

Cross-wires will now appear on the screen. Bring the cross-wires to the correct position and press any key on the console except for '@' or 'RETURN'. It is important to get E0 right as this calibrates the EXAFS spectrum.

* ENTER 1 if POINT IS OK 0 TO SELECT AGAIN
  1

* SELECT N1 AND N2

The cross-wires will appear again. With them choose N1 and N2 respectively. The fit is then plotted.

* ENTER 1 IF FIT IS OK 2 TO SELECT AGAIN
  1
* ENTER 0 TO REPLOT 1 TO GO ON
  1
* SELECT N3 AND N4

Again, the cross-wires appear and you choose N3 and N4. The fit is plotted and this should approximate to the atomic absorption after the edge.

* ENTER 1 IF FIT IS OK 2 TO SELECT AGAIN
  1
* ENTER 1 TO REPLOT 0 TO GO ON
  1
* 1 TO SELECT N5, 2 N5=EZERO
  2

N5 can be chosen anywhere as the calibration has already been made. N5 is the point from which the background subtracted data will be saved and plotted.
The background subtracted spectrum is then plotted from N5.

* 1 TO GO ON, 2 CHOOSE N5, 3 CHOOSE N1, 4 CHOOSE N3 ?

If a user is not satisfied with the background subtracted he can choose to go back to pre- or post- edge subtraction or to simply redefine N5.

READY

3.3 EXCURVE

This is a comprehensive interactive programme starting from a normal spectrum (e.g. fig.9). It involves curve fitting to the normalised spectrum or its Fourier transform using calculated phaseshifts and the curved wave approximation. It can be executed simply by typing:

EXCURVE 'carriage return'

The following notes demonstrate only the basic options of EXCURVE. Other aspects of this comprehensive programme can be obtained from the documentation. The data sets used below serve only as examples of the required input to the programme.

* UNITS?
  1 EV+ANGSTROMS
  2 BOHR RADII+HARTREES
  1

* POINT FREQUENCY ?
  1

* DSN FOR EXPERIMENT ?
  A708.EXBACK

The .DATA qualifier is not required.

* COLUMN COMBINATION ?
  32

* NO. OF HEADER LINES ?
  10

* NO. OF DATA POINTS READ = xxx

This should be less than 200 if the iteration facility will be required later on. If not, either reduce the range or increase the point frequency.

* DSN FOR PARAMETERS ?
'EXOUTA'

A response from you of '*' will bring the default DS into action. Again, the .DATA qualifier is not required.

* ENTER NUMBER OF PHASESHIFT FILES
2

The phaseshift files are usually in partitioned data sets as in this example. Here we have data set PHCAO6.DATA with members SC and O.

* ENTER DSN FOR CENTRAL ATOM
PHCAO6.DATA(SC)
* ENTER DSN FOR SECOND ATOM
PHCAO6.DATA(O)

* ENTER COMMAND
L

Command L lists the parameters. Note - all parameters are either in atomic units or in Ångstroms and eV, including VPI, They come in the following tabular form:

SHELL	N1 = x.xxx	T1 = x.xxx	R1 = x.xxx	A1 = x.xxx
"	"	"	"	"
"	"	"	"	"
"	"	"	"	"

* ENTER COMMAND
P

Command P calculates and plots the EXAFS spectrum with the experiment.

Here are some more examples of EXCURVE commands:

CP Calculates and plots EXAFS and Fourier transforms with the experiment. Note - FI, the fit index, is printed on the graph.

GS This command sets various options, e.g.:
Device options - D 1 Tektronix, D 2 Tektronix and Versatec, D 3 Versatec.
By typing D 2 spectra will be displayed on the Tektronix and stored in a file for the Versatec.
x-axis options - X 1 energy, X 2 wavenumber.
Typing X 2 will result in plots against k.
Weighting options - W 1 none, W 2 k, W 3 k^2, W 4 k^3.
Typing W 2 will produce a k-weighted spectra.

Other options are available and information on these is obtainable by typing

GS

You then get the response
ENTER KEYWORD + OPTION NUMBER, LIST, RESET OR EXIT
Typing 'L' will list all the GS command options.

After making your choice or choices type E to exit out of the GS command.

IT DR This command iterates all the shell radii values (Rx) although you may choose only to refine a few distances. You will be asked

HOW MANY STEPS ?

to which an adequate reply would be 20. During the iteration process the current spectrum can be plotted on the Tektronix. Also the spectrum can be stored in the data set PLOTFL.DATA for Versatec if device 2 is in operation (see above notes on command GS).

END On executing this command, the programme asks

GRAPHICS DATA IN PLOTFL.DATA
VERSATEC PLOTTER
DO YOU WISH TO SUBMIT PLOTS ?

If the answer is 'yes' then

JOB SJBPLOT SUBMITTED
READY

Should you need more information whilst executing the programme, type H.

APPENDIX

Details of edge positions, spectral ranges and imitation chamber gas partial pressures for K and L_{III} edges in the wavelength range 3.07 to 0.374 Å. Monochrometor positions are given in millidegres for Si(111) and Si(220) crystals.

```
  5 THE VALUES QUOTED ARE FOR THE K EDGE OF THESE ATOMS
 10 ELEMENT         EDGE POSITION                SCAN RANGE (IN TERMS OF MOTOR
 20 :        LAMDA IS IN ÅNGSTROMS               POSITION) FOR A TYPICAL SCAN          GAS PARTIAL PRESSURES
 30 :        SI(220) & SI(111) ARE IN            300EV BELOW AND 600EV ABOVE
 40 :        MOTOR POSITION                      THE EDGE
 50 :      LAMDA     KEV     SI(220)  SI(110)    SI(220)       SI(111)              20%               80%
 60 K     3.43645   3.689    63497    33235     72310-47998   35696-27454
 70 Ca    3.07016   4.038    53084    29318     59742-44119   31938-25236       5.4 Torr A       39    Torr A
 80 Sc    2.75720   4.697    45891    26088     47249-37556   26726-21920       7.1 Torr A       51.4 Torr A
 90 TIi   2.49730   4.965    40567    23472     43790-35464   25080-20814       9.1 Torr A       66    Torr A
100 V     2.26902   5.464    36220    21216     38700-32171   22515-19032      12.1 Torr A       87.3 Torr A
110 Cr    2.07012   5.989    32622    19279     34579-29342   20340-17464      15.1 Torr A      108.9 Torr A
120 Mn    1.89636   6.538    29594    17605     31171-26893   18481-16083      19.2 Torr A      138.5 Torr A
130 Fe    1.74334   7.112    27000    16144     28293-24750   16875-14857      24.1 Torr A      174.2 Torr A
140 Co    1.60811   7.710    24758    14861     25832-22864   15477-13766      30.8 Torr A      222.5 Torr A
150 Ni    1.48802   8.332    22799    13729     23702-21191   14252-12790      38.4 Torr A      277.1 Torr A
160 Cu    1.38043   8.982    21069    12719     21832-19692   13165-11910      47   Torr A      338.6 Torr A
170 Zn    1.28330   9 661    19523    11810     20177-18340   12195-11111      56.3 Torr A      406.4 Torr A
180 Ga    1.19567  10.369    18142    10993     18703-17119   11326-10386      69.7 Torr A      502.9 Torr A
190 Ge    1.11652  11.105    16903    10258     17387-16012   10545-9726       88   Torr A      635   Torr A
200 As    1.04497  11.865    15791     9594     16211-15012    9845-9128      102   Torr A      736   Torr A
210 Se    0.97978  12.654    14783     8990     15150-14099    9211-8580      124.3 Torr A       97.4 Torr Xe
220 Br    0.91994  13.477    13861     8437     14184-13260    8631-8075      147   Torr A      115.5 Torr Xe
230 Kr    0.86546  14.326    13025     7934     13309-12493    8105-7613      179   Torr A      140   Torr Xe
240 Rb    0.81549  15.204    12261     7473     12512-11788    7624-7188      211   Torr A      161   Torr Xe
250 Sr    0.76969  16.108    11563     7051     11785-11142    7186-6797      249   Torr A      150   Torr Kr
260 Y     0.72762  17.040    10922     6664     11051-10547    6784-6436      295   Torr A      174   Torr Kr
270 Zr    0.68877  18.001    10333     6307     10510-9996     6414-6102      341   Torr A      198   Torr Kr
280 Nb    0.65291  18.989     9789     5977      9948-9487     6074-5507      406   Torr A      231   Torr Kr
290 Mo    0.61977  20.005     9288     5673      9431-9015     5759-5507      463   Torr A      273   Torr Kr
300 Tc    0.58888  21.054     8821     5389      8950-8575     5467-5239      589   Torr A      297.5 Torr Kr
310 Ru    0.56047  22.121     8393     5128      8509-8170     5199-4993      621   Torr A      341.6 Torr Kr
320 Rh    0.53378  23.228     7990     4884      8095-7788     4948-4760      725   Torr A      386   Torr Kr
330 Pd    0.50915  24.351     7619     4592      7715-7435     4716-4546       60.9 Torr Kr     439   Torr Kr
340 Ag    0.48582  25.521     7268     4444      7355-7100     4497-4342       70.4 Torr Kr     503   Torr Kr
350 Cd    0.46408  26.716     6941     4245      7021-6788     4293-4151       78.5 Torr Kr     564   Torr Kr
360 In    0.44397  27.926     6639     4060      6712-6499     4105-3975       90.3 Torr Kr     656   Torr Kr
370 Sn    0.42468  29.195     6350     3884      6416-6221     3924-3805       99.6 Torr Kr     718   Torr Kr
380 Sb    0.40663  30.491     6079     3718      6074-5961     3755-3647      118.4 Torr Kr     639   Torr Kr
390 Te    0.38972  31.814     5825     3564      5881-5717     3598-3498      186.3 Torr Kr     681   Torr Kr
400 I     0.37379  33.169     5586     3418      5637-5487     3449-3357      140.3 Torr Kr     757   Torr Kr
410 END
```

```
410 THE VALUES QUOTED ARE FOR THE L(111) EDGE OF THESE ATOMS
420 ELEMENT        EDGE POSITION               SCAN RANGE (IN TERMS OF MOTOR
430 :          LAMDA IS IN ÅNGSTROMS           POSITION) FOR A TYPICAL SCAN      GAS PARTIAL PRESSURES
440 :          SI(220) & SI(111) ARE IN        300EV BELOW AND 600EV ABOVE
450 :          MOTOR POSITION                  THE EDGE
460 :       LAMDA     KEV     SI(220)  SI(111)    SI(220)       SI(111)          20%             80%
470 Mo    4.90930   2.525    -----    51534    ---------     62714-39255
480 Ic    4.62537   2.581    -----    47536    ---------     56150-37063
490 Ru    4.36632   2.840    -----    44138    ---------     51124-35088
500 Rh    4.13889   2.996    -----    41308    ---------     47178-33360
510 Pd    3.89688   3.182    -----    38427    ---------     43324-31524
520 Ag    3.67283   3.376    -----    35858    ---------     40005-29824
530 Cd    3.50070   3.542    65733    33940    84818-51216   37585-28516
540 In    3.32154   3.733    59881    31989    70136-48172   35170-27153     4.7 Torr A      33.7 Torr A
550 Sn    3.16952   3.912    55629    30365    63367-45692   33193-25993     5.2 Torr A      37.7 Torr A
560 Sb    2.99637   4.138    51288    28548    57273-42958   31012-24668     5.8 Torr A      41.9 Torr A
570 Te    2.85162   4.384    47954    27052    52903-40733,  29242-23556     6.3 Torr A      45.2 Torr A
580 I     2.71901   4.560    45079    25700    49281-38736   27657-22533     7.3 Torr A      53   Torr A
590 Xe    2.59330   4.781    42480    24431    46099-36872   26186-21560     8.3 Torr A      60   Torr A
600 Cs    2.47227   5.015    40077    23222    43219-35101   24796-20620     9.4 Torr A      68   Torr A
610 Ba    2.36114   5.251    37943    22122    40703-33493   23541-19753    10.6 Torr A      76.8 Torr A
620 La    2.25792   5.491    36015    21107    38462-32011   22391-18944    12   Torr A      86.6 Torr A
630 Ce    2.16410   5.729    34303    20191    36493-30620   31360-18176    13.5 Torr A      97   Torr A
640 Pr    2.07707   5.969    32745    19346    34718-29440   20415-17519    15.1 Torr A     108.9 Torr A
650 Nd    1.99452   6.216    31292    18548    33077-28275   19527-16865    16.7 Torr A     120.4 Torr A
660 Pm    1.91888   6.461    29981    17821    31605-27211   18721-16263    19.2 Torr A     138.5 Torr A
670 Sm    1.84464   6.721    28710    17110    30188-26169   17936-15670    20.6 Torr A     149   Torr A
680 Eu    1.77491   6.985    27530    16444    28880-25193   17205-15112    23.2 Torr A     167   Torr A
690 Gd    1.70955   7.252    26436    15822    27674-24280   16525-14586    25.8 Torr A     186   Torr A
700 Tb    1.64840   7.521    25421    15242    26560-23427   15893-14093    28.4 Torr A     205   Torr A
710 Dy    1.59025   7.797    24464    14692    25510-22613   15293-13621    31.3 Torr A     226   Torr A
720 Hd    1.53529   8.076    23567    14174    24533-21848   14732-13175    34.9 Torr A     251   Torr A
730 Er    1.48242   8.364    22709    13676    23603-21112   14195-12744    38.4 Torr A     277   Torr A
740 Tm    1.43140   8.662    21886    13197    22713-20402   13679-12327    42.3 Torr A     305   Torr A
750 Yb    1.38518   8.951    21145    12763    21915-19758   13213-11949    47   Torr A     338.6 Torr A
760 Lu    1.34039   9.250    20430    12344    21147-19135   12764-11581    51   Torr A     367   Torr A
770 Hf    1.29570   9.569    19720    11926    20386-18512   12318-11213    55.5 Torr A     400   Torr A
780 Ta    1.25427   9.885    19065    11539    19685-17935   11906-10871    62   Torr A     448   Torr A
790 W     1.21529  10.202    18450    11176    19030-17392   11519-10548    67.2 Torr A     485   Torr A
800 Re    1.17720  10.532    17852    10822    18394-16860   11143-10232    74   Torr A     532   Torr A
810 Os    1.14143  10.862    17292    10489    17800-16361   10787-9934     80.6 Torr A     581   Torr A
820 Ir    1.10599  11.210    16739    10160    17214-15866   10442-9639     89.3 Torr A     644   Torr A
830 Pt    1.07306  11.554    16227     9854    16672-15406   10120-9363     95.2 Torr A     686   Torr A
840 Au    1.04028  11.918    15718     9550    16135-14947    9800-9089    102   Torr A     736   Torr A
850 Hg    1.00944  12.282    15241     9265    15633-14515    9499-8830    117   Torr A      92.3 Torr Xe
860 Tl    0.97968  12.656    14781     8989    15148-14097    9209-8579    124.3 Torr A      97.4 Torr Xe
870 Pb    0.95112  13.036    14341     8725    14686-13697    8932-8338    136   Torr A     106   Torr Xe
880 Bi    0.92459  13.410    13933     8480    14258-13324    8675-8114    147   Torr A     115.5 Torr Xe
890 Po    0.89761  13.813    13518     8231    13824-12945    8415-7886    158   Torr A     123   Torr Xe
900 At    0.87234  14.213    13131     7997    13419-13590    8171-7671    172   Torr A     133   Torr Xe
910 Rn    0.84845  14.613    12765     7777    13037-12253    7941-7469    187   Torr A     144   Torr Xe
920 END
```
SC

FIGURE CAPTIONS

Fig.1 Schematic of the EXAFS equipment

Fig.2 Transmission spectrum of Ni foil.

Fig.3 XANES of V metal foil with different amounts of harmonic contamination with monochromatised beam. The percentages on the fight refer to I/I_{max}, the intensity used, I, compared to the maximum available when the two crystals are aligned, I_{max}.

Fig.4 Arrangement of scintillation detectors for fluorescence measurements.

Fig.5 Fluorescence excitation spectrum of $CuSO_4$ solution obtained in a single scan of 6 sec per energy point for a 5 m molar, 1 m molar and 250 μ molar solution.

Fig.6 Order sorting Si 220 monochromator. M is a ferrite magnet influenced by solenoid S. C is a stepper motor driven screw and provides coarse adjustment about pivot P.

Fig.7 Layout of control rack panel for order sorting monochromator and ion chamber currents.

Fig.8 Absorption at the Ge K-edge of liquid $GeCl_4$ showing the pre(1) and post (2) edge polynomials used for the background subtracting programme EXBACK.

Fig.9 Normalized EXAFS for the $GeCl_4$ absorption spectrum shown in fig.8.

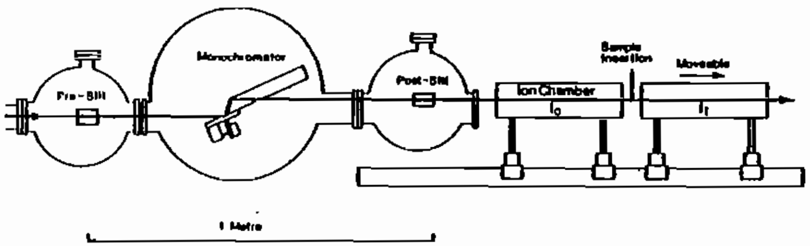

Pre - Slit
Monochromator
Post - Slit
Ion Chamber
I_0
Sample insertion
Moveable
I_t
1 Metre

Fig.1

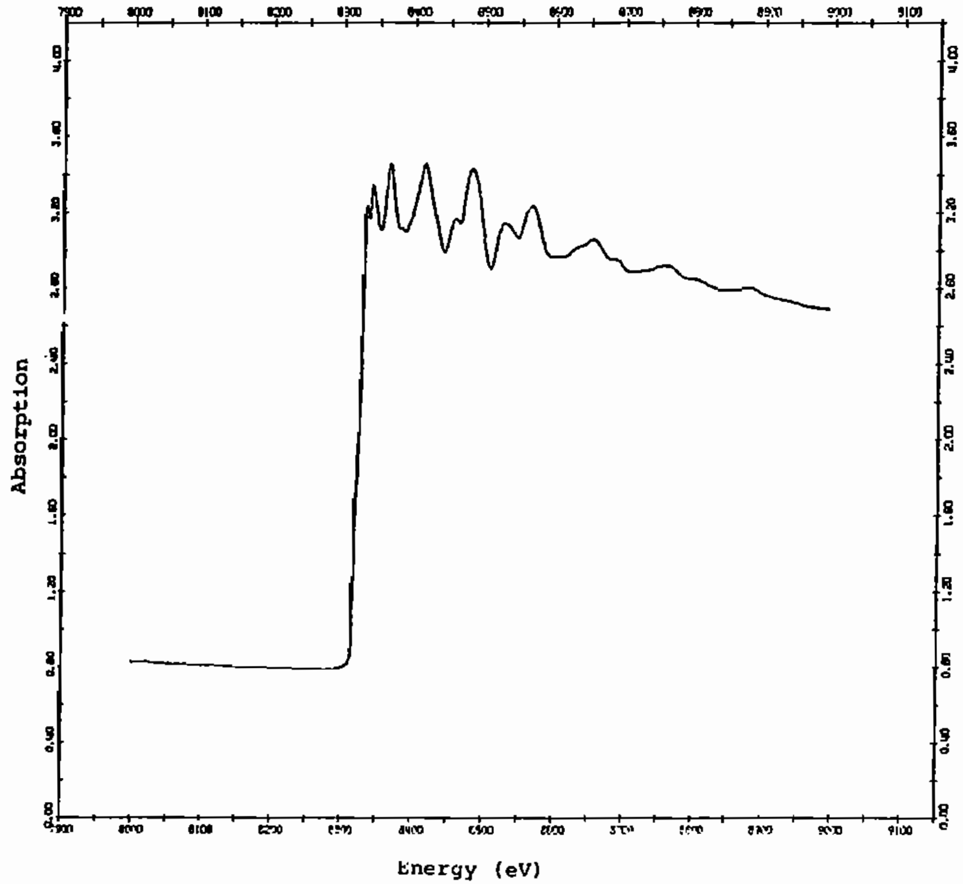
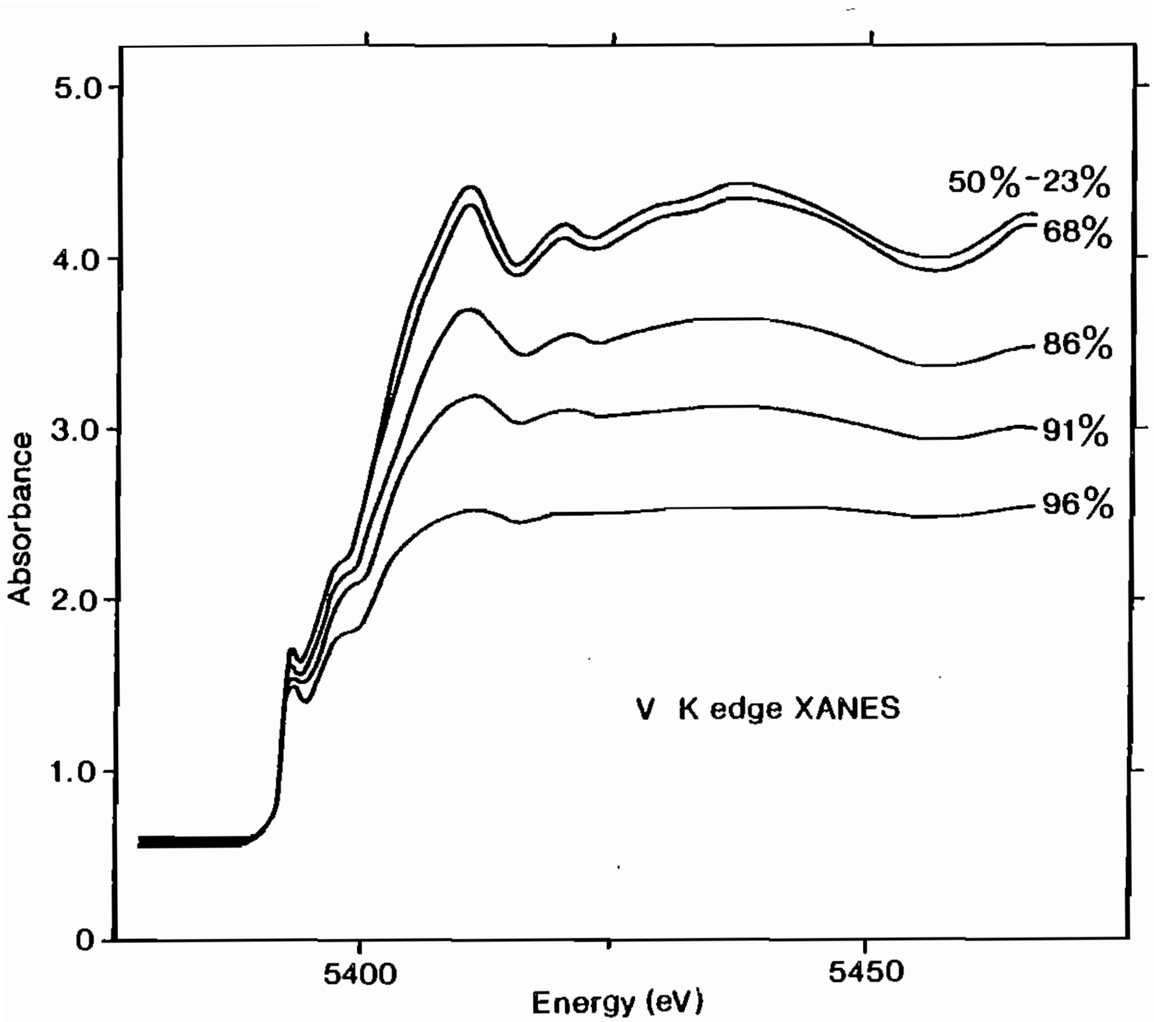

Absorption
Energy (eV)

Fig.2



Absorbance
5.0
4.0
3.0
2.0
1.0
0
5400
5450
Energy (eV)
50%-23%
68%
86%
91%
96%
V K edge XANES

Fig.3

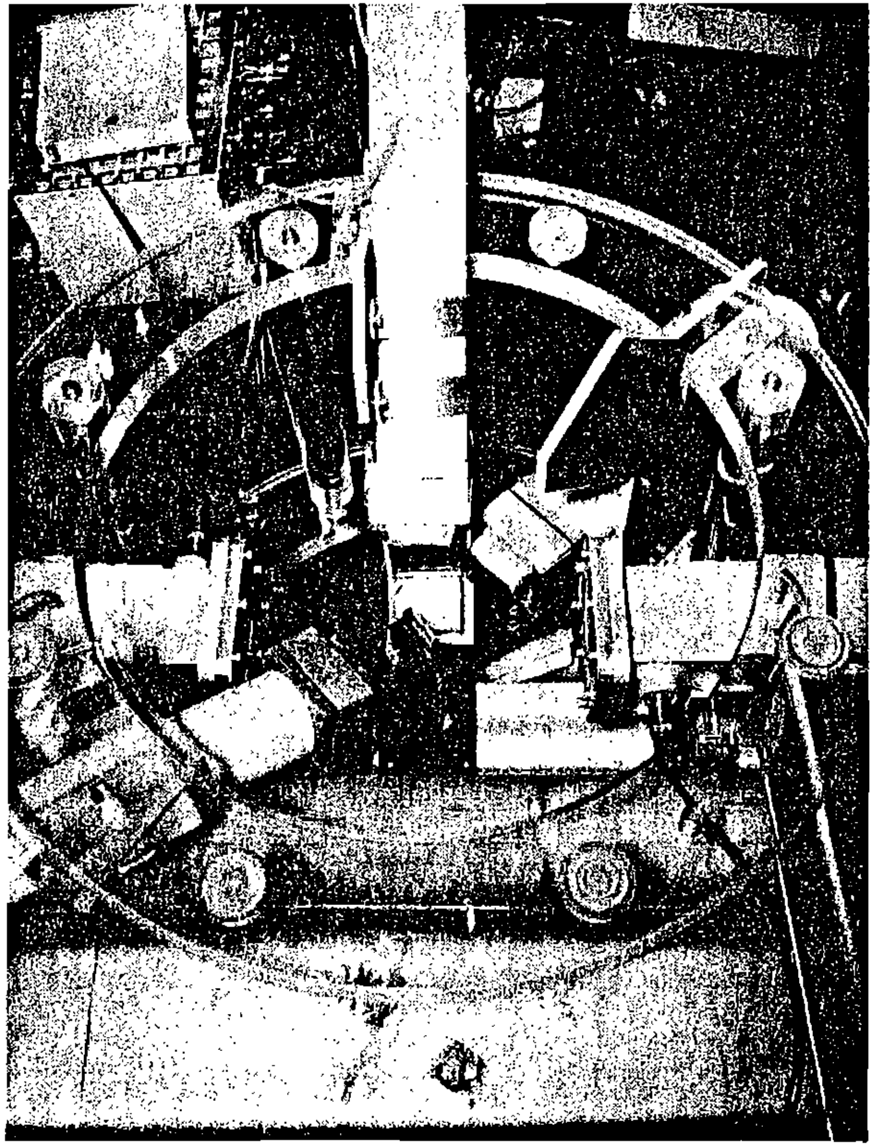


Fig.4

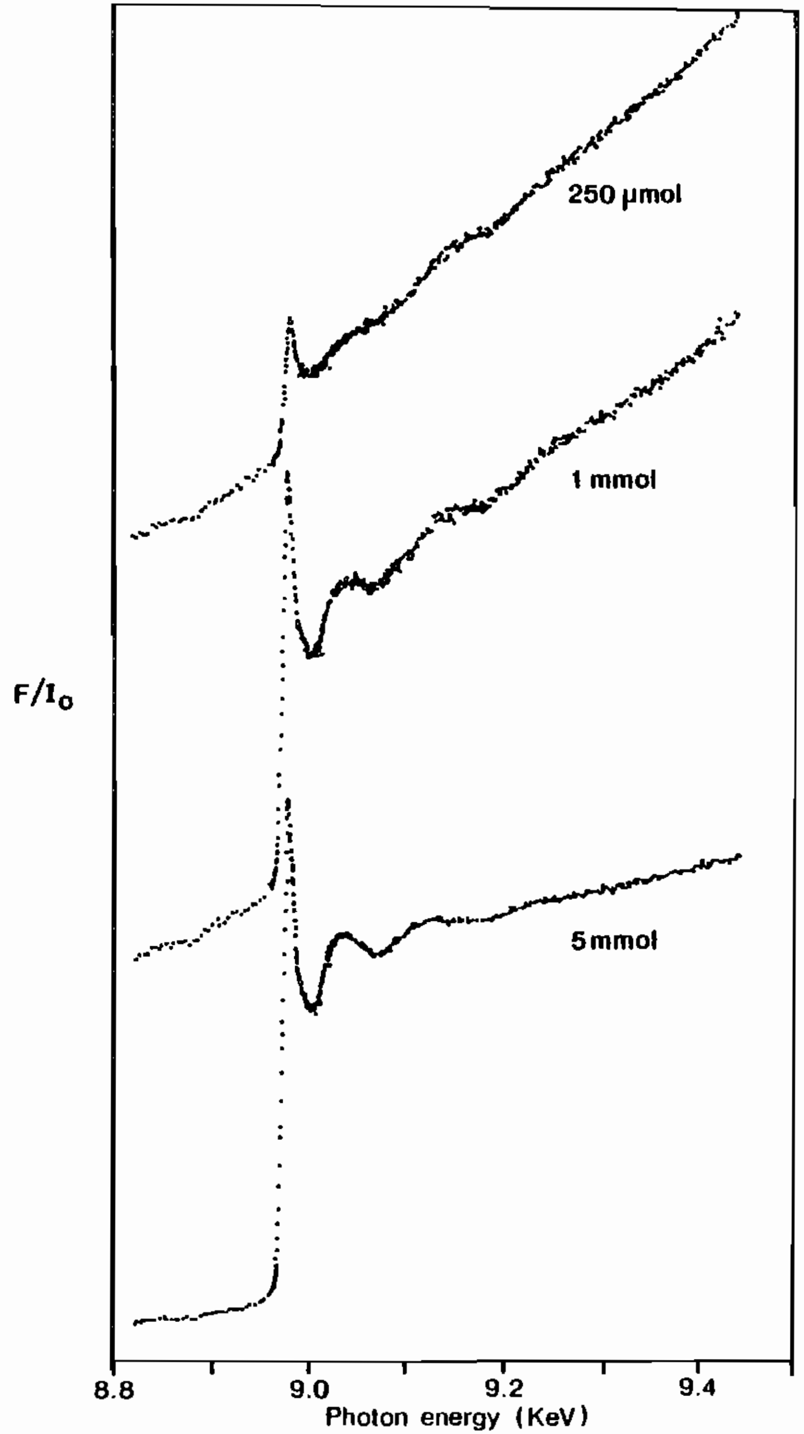


Fig.5

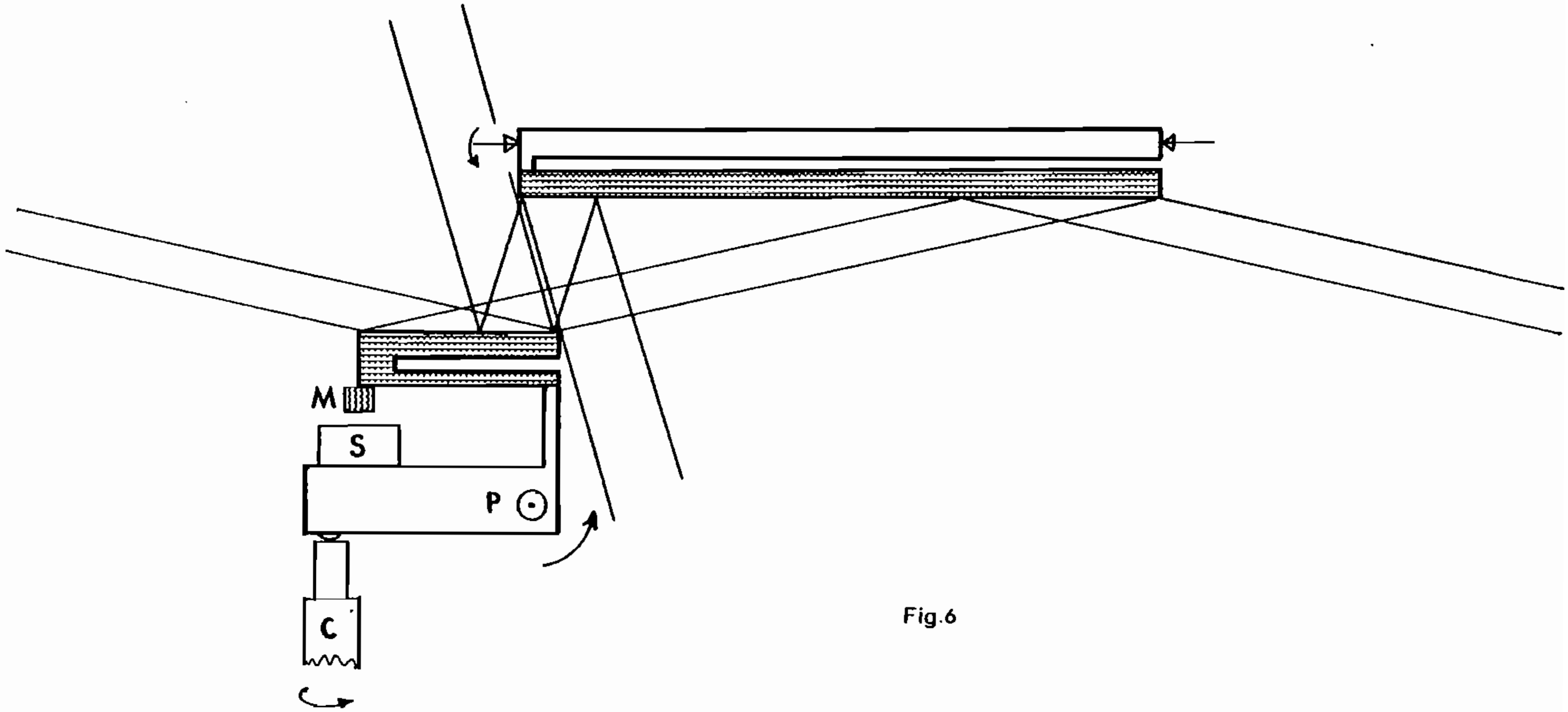


Fig.6

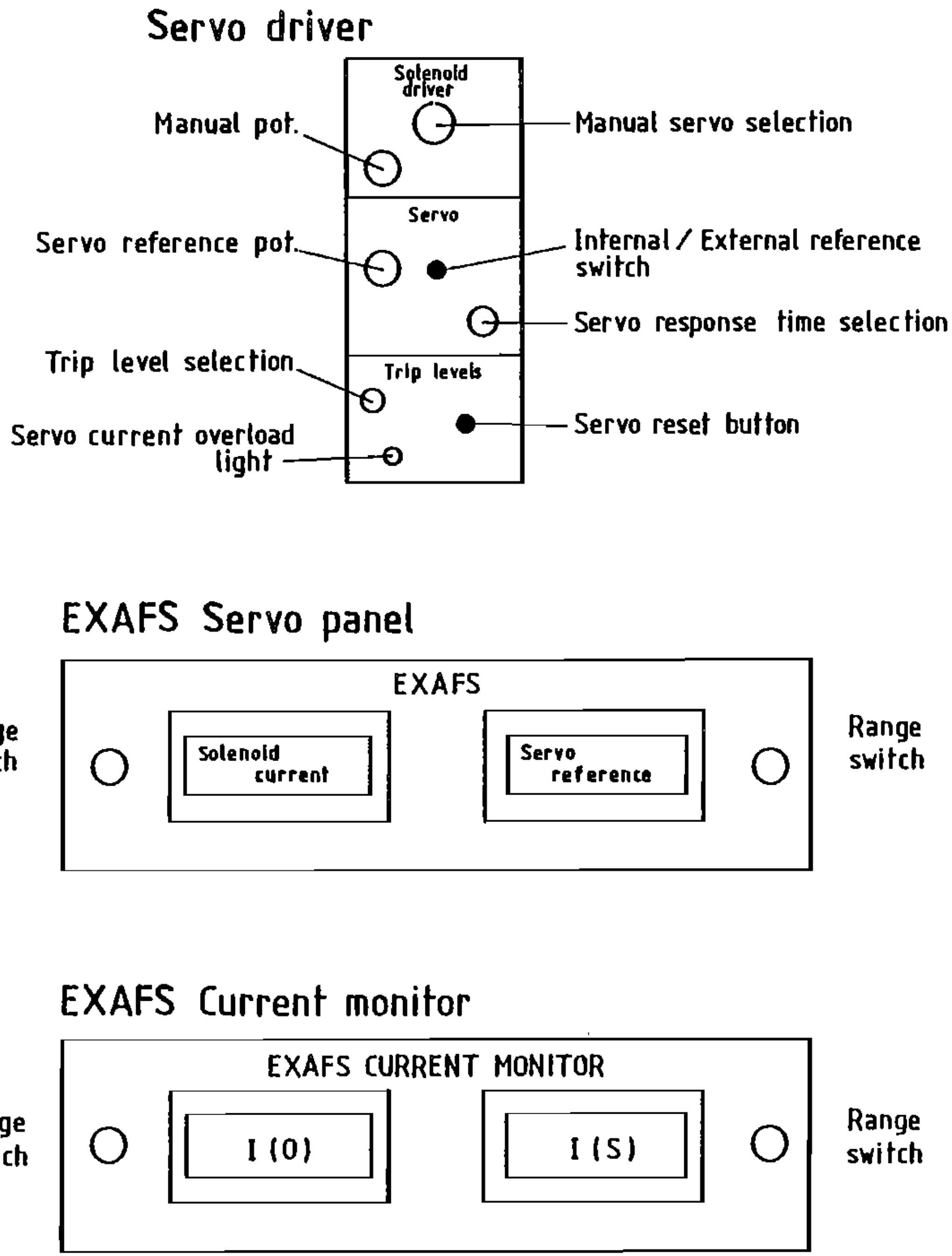

Servo driver
Solenoid driver
Manual pot.
Manual servo selection
Servo
Servo reference pot.
Internal / External reference switch
Servo response time selection
Trip level selection
Trip levels
Servo current overload light
Servo reset button
EXAFS Servo panel
EXAFS
Range switch
Solenoid current
Servo reference
Range switch
EXAFS Current monitor
EXAFS CURRENT MONITOR
Range switch
I (0)
I (S)
Range switch

Fig.7

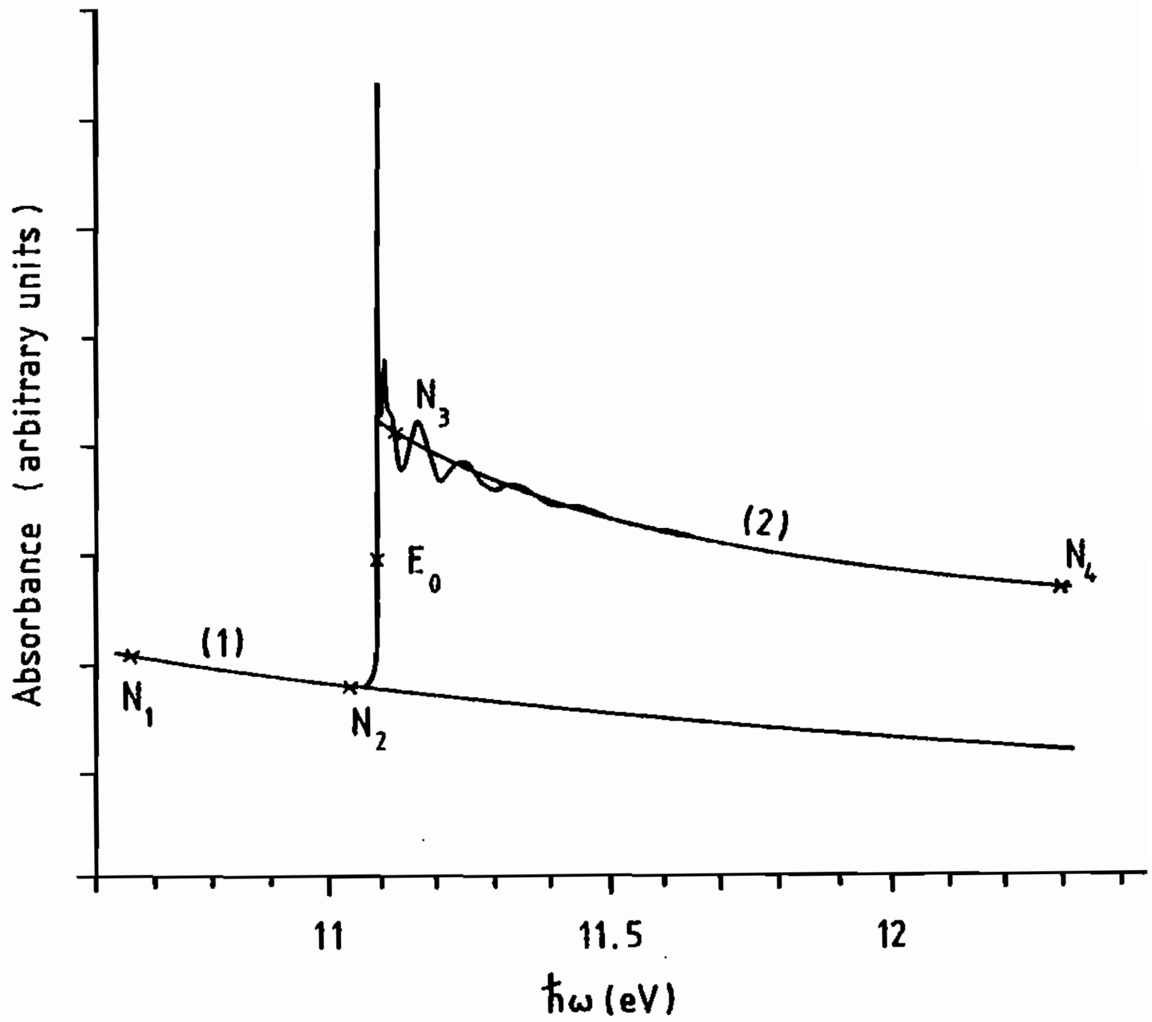


Fig.8

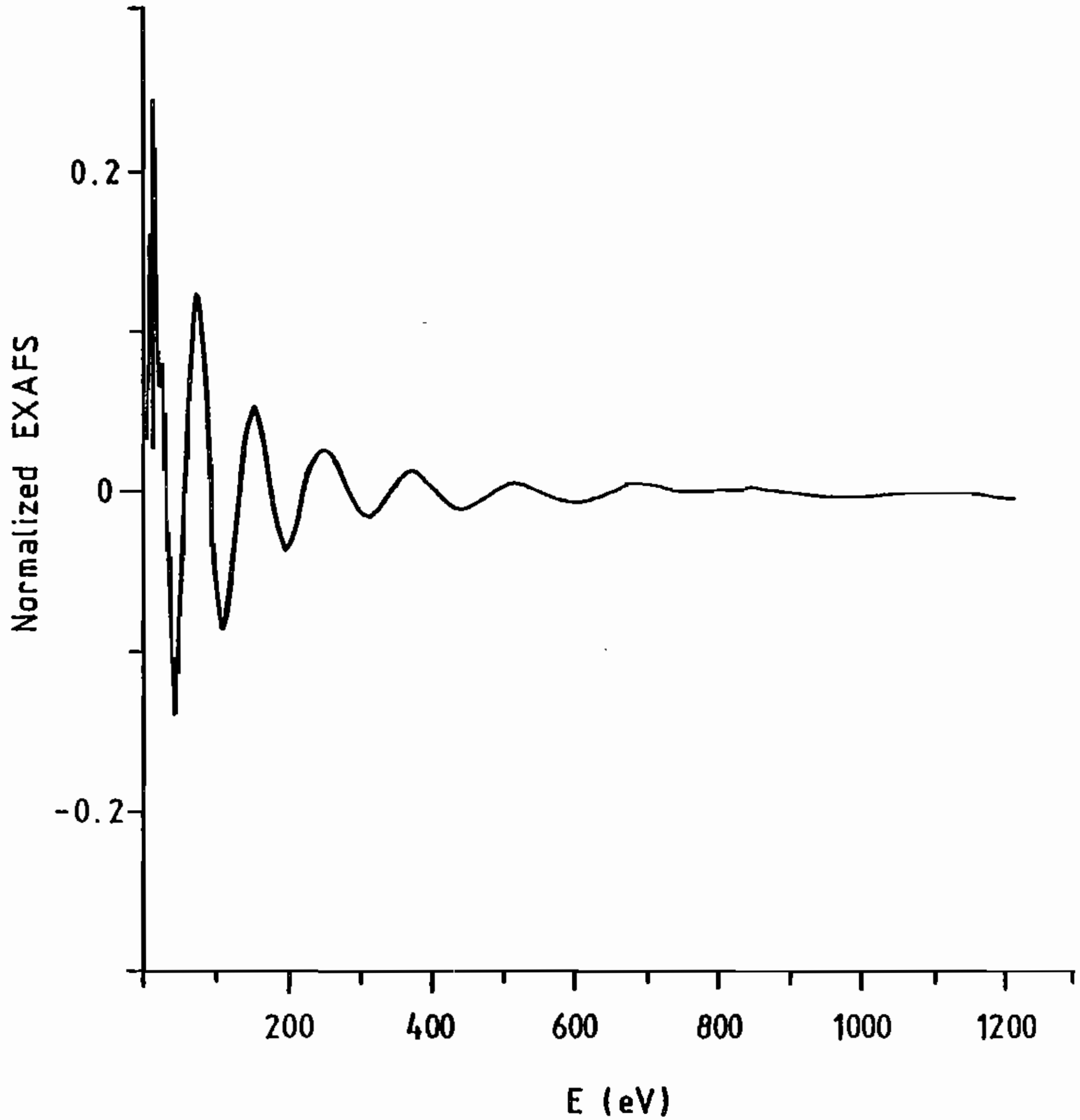


Fig 9