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RIETVELD REFINEMENT OF HIGH PRESSURE POWDER DIFFRACTION DATA COLLECTED WITH AN IMAGING PLATE DETECTOR

by

A.M.T. BELL, University of Keele; and
R.J. CERNIK, Daresbury Laboratory

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IMPORTANT

Rietveld refinement of high pressure powder diffraction data collected with an imaging plate detector.

A.M.T.Bell[1]   R.J.Cernik[2]

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Abstract

This report describes the Rietveld refinement of synchrotron powder diffraction data collected using an image plate detector on beamline 6B at the Photon Factory, Tsukuba, Japan before December 1990. Data were collected for silver at ambient pressure and for iodine at 0.6GPa.

[1] Department of Chemistry, University of Keele, Keele, Staffordshire, ST5 5BG.
[2] SERC Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD.

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0.1 Introduction

A collaboration between Daresbury Laboratory and the University of Edinburgh (Prof. R.J.Nelmes) is currently investigating the use of an image plate system for collecting powder diffraction data from small volume polycrystalline specimens. This is primarily aimed at high pressure research using diamond anvil cells where small samples necessitate the use of beams $\sim 100\mu m$ in diameter. Conventional powder scans with samples and

beams this small yield data of very poor statistical quality. A major advantage of the image plate area detector system over a conventional angle scan is that the diffracted intensity of each Debye-Scherrer ring can be radially integrated improving the counting statistics by a factor of 50-100 in the case of the larger rings. In addition the random noise in the background is also radially integrated thus reducing unwanted statistical fluctuations. The effects of a poor powder average caused by a small sample volume can also be clearly seen. Providing this is not too severe radial integration can also compensate for this effect, however, it should be stressed that if reliable integrated intensities are required then considerable attention must be paid to sample preparation.

The ultimate aim of the Daresbury and Edinburgh groups is to extract accurate positional parameters from specimens at high pressures. Before such data were available at Daresbury the Photon Factory group (Y.Fujii and O.Shimomura) sent some sample data sets to be refined initially to establish whether these data would be suitable for full Rietveld refinement[1].

Data were recieved for 2 different samples, silver (data collected at ambient pressure) and iodine (data collected at 0.6 GPa). Silver is commonly used by the Japanese group to calibrate the sample-film distance.

0.2 Experimental

The data were collected on beamline 6B of the Photon Factory at Tsukuba. Figure 1 shows the experimental arrangement with the diamond anvil cell mounted on an xyz stage. The collimation equipment, image plate holder and general assembly are also shown.

For both samples synchrotron radiation with a wavelength of 0.6888Åwas used. The data for the silver was collected between 13 and 49.96°2θ, the iodine data was collected between 6 and 32.96°2θ, in both cases the step width was 0.02°2θ. The data were mapped onto a 2θ scale by the Japanese group.

0.3 Data manipulation

The data were recieved on magnetic tape in two column format (2θ and intensity). The data were then converted to six column format (dummy SRS format) by Mike Miller (CST division). This enabled the data to be processed using software from the Powder Diffraction Program Library (PDPL)[3].

As the Bragg angle increases the absorption of the beam by the sample also increases, this is corrected for by dividing the diffracted intensity by $\exp(-(\mu(d/\cos\theta)))$ where μ is the linear absorption coefficient and d is the sample thickness. In this work this sample was approximately 0.2 mm thick. The absorption coeffiecients for Mo Kα radiation ($\lambda = 0.7107$Å)[2] were used. To a first approximation the Lorentz factor was taken to be the same as that for Debye-Scherrer geometry.

0.4 Rietveld refinement results

The data were corrected for the effects discussed in the previous section using a local computer program. Prior to Rietveld refinement these corrected data were converted into PDS format using the program PODSUM. The program CELREF was used to determine initial lattice parameters for the samples and the program DRAGON was used to provide an input file for the preprofile preparation program, MPREP.

MPREP was used to provide an input file for the Rietveld program MPROF. MPROF produced the refined structural parameters for the sample.

0.4.1 Refinement of the silver structure.

The powder diffraction data for silver was indexed from the JCPDS powder diffraction file[4] pattern 4-783. The structure was refined from the face centred cubic structure given by Wyckoff[5].

MPROF was able to satisfactorily refine the silver structure, a plot showing the observed, calculated and difference profiles is given as Figure 2. Only data from 13 to 48°2θ was used for refinement as the highest Bragg angle data (from 48 to 49.96°2θ) was of poorer quality. The Rietveld output is shown in Table 1.

As a comparison the uncorrected raw data was also refined. A plot showing the observed, calculated and difference profiles is given as Figure 3 and the Rietveld output is shown in Table 2.

0.4.2 Refinement of the iodine structure.

The powder diffraction data for iodine was indexed from the JCPDS powder diffraction file pattern 5-558. The structure was refined from the orthorhombic structure (determined at 20.6GPa) given by Shimomura et al[6].

MPROF was able to refine the iodine structure although the refinement is not of as high a quality as that for the silver. The Rietveld output is shown in Table 3. Not all of the data was used in the refinement, data between 16.71 and 17.83°2θ and 20.17 and 20.27°2θ were excluded due to the presence of impurity peaks (possibly from the diamond anvil cell), data between 30.50 and 32.96°2θ was also excluded as the highest Bragg angle data was of poorer quality. A plot showing the observed, calculated and difference profiles for the whole pattern is shown in Figure 4, more detailed plots are given as Figure 5 (10 to 20°2θ) and Figure 6 (21.5 to 30.5°2θ).

As a comparison the uncorrected raw iodine data was also refined, this refinement was less satisfactory as no absorption correction was made. The Rietveld output is shown in Table 4. A plot showing the observed, calculated and difference profiles for the whole pattern is given as Figure 7, more detailed plots are given as Figure 8 (10 to 20°2θ) and Figure 9 (21.5 to 30.5°2θ).

0.5 Discussion

0.5.1 silver

The face centred cubic silver structure was satisfactorily refined from the corrected data and converged to RI = 1.67 and Rwp = 8.81. However, the cubic lattice parameter determined for silver (a = 4.0805(1)Å) is slightly lower than that given on JCPDS powder diffraction file pattern 4-783 (a = 4.0862Å). This could be because the diamond anvil cell containing the silver was slightly pressurised. The isotropic temperature factor determined for silver in this refinement (B = 1.15Å^2) is larger than expected, this may be an artifact of refinement process as the refinement was carried out with data up to a relatively low Bragg angle. The silver structure was also satisfactorily refined from the uncorrected data and converged to RI = 1.66 and Rwp = 8.60. However, the isotropic temparature factor from this refinement (B = 1.99Å^2) was larger than that for the corrected data. Figures 2 and 3 show a good fit between the observed and calculated peak shape for the silver data.

0.5.2 iodine

The refinement of the orthorhombic iodine structure from the corrected data converged to RI = 10.67 and Rwp = 13.67 the structure of iodine at 0.6GPa is similar

to that at 20.6GPa[6] and at ambient pressure[7]. The refined structural parameters for iodine determined in this work are given in Table 5 together with those given in[6] and[7]. However, there were some problems in determining the best peak shape to fit the profiles of the observed Bragg reflections. At "low" Bragg angles the fit is reasonably good (see Figure 5) but at "high" angles the fit is worse (see Figure 6). This could be due to some lattice strain and/or preferred orientation due to the sample being under pressure. As for the silver the isotropic temperature factor ($B = 3.07\text{Å}^2$) is larger than expected.

The refinement of the iodine structure from the uncorrected data was not satisfactory, the refinement converged to RI = 44.86 and Rwp = 12.63. The peak shape fit for this data is worse than that for the refinement of the corrected data, this is particularly evident if Figures 6 and 9 are compared. As was found for silver the isotropic temperature factor ($B = 3.65\text{Å}^2$) is larger than that for the corrected data.

Table 1 - corrected silver data

```
Ag     1   1    0.00000      0.00000     0.00000    1.14879   1.00000  0
          0.26434669E-01                0.00000
              -2.896
          -707.641         539.031       144.372       0.665      0.000
        4.0805     4.0805    4.0805   90.000    90.000    90.000
# R FACTORS;  RI =      1.67, Rwp =     8.81, Re =     0.56
```

Table 2 - uncorrected silver data

```
Ag     1   1    0.00000      0.00000     0.00000    1.99232   1.00000  0
          0.11801014E-03                0.00000
              -2.981
          -979.782         669.806       132.253       0.656      0.000
        4.0803     4.0803    4.0803   90.000    90.000    90.000
# R FACTORS;  RI =      1.66, Rwp =     8.60, Re =     9.13
```

Table 3 - corrected iodine data

```
I      1   1    0.00000      0.15896     0.11665    3.07026   1.00000  0
          0.40354710E-01                0.00000
              -6.970
          9589.811        -1720.474      180.989       2.360      0.000
        7.0186     4.6542    9.6908   90.000    90.000    90.000
# R FACTORS;  RI =     10.67, Rwp =    13.67, Re =     2.11
```

Table 4 - uncorrected iodine data

```
I      1   1    0.00000      0.15829     0.11640    3.64986   1.00000  0
          0.79258642E-03                0.00000
              -6.959
         32679.711       -7300.840      516.874       2.986      0.000
        7.0187     4.6532    9.6933   90.000    90.000    90.000
# R FACTORS;  RI =     44.86, Rwp =    12.63, Re =    15.55
```

Table 5 - iodine structural parameters

reference	Harris et al	This work	Shimomura et al
pressure	ambient	0.6GPa	20.6GPa
space group	Cmca (64)	Cmca (64)	Cmca (64)
a	7.136(10)	7.0186(9)	5.779(8)
b	4.686(70)	4.6542(7)	3.943(14)
c	9.784(15)	9.6908(10)	9.076(10)
V	327.17	316.57(11)	206.8(12)
x	0	0	0
y	0.15	0.1590(5)	0.194(4)
z	0.117	0.1167(4)	0.128(3)
Z	4	4	4
B	not given	3.07(12)	0.3

For a more satisfactory refinement of this structure data of better quality would be needed especially for satisfactory Rietveld refinement of structures more complex and of lower symmetry than that of iodine.

0.6 Conclusions

- 1. The face centred cubic structure of silver at ambient pressure has been satisfactorily refined.

- 2. The orthorhombic structure of iodine at 0.6GPa has been refined and agrees reasonably well with the structure found at ambient pressure and at 20.6GPa.

- 3. Better quality data than that supplied for this work would be required for satisfactory rietveld refinement of more complex structures than those refined in this work.

- 4. The isotropic temperature factors determined from these refinements are higher than expected. This may be because the refinements were carried out with a relatively low angular range for the data and a rather elementary absorption correction.

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[4] Powder Diffraction File, JCPDS-International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081, USA.

[5] R.G.Wyckoff, Crystal Structures, 2nd edition, volume I, page 10. Published by Interscience, New York (1964).

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collimator

sample

(50×50×55   )

DAC

microscope
for alignment

IP

SR

modified
(See drawings)

25
13

閉気

3月取付ボルト
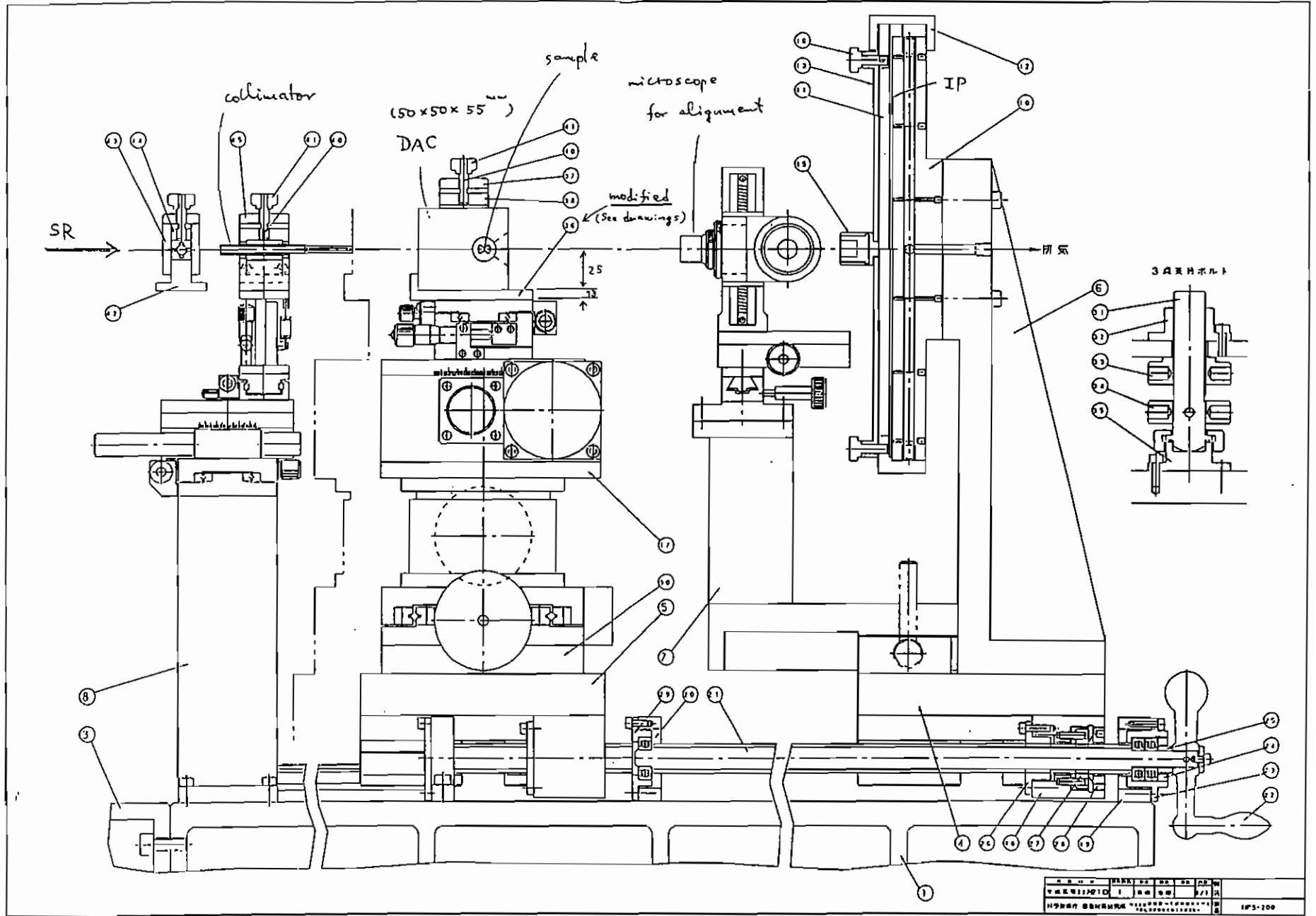
Fig.1

Fig 2 Silver at ambient pressure - corrected data
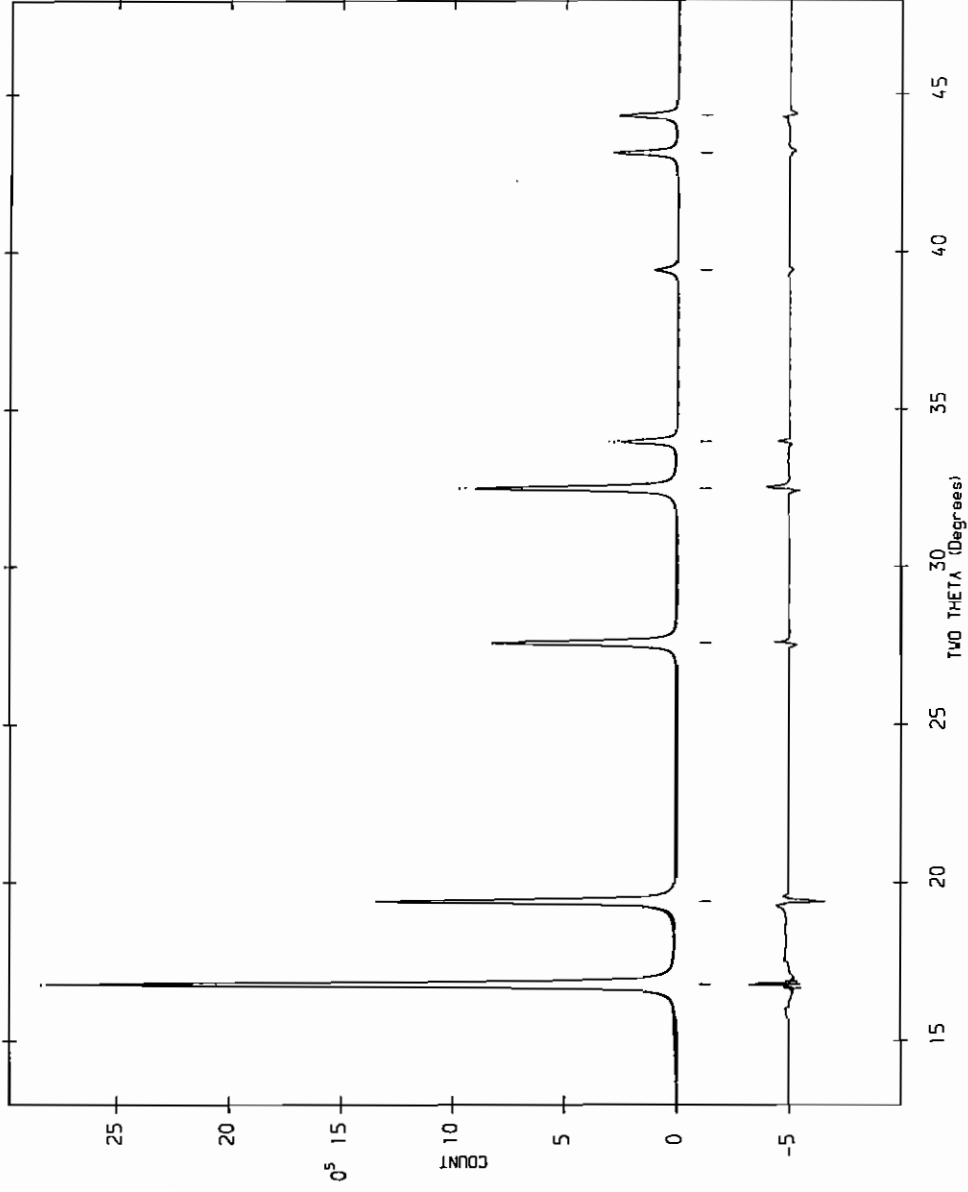
Fig 3 Silver at ambient pressure - uncorrected data
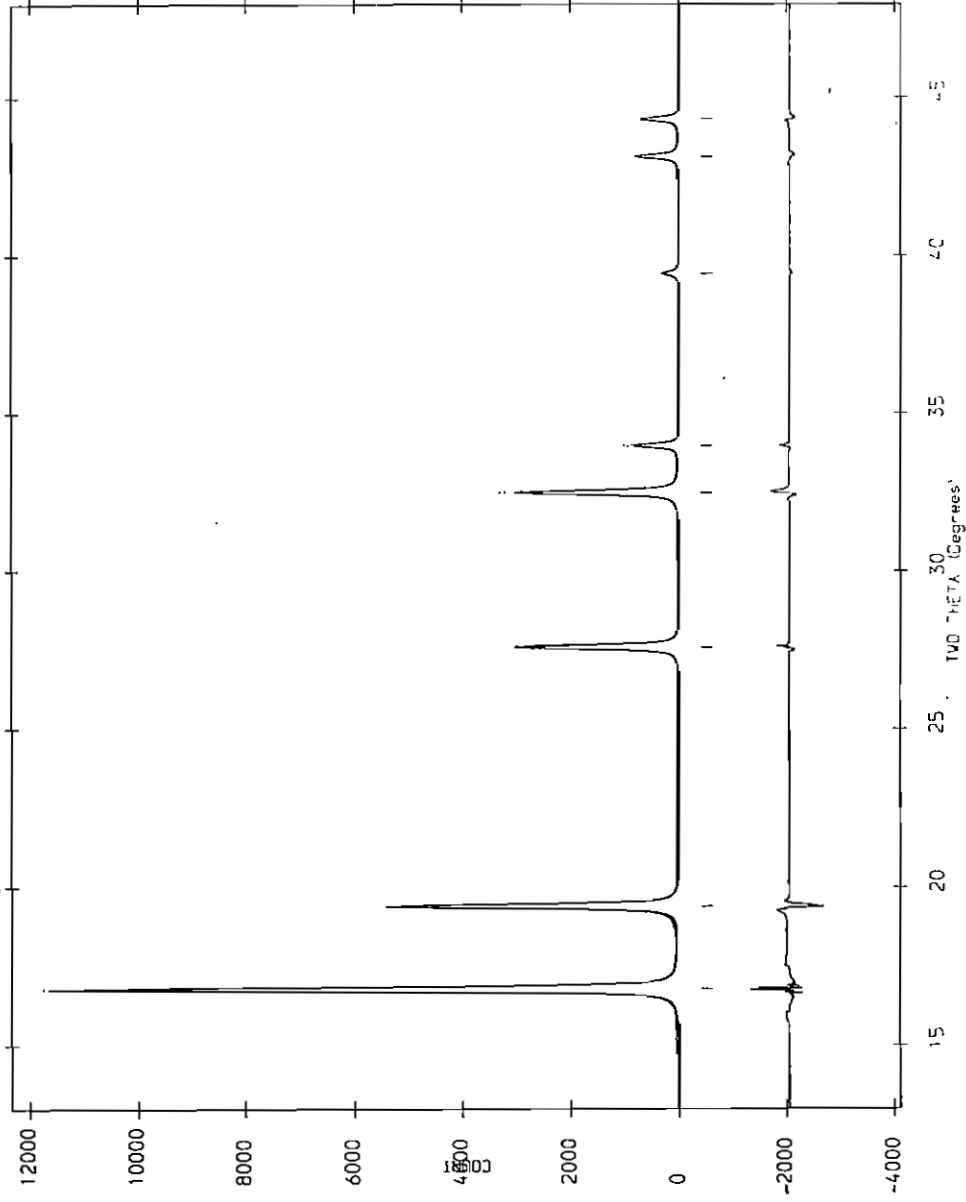
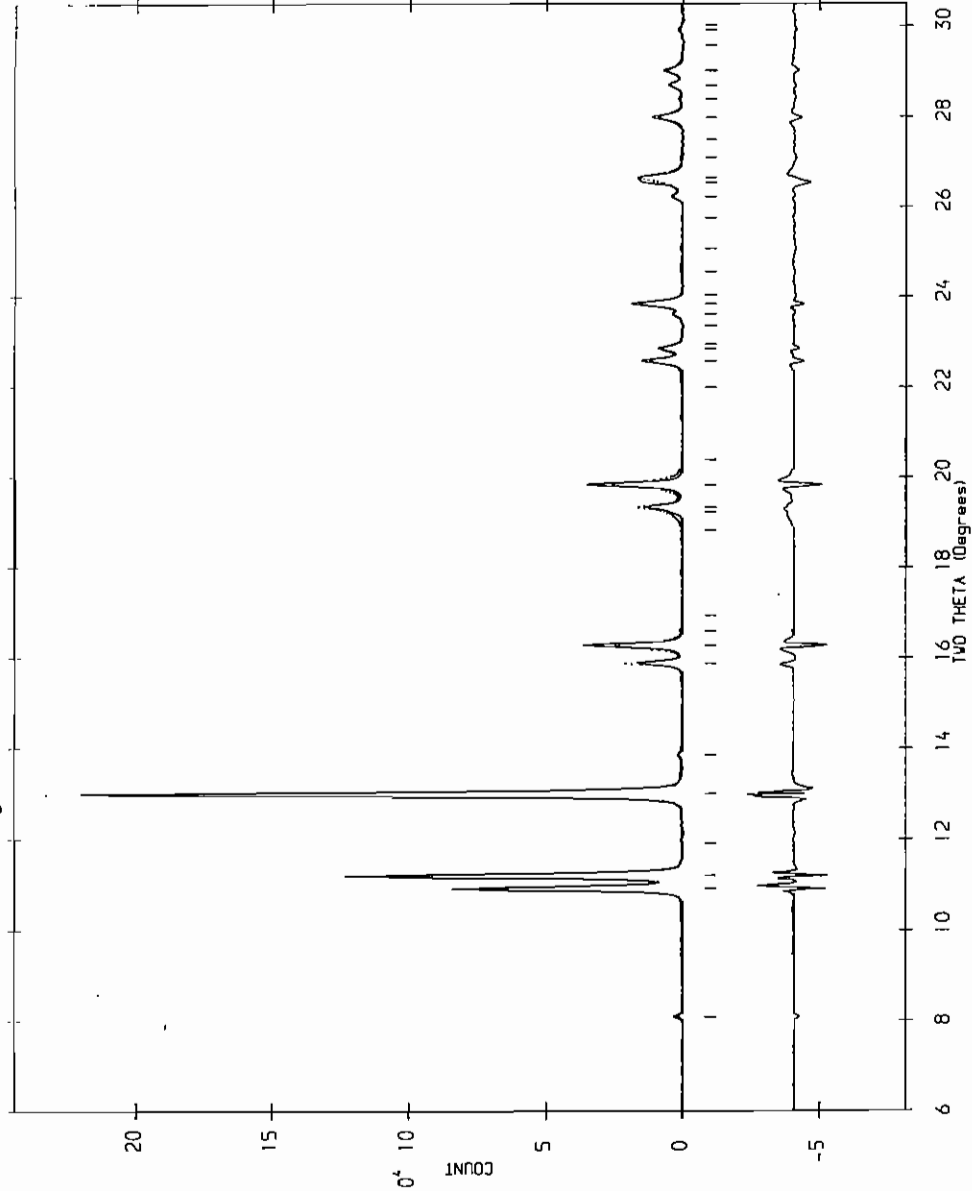Fig 4   Iodine at 0.6 GPa - corrected data
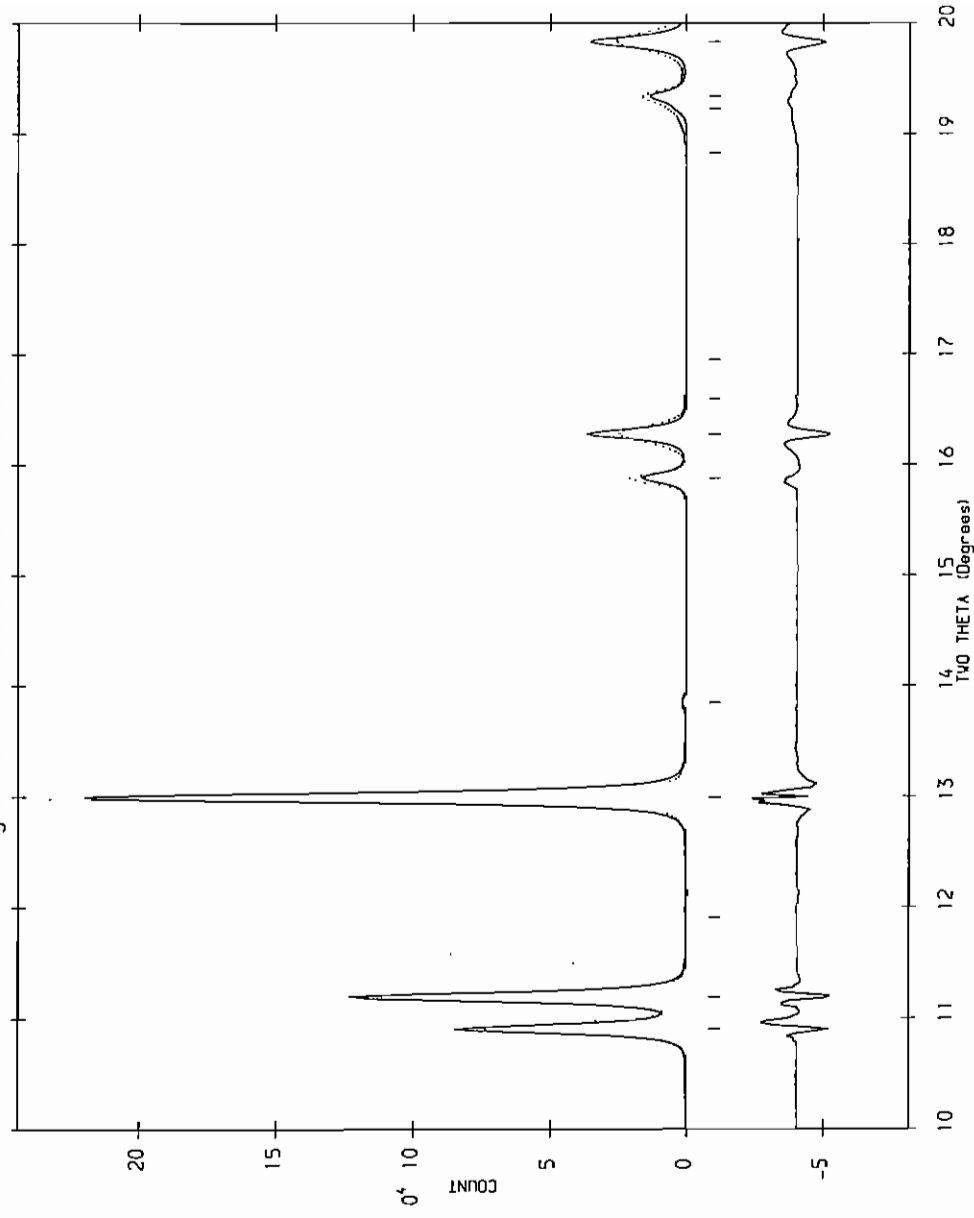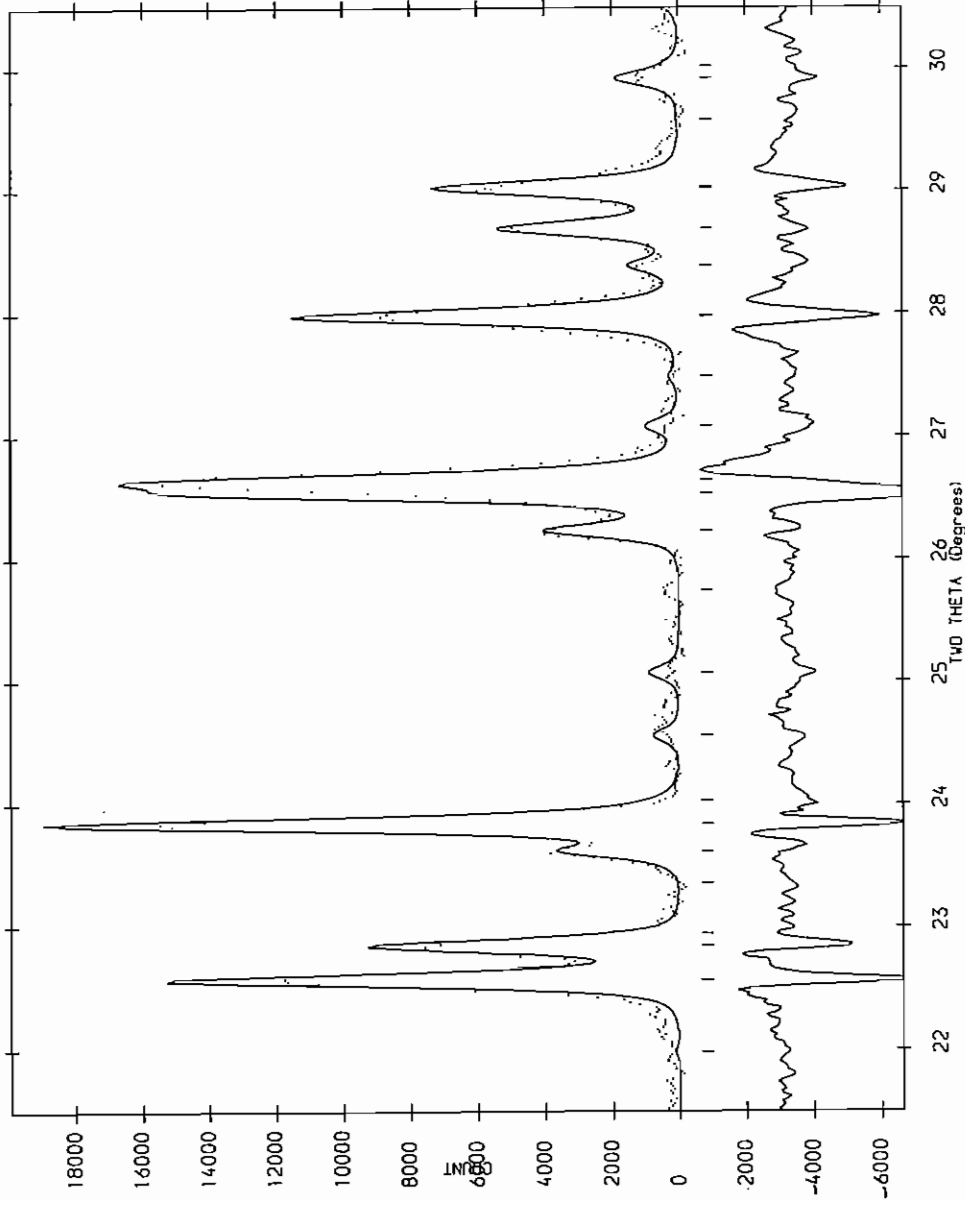
Fig 5   Iodine at 0.6 GPa - corrected data

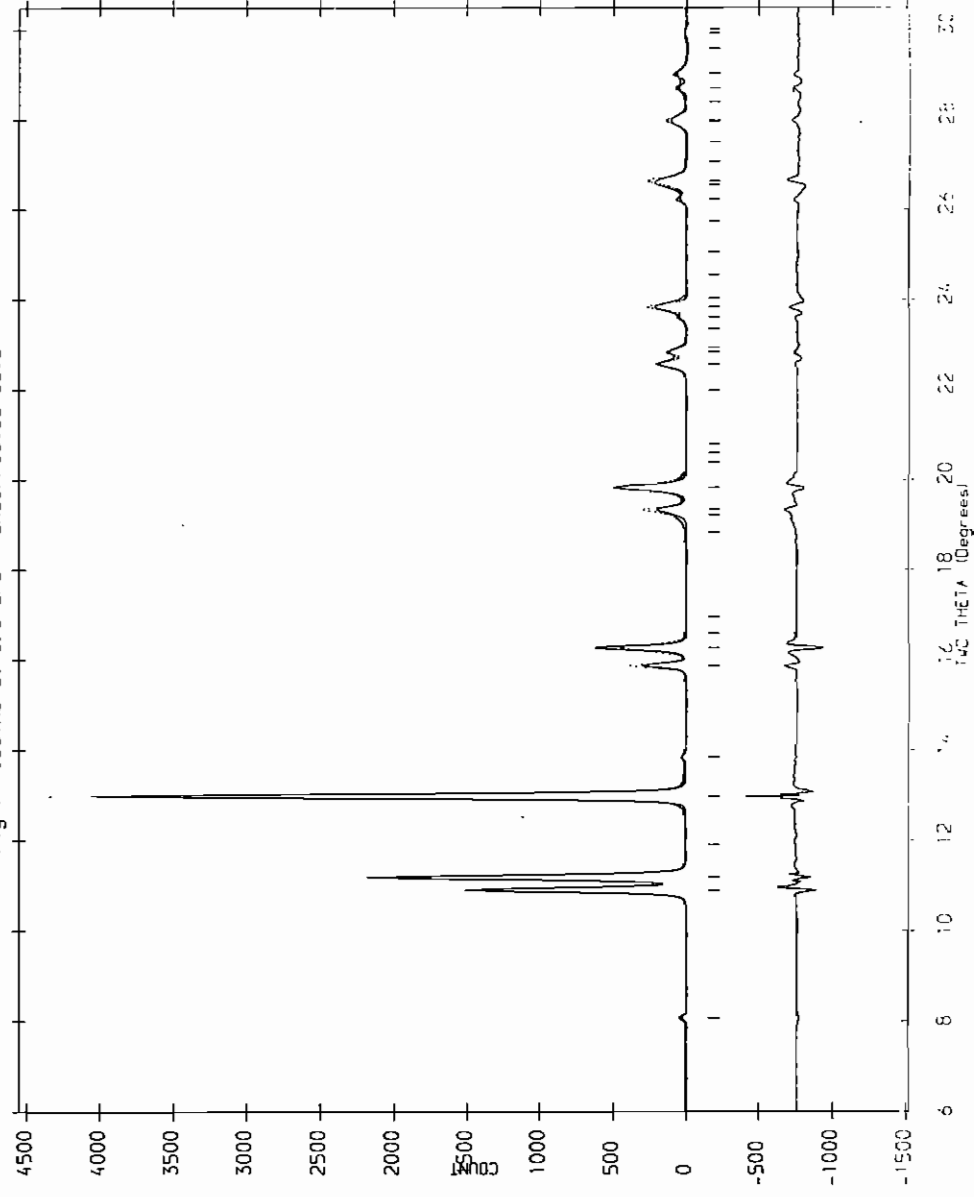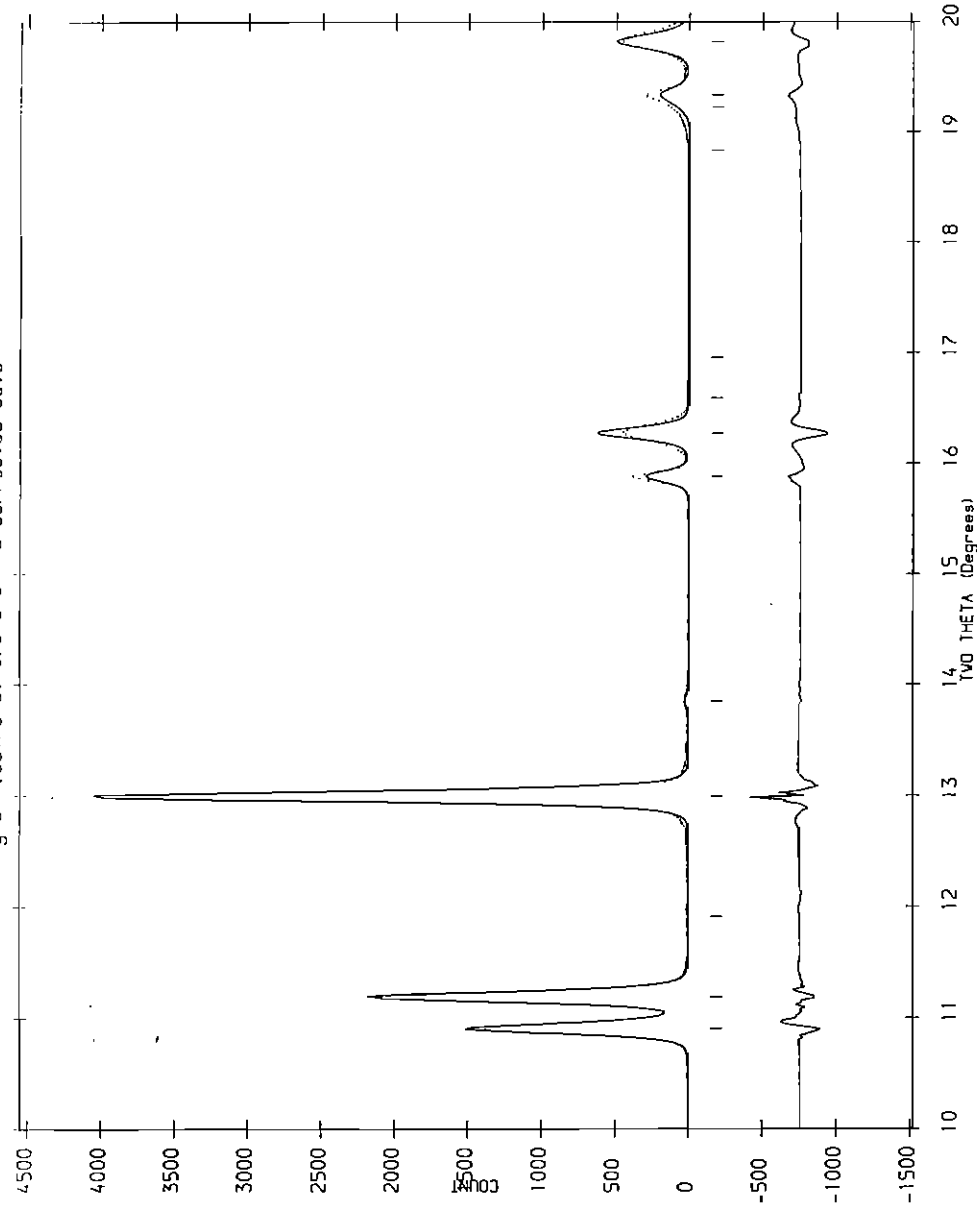Fig 6 Iodine at 0.6 GPa - corrected data

Fig 7 Iodine at 0.6 GPa - uncorrected data

Fig 9 Iodine at 0.6 GPa - uncorrected data

Fig 9 Iodine at 0.6 GPa - uncorrected data