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SYNCHROTRON ENERGY DISPERSIVE POWDER DIFFRACTION

by

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SYNCHROTRON ENERGY DISPERSIVE POWDER DIFFRACTION:

A report on trial experiments conducted on station 9.7 at the Daresbury Synchrotron Radlation Facility

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ABSTRACT

During four weeks of useful beam time during the summer of 1986, the authors of this report used the test station 9.7 to explore the possibilities for developing Energy Dispersive Diffraction (EDD) as a separate facility at Daresbury. Novel applicatlons of EDD were made in three areas: which are detailed in this report.

1) real time EDD of hydratlng cements;
2) monitoring crystallisation of alkanes using EDD;
3) use of EDD in high pressure lattice parameters and intensity measurements;

The longer-term conclusions from these trials are that useful EDD can be effective and cheaply developed on 9.7 after the HBL alterations of 1986/87. The experiences gained during these trials would enable us to design and build an improved system that would place the Daresbury synchrotron at the forefront of EDD technology.

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INTRODUCTION

Although energy dispersive powder X-ray diffraction has always been recognised as one of the three main modes of operatlon of statlon 9.1, lts development has lagged behind that of the more conventional angle-scannlng mode. The three designated modes of operation on 9.1 in the past have been:

1) Angle scanning mode for medium resolution work such as anomalous dispersion experiments.
2) High resolution powder diffraction mode with analyser crystal.
3) And the energy dispersive mode for studying fast reactions and transformations, with time resolved powder diffraction.

Although 9.1 is capable of accommodating all these modes, a significant amount of beam time has been wasted changing from one mode to another. There has also been a sharp increase in demand for beam time in the angle scanning mode on 9.1. A high resolution diffractometer on station 8.3 (shared with EXAFS TEST) will alleviate the overcrowding but the need for a purpose-built dedicated energy dispersive station is well recognised.

An ideal site for the development of EDD is station 9.7 (formerly Interferometry/test), this will be shared with the protein crystallography Laue section. Both techniques use the white beam so a new front end can be developed jointly at very low cost. It was demonstrated in the summer of 1986 that both groups could use this station efficiently wlth a very short change-over time.

In this memorandum we describe the EDD arrangement that was successfully set up on station 9.7 using various equipment available from other Daresbury stations and at the users' home bases (Birkbeck College London, King's College London, and University of Strathclyde). A detailed descrlption of hardware, electronics and software is available from the authors.

BACKGROUND TO EDD METHOD

Although the applicatlon of synchrotron radiation to powder diffraction is more recent, the concept of EDD has been known for some time[1], using laboratory-based white X-ray sources. The basic idea of EDD is to irradiate

the powder-specimens with white (rather than monochromatic) X-rays and collect powder diffraction data at fixed sample and detector angles. The range of diffraction states implied by Bragg's law is then registered as a spectrum of diffraction intensity versus X-ray photon energy rather than against detector angle. The Bragg equation then becomes:

$$\frac{nhc}{E} = 2d \sin\theta; \quad \text{or alternatively} \quad Ed \sin\theta = \text{constant}$$

The aberrations peculiar to EDD geometries have been outlined by Wilson[2]. Fukamachi, Hosoya and Terasaki[3] have claimed that, by using laboratory white radiation from a Cr-target, a precision of 0.01% could be obtained for d-spacings of Al. However, there is now evidence (see project (2) below) that this accuracy cannot be achieved consistently and predictably over the whole energy range. A substantial paper by Mantler and Parrish[4] examined the question of separation of peaks with EDD: clearly since the value of θ in the above Bragg equation can be chosen at will, it can be set experimentally at values which will either shift and contract (large θ) or expand (small θ) the pattern as required. However, the relative separation and intensity of the peaks also varies with the chosen θ, so the final choice of θ becomes a complex compromise.

EDD studies using synchrotron radiation date back to the late seventies using the earlier generation of synchrotrons such as NINA at Daresbury[5-8]. The major instrumental limitation was judged to be the counting rate of the soiid state detector. Solid state detectors have also been used in conjunction with a pre- or post-sample X-ray monochromator for other diffraction modes. However, for the purposes of this report we will restrict the meaning of EDD to refer only to white X-ray diffraction experiments without the use of any monochromatisation. In the following sections we summarise the various projects that were undertaken.

PROJECT 1 Real Time Energy Dispersive Powder Diffraction of Hydrating Cement

by P. Barnes, S.M. Clark, E. Polak and S.E. Tarling
Industrial Minerals Group, Department of Crystallography, Birkbeck College, London, UK.

(a) Introduction

Previous attempts had been made on 9.1, using monochromatic radiation and a position sensitive detector (PSD) to collect time-resolved diffraction data on hydrating cement. The detector had an active straight wire length of 9 cm and was borrowed with it's accompanying electronics from the Small Angle Scattering station with the help of Dr. C. Nave and Dr. A. Fitch). These trials served usefully as a means of standardising the experimental procedures (such as controlled cement mixing, and specimen transfer). Preliminary powder diffraction patterns are given in fig.1 for hydrating Portland cement and for silicon powder which illustrate the time resolution of the experiment.

(b) Energy Dispersive PXRD Trials

The experimental arrangement for the EDD trials of summer 1986 is illustrated in fig.2. The main experimental conditions are listed below:

Beam size at specimen (defining slit imposed by trial goniometer)		: 0.1 × 0.3 mm
Pre-collimation anti-scatter slits		: 0.1 mm wide
Detector collimators:	1 pair Mo-flats	: 50 cm long × 0.1 mm separation
	Specimen angle	: θ = 5°,10°,15°
	Specimen rotation	: 2 revs per minute
	Detector angle	: 2θ = 10°,20°,30°

In view of the complexity of intensity relationships between peaks spread across an EDD pattern, we decided that we should start by collecting reference patterns on NBS standard powders. This pre-exercise was aimed at establishing the $I_{peak}(E,2\theta,\mu)$ relationships which would act as calibrtion functions for extracting intensity data for various energy, 2θ-angle, and sample absorption parameters. Thus reference patterns were obtained in transmission for five NBS standards; CeO_2, ZnO, TiO_2, Cr_2O_4 and Al_2O_3 at

three detector angles 2θ = 10°, 20° and 30°. A selection of these patterns for CeO_2 is given in fig.3.

The cement-hydration trials were performed with selected Portland cement and tricalcium silicate (C_3S), which is the major constituent of Portland cement. The specimens were supplied by Blue Circle. The cement hydration was initiated by mixing the cement and water in the appropriate ratio in a nitrogen atmosphere for three minutes. The nitrogen atmosphere was necessary in order to combat the reaction of the alkalls in the reaction mixture with carbon dioxide in the air to form calcium carbonate. The diffractometer sample holder was filled with the mix and the top of the sample smoothed with a glass slide then covered to prevent rapid evaporation of water from the sample. The data acquisition program was run in "automatic" mode which cycles over the initialisation, collection, comparison with the ion chamber, and writing the file for each required collection period. The limit of collection was set by the LSI computer's disc (4096 blocks) which can store 48 cycles each of 85 blocks. For example, one could collect for 4 hours at 5 minutes per cycle or 8 hours at 10 minutes per cycle. Once the disc became full the data had to be transferred to another storage device before continuing the next data collection. An example of a time-resolved diffraction output is shown in fig.4.

The counting statistics associated with these patterns were limited by the inadequate slit geometry that was available for these trials. It is expected that order of magnitude improvements in peak:background ratios and time resolution would be obtained with a properly designed and carefully built EDD experiment. Nevertheless fig.4 clearly demonstrates the feasibility of the EDD method for monitoring cement hydration and similar reactions. In the case of fig.4, the main $Ca(OH)_2$ peak grows over 22 hours whlle the C_3S peaks diminish in accordance with expectation.

The long-term aims of this study are to establish and explain the variations with time of all the various hydrated phases, and to relate these to what is known about the structural chemistry and chemlcal substitutions made to the cement material.

PROJECT 2 High Pressure studies of Industrially Relevant Materials Uslng High Energy Synchrotron Radiation

by D. Hausermann, Department of Physics, King's College, London, UK

Preliminary Energy Dispersive Powder X-ray Dlffraction work was conducted on station 9.7 during three weeks of summer in 1986. All the high pressure results described in this section were obtained during that period.

All measurements were made using the EDD method in transmission at low Bragg angles (4° to 5°) and thus made full use of the advantages offered by the high energy radiation from the Wiggler; that is, optimum resolution[8] and a simple geometry in which sample positioning is not critical[9].

A low cost diffractometer was custom-built to operate at these small angles of diffraction and give the fine collimation required to achieve a final resolution with a negligible geometric contributlon. The diffractometer, used for all the measurements, is shown in flg.5.

(a) High Pressure Studies

A Drickamer-type high pressure cell (fig.5) was used to measure the compressibility of TiB_2. In such a cell, pressure is applied by tungsten carbide anvils to a mixture of sample and pressure calibrant surrounded by several millimetres of pressure-transmitting material, hence the need for high energy X-rays. Further, as the spectra consist of reflectlons from the sample and calibrant the wide dynamic range of energies produced by the Wiggler is an extremely important feature of the technique. In the measurements on TiB_2 it was possible to use four or five copper reflections to determine the pressure and six to eight reflections from TiB_2 to calculate the changes in both the a and c lattice parameters (TiB_2 has a hexagonal structure with space group P6/mmm). Two spectra obtalned at 25.2 and 123.5 kbar are shown in fig.6. The spectra were analysed by fitting a sum of Gaussians and a polynomial background to parts of the diffraction patterns. Very good signal-to-noise ratios and statistics ensured an accuracy of 2 to 3 parts ln 10^4 in calculations of d/d_o, giving a corresponding accuracy in the pressure calibration of typically 0.5% (on the copper scale) between 0 and 130 kbar. From the variation of V/V_o with pressure, the bulk modulus K_o of TiB_2 was determined as 4.1 (± 0.2) Mbar. This shows TiB_2 to be one of the least compressible materials known (diamond has $K_o \sim 4.4$ Mbar) and hence a

potentially useful industrial material.

(b) EDD and Lattice Parameter Measurements

EDD from thick samples in transmission has the potential of being a simple and accurate technique for lattice parameter measurements. Spectra from LiF, Al, Ti, Cu, Ag, and mixtures of all these with silicon (NBS SRM 640a), silicon itself, Al_2O_3, Cr_2O_3, TiO_2, CeO_2 and ZnO (NBS SRMs 674) were collected. The spectra obtained from these five compounds are shown in fig.7 together with an example of the obtained quality of fit.

These data will be used to determine the accuracy of lattice parameter measurements using EDD. Although Fukimachi et al[3] claimed 2 parts in 10^4, a closer examination of their data shows a range of error more than ten times larger[8]. Further work, comparing reflection and transmission and testing the expressions for axial divergence and sample absorption effects[2] is also planned.

(c) EDD and Intensity Measurements

The high collimation achievable with synchrotron radiation has one notable drawback, that of small effective sample volumes, typically less than 0.1 mm^3. With a smallest grain size of 2 μm, this represents a sample containing only a few million crystallites, few of which satisfy the conditions for reflection. Early calculations based on the data collection so far indicate that rotation of the sample about the beam axis should reduce this effect from the present 10-20% to 1% or less.

PROJECT 3 An Initial Study of the Precipitation of n-Alkanes from Solution Using Energy Dispersive X-ray Diffraction

by J.N. Sherwood, S. Doyle and K.J. Roberts
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 XL

(a) Introduction

Hydrocarbon petroleum products are usually blends of several distillate fractions, with characteristic distributions of alkane chain length. Increasing demands for low and high molecular weight hydrocarbons, for aircraft fuel and industrial feedstock respectively, have led oil companies to extract more and more fractions from crude distillates, the result being narrower molecular weight distributions in the medium weight fraction which is used in diesel oils. The narrower distribution of molecular weights has a deleterious effect on the crystallisation of the components, leading to problems for the diesel user.

Figure 8 shows two typical curves; the first, designated BBD (broad boiling distillate), has a wide molecular weight distribution with a mean around C24, while the NBD (narrow boiling distillate) has a mean at about C20. Both these mixtures have significantly different crystallisation behaviour. In the case of the BBD, supersaturation by cooling results in the formation of large numbers of nuclei of the heavier alkanes followed by rapid crystallisation of the bulk wax on the nuclei. The result is large numbers of small crystals. In the case of NBD mixtures, the freezing range is narrow, supersaturation build-up is slow and co-crystallisation of close homologues is likely. This results in nucleation and growth occurring simultaneously with the consequent production of a small number of large crystals. The crystal growth mechanism produces crystals with plate-like habit and the consequences of this process for diesel fuels is that during cold weather fuel filters become blocked, the diesel is prvented from reaching the combustion chamber and engine failure results.

There are two possible ways of dealing with the problem. Firstly the nucleation rate in NBD mixtures could be increased, the result being a larger number of crystallites which must therefore attain smaller sizes.

Secondly it may be possible to devise habit modifiers which cause the crystals to grow in preferred directions, giving rise to needle-like habits rather than plates. This would substantially decrease the likelihood of fuel line blockage.

Since the major component of NBD mixtures is C20 (n-eicosane), initial studies of the crystallisation behaviour of fuel oils concentrated on the crystallisation of this alkane from solution, both in the presence and absence of its close homologues C18,19,21 and C22. To this end energy dispersive X-ray diffraction was considered as a useful probe of the crystallisation process. One of the advantages of using synchrotron radiation is that it allows real time study of phenomena such as crystallisation and thus (ED) in principle should allow us to identify each component of a hydrocarbon mixture as it crystailises, and should therefore allow the observation of co-crystallisation and mixed crystals.

(b) Experiment and Initial Results

The experiment was conducted on sataion 9.7 at the SRS. The incident beam consisted of polychromatic radiation and the diffraction pattern was recorded via an energy dispersive detector. A small cell was constructed which allowed the beam to pass through about 12 mm of solution. The solution was cooled and the diffraction pattern recorded at various points at which the beam passes through the solution as shown in fig.9.

Initial results, while not exhaustive, confirm that EDD is capable of following the crystallisation process in solution. An extremely useful addition to this experiment would be the ability to make simultaneous light scattering measurements during the cooling cycle, since in this way the size of the diffracting nuclei could be measured, providing a unique insight into precipittion processes. The detailed analysis of this material and more complex mixtures is the next step in this project, after the HBL is installed at Daresbury.

CONCLUSIONS AND RECOMMENDATION

The short trial period has demonstrated the viability and usefulness of Synchrotron EDD as a prime method for obtaining time-resolved powder x-ray diffraction data. It would have been impossible to have accommodated these experiments within the 9.1 programme. We summarise the progress as follows:

Project 1: This showed that kinetic studies can be performed using Synchrotron EDD, including the early hydration of cement. The main problems were the relatively low beam intensity through the available equipment rather than the detector at this stage, though the indication are that the eventual signal-to-noise ratios should be good. With the planned future design incorporating optimised soller slits we should be able to improve significantly both signal-to-noise ratios and data collection speed.

Project 2: This work demonstrated the viability of Synchrotron EDD for high pressure studies (up to 250 kbar) on TiB_2. This resulted in accuracies in d/d_0 of a few parts in 10^4, and ~ 0.5% in pressure. The trials also outlined the problems to be dealt with in improving lattice parameter measurements (currently around parts per 10^3) and intensity measurements that would be required for Rietveld refinements.

Project 3: The experiment showed that crystallisation of alkanes from fuel oil with decreasing temperature can be monitored with EDD. The main problems experience during these trials were low signal throughput and poor cryostat control. Both of these features could be improved enabling actual kinetics of crystallisation to be determined.

The main recommendation now is for a permanent EDD facility to be designed, built and installed in 9.7. The concept of fixed 2θ-angle EDD fits in naturally with the research interests in other work involving high temperature, cryostat and diamond anvil high pressure cells. The clear preference is to have a system which is simple and stable in order to minimise set-up procedures and maximise beam time. The eventual system will probably utilise a vertical plane goniometer for the detector and soller slits, and simple interchangeable defining slits. A versatile XYZ-stage would be

suitable for supporting specimen holders and any environmental cells built by individual users. The main requirements would be simplicity and freedom of access to the specimen area.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. A. Fitch for his collaborations in the preliminary studies of cement hydration using the linear detector. Discussions and advice from Professors C.R.A. Catlow and M. Hart are also acknowledged.

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Fig.1. Preliminary powder diffraction data collected using a trial p.s.d. set up on station 9.1. The cement hydration sequence covers the first hours of hydration: these sequences have now been more fully studied with the Energy Dispersive arrangement (fig.4). The silicon powder spectra illustrate the time resolution of the p.s.d. The horizontal scale is in p.s.d. channels and corresponds to a 2θ-range of ~ 7° centred on ~ 19°.

Fig.2. Simplified diagram illustrating the experimental set-up used during the EDD trials on station 9.7.

Fig.3. A set of Energy Dispersive Powder patterns of cerium oxide collected in reflection on station 9.7. Three detector (2θ) angles are used, (a) 2θ = 10°, (b) 2θ = 20°, (c) 2θ = 30°. A typical laboratory diffractometer output is shown in (d). Note the considerable change in pattern for different 2θ settings and laboratory (monochromatic) output.

Fig.4. Time-resolved EDD pattern obtained on station 9.7 during the 1986 trials. The calcium hydroxide peak (marked) grow with time. All other peaks are C_3S and are seen to decrease with time. The traces are separated by 3-6 hours and each pattern took 10 minutes to collect.

Fig.5. Photograph of the Energy Dispersive-Diffractometer - High Pressure Cell arrangement used in the Synchrotron EDD trial in 1986. The system operates at a fixed angle of diffraction between 6° and 10°, and the vertical divergence of the diffracted beam is controlled by two 50 cm molybdenum parallels (to the left of the pressure cell).

Fig.6. Energy Dispersive spectra from TiB_2 at 2θ = 9°, the data collection time was 45 minutes. Two spectra are shown, one at 25.2 kbar the other at 123.5 kbar. The SRS was operating at 2 GeV and the current varied from 300 to 100 mA. The pressure was determined from the Cu peaks (shown in black), while the LiF peaks were produced by the packing. The peaks labelled 'hkl' are due to TiB_2.

Fig.7. Examples of EDD spectra obtained in transmission on five NBS standards. Fig. (c) also shows an expanded view of ZnO showing the difference in the data from a Gaussian fit.

Fig.8. Molecular weight distributions in crude distillates: BBD, broad boiling distillate, NBD, narrow boiling distillate.

Fig.9. Crystallisation of n-eicosane from dodecane as a function of temperature. The spectra were collected using the Energy Dispersive mode on station 9.7. The sharp edge is believed to be molybdenum absorption.

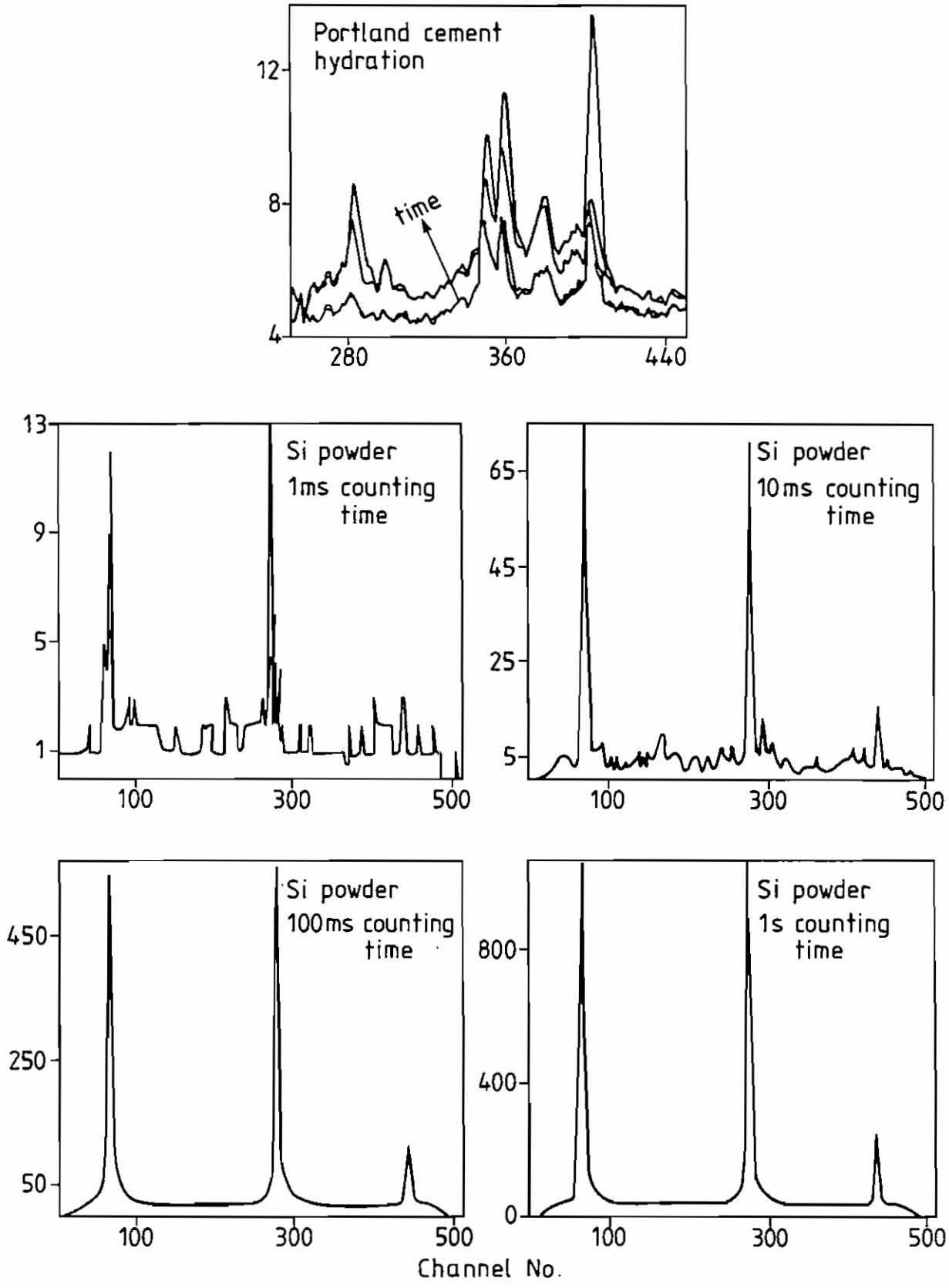
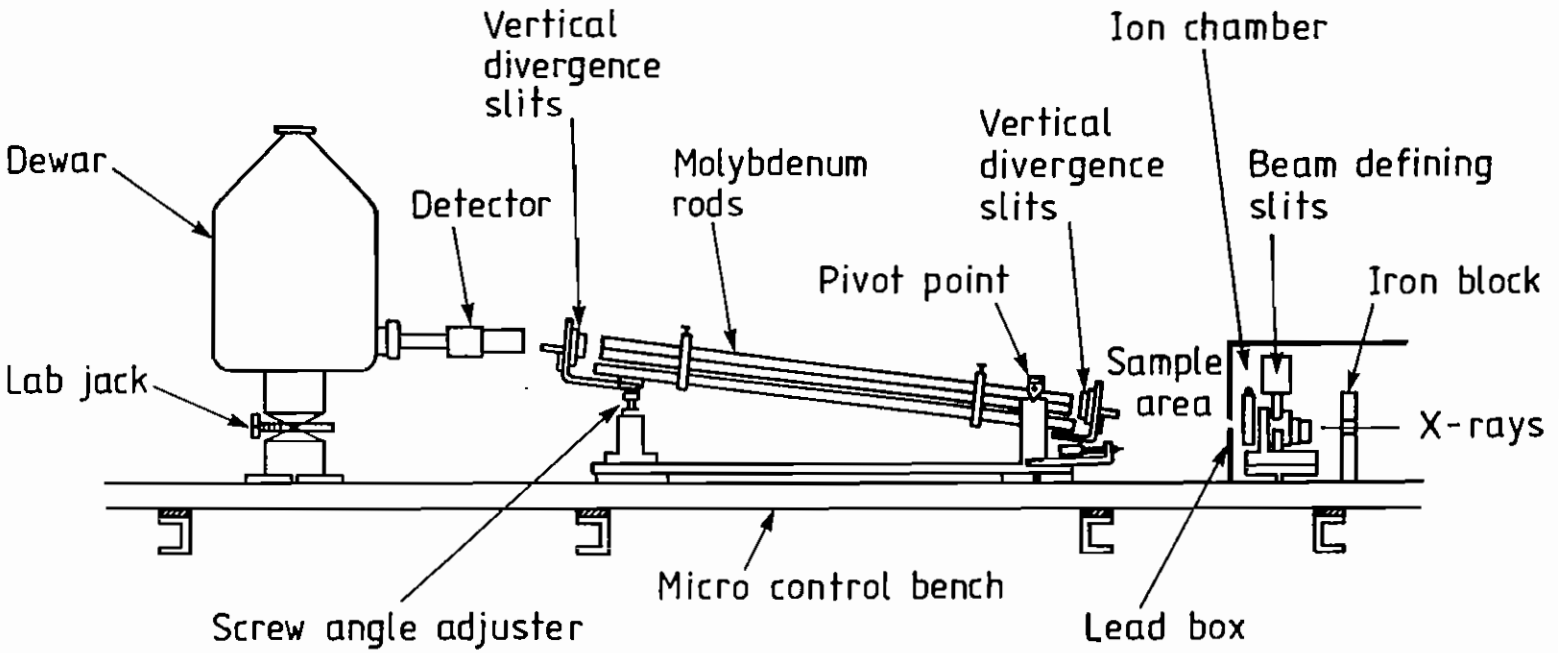

Portland cement hydration
time
12
8
4
280
360
440
Si powder
1ms counting time
13
9
5
1
100
300
500
Si powder
10ms counting time
65
45
25
5
100
300
500
Si powder
100ms counting time
450
250
50
100
300
500
Si powder
1s counting time
800
400
0
100
300
500
Channel No.

Fig. 1


Vertical
divergence
slits
Ion chamber
Dewar
Detector
Molybdenum
rods
Vertical
divergence
slits
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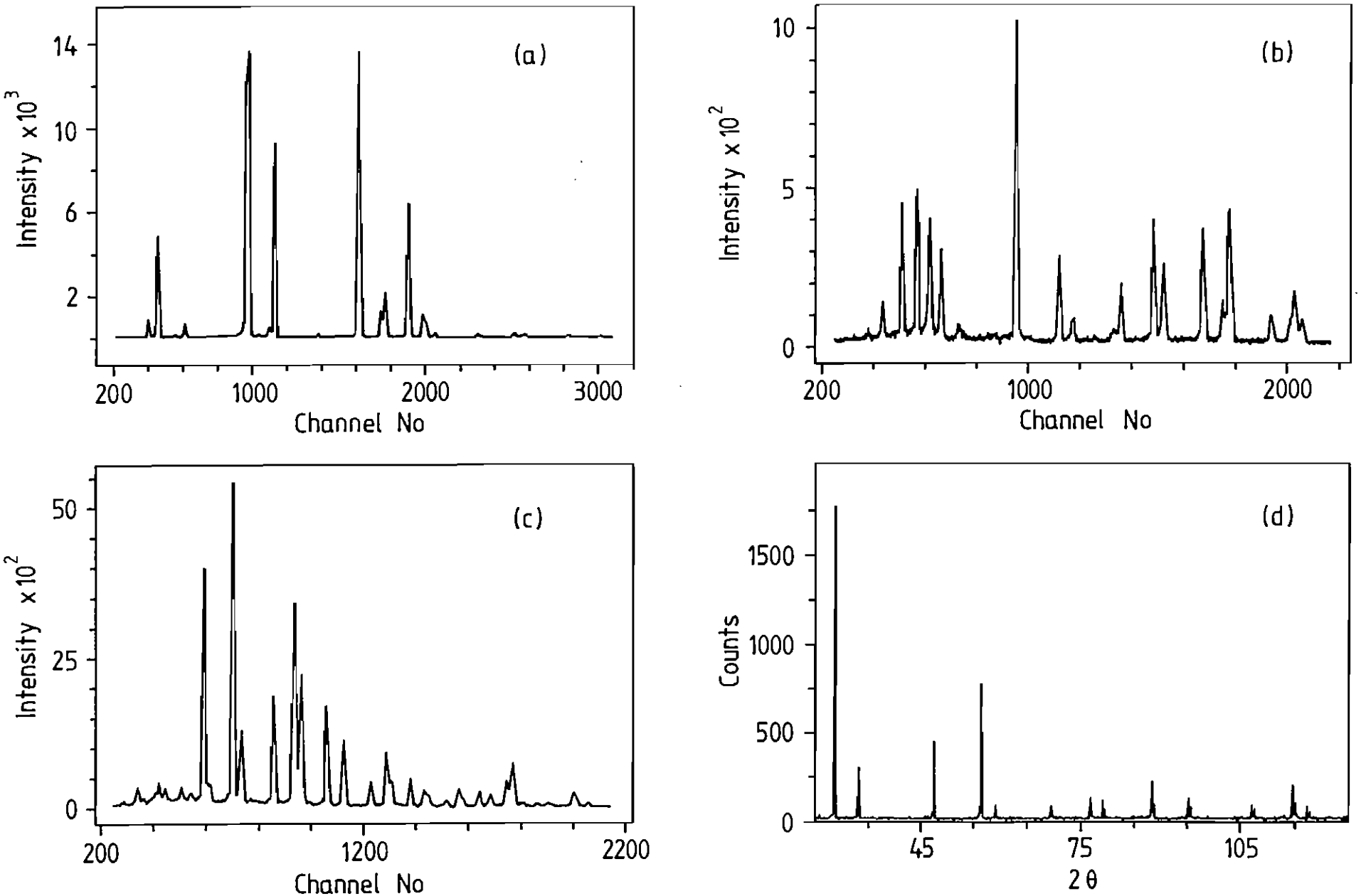
Sample
area
X-rays
Micro control bench
Screw angle adjuster
Lead box

Fig. 2


(a)
Intensity x 10^3
14
10
6
2
200
1000
2000
3000
Channel No
(b)
Intensity x 10^2
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5
0
200
1000
2000
Channel No
(c)
Intensity x 10^2
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Channel No
(d)
Counts
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1000
500
0
45
75
105
2θ

Fig. 3

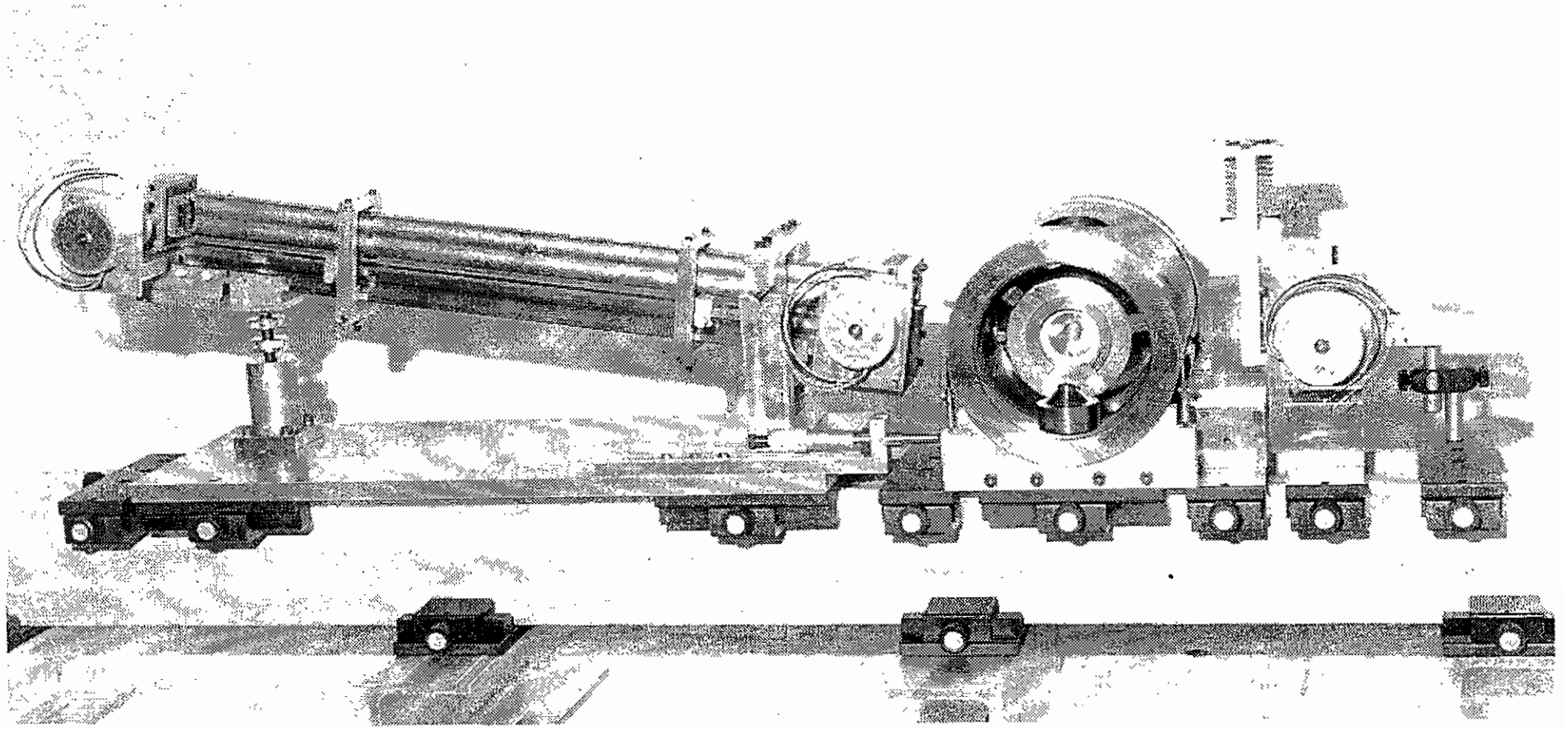


Fig. 5

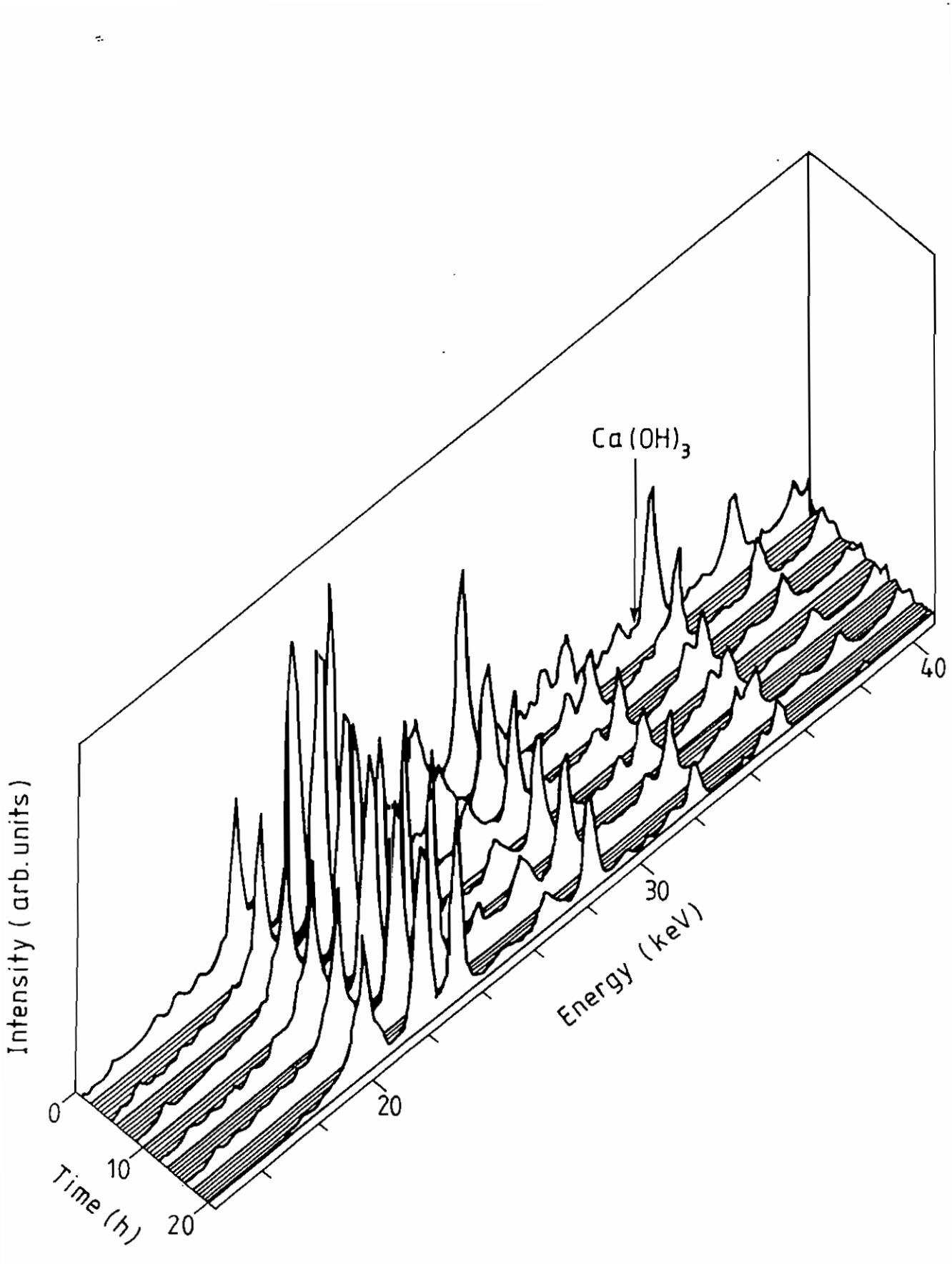
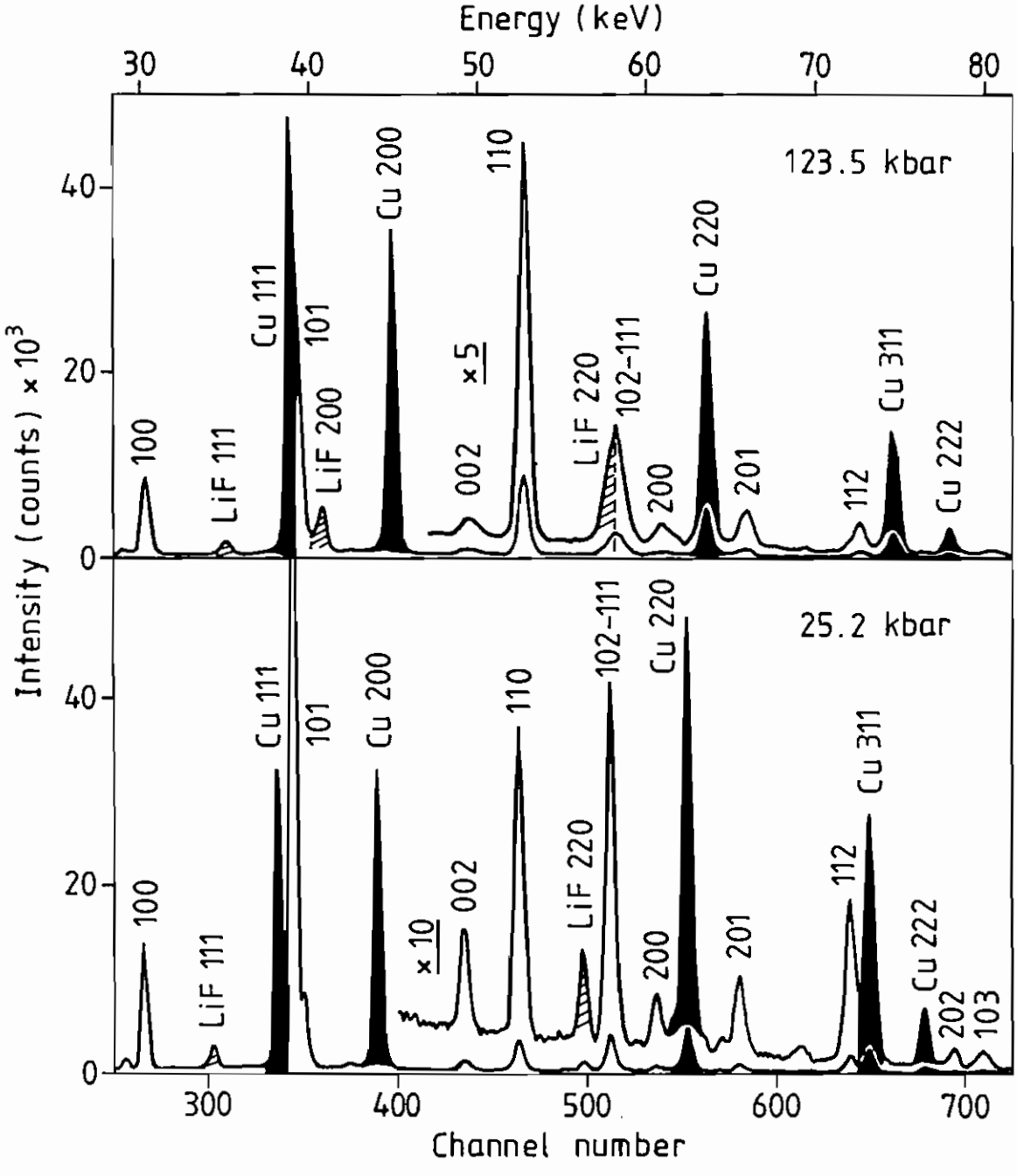


Fig. 4


Energy (keV)
30
40
50
60
70
80
123.5 kbar
25.2 kbar
Intensity (counts) x 10^3
0
20
40
100
LiF 111
Cu 111
101
LiF 200
Cu 200
002
×5
110
LiF 220
102-111
200
Cu 220
201
112
Cu 311
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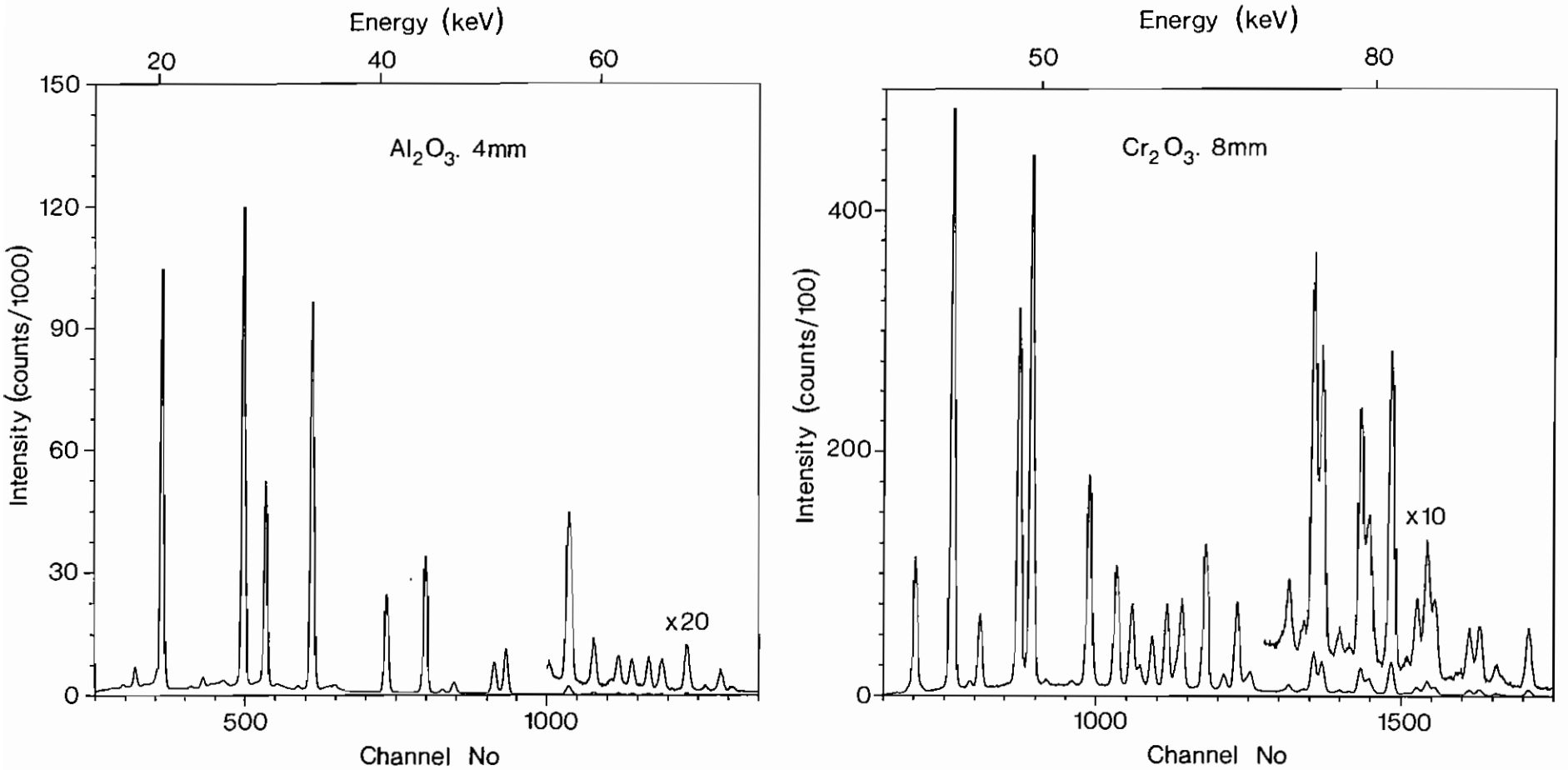
202
103
300
400
500
600
700
Channel number

Fig.6


Energy (keV)
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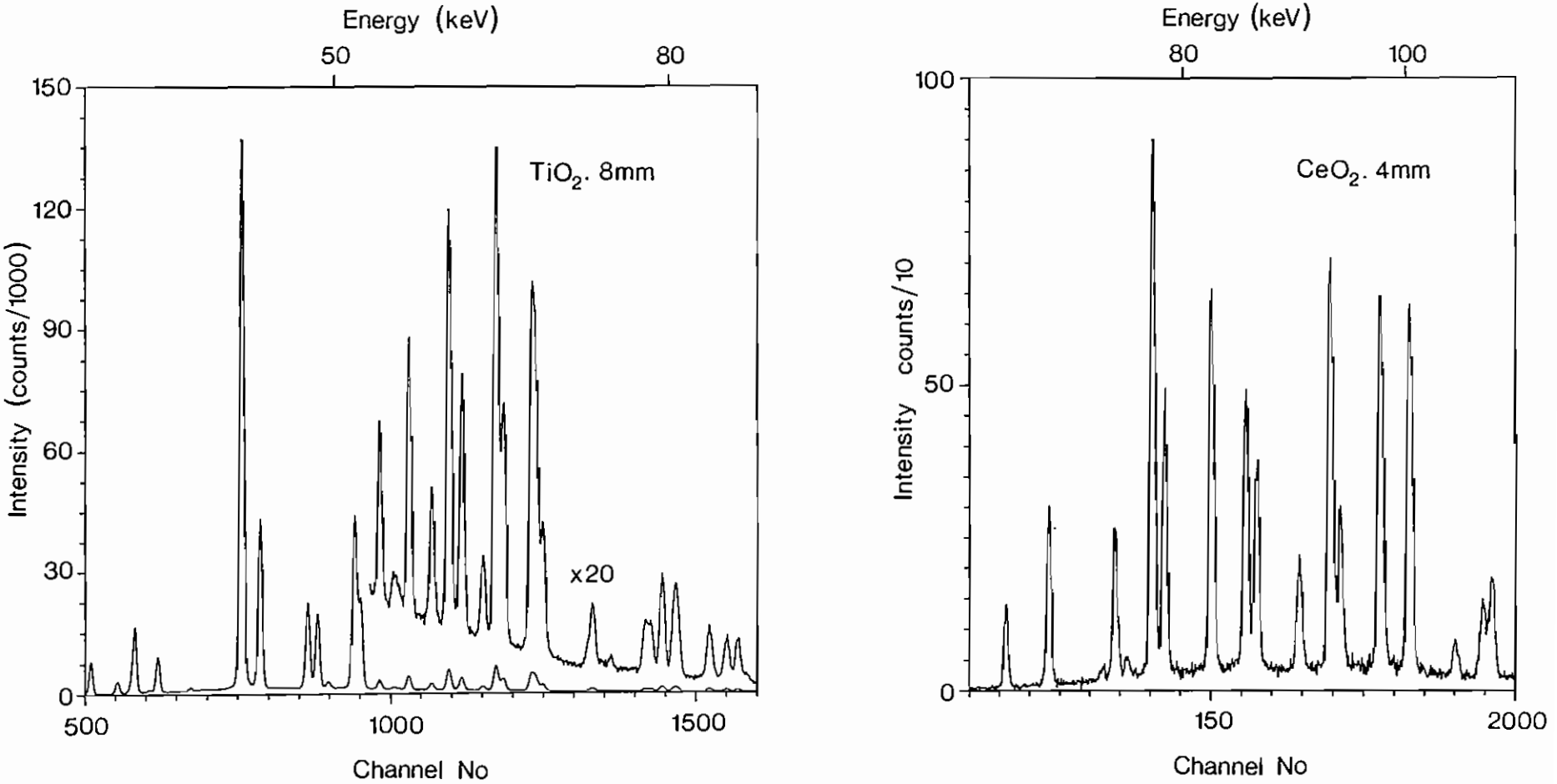
40
60
150
120
90
60
30
0
Al_2O_3. 4mm
x20
Intensity (counts/1000)
500
1000
Channel No
Energy (keV)
50
80
400
200
0
Cr_2O_3. 8mm
x10
Intensity (counts/100)
1000
1500
Channel No

Fig 7 (a)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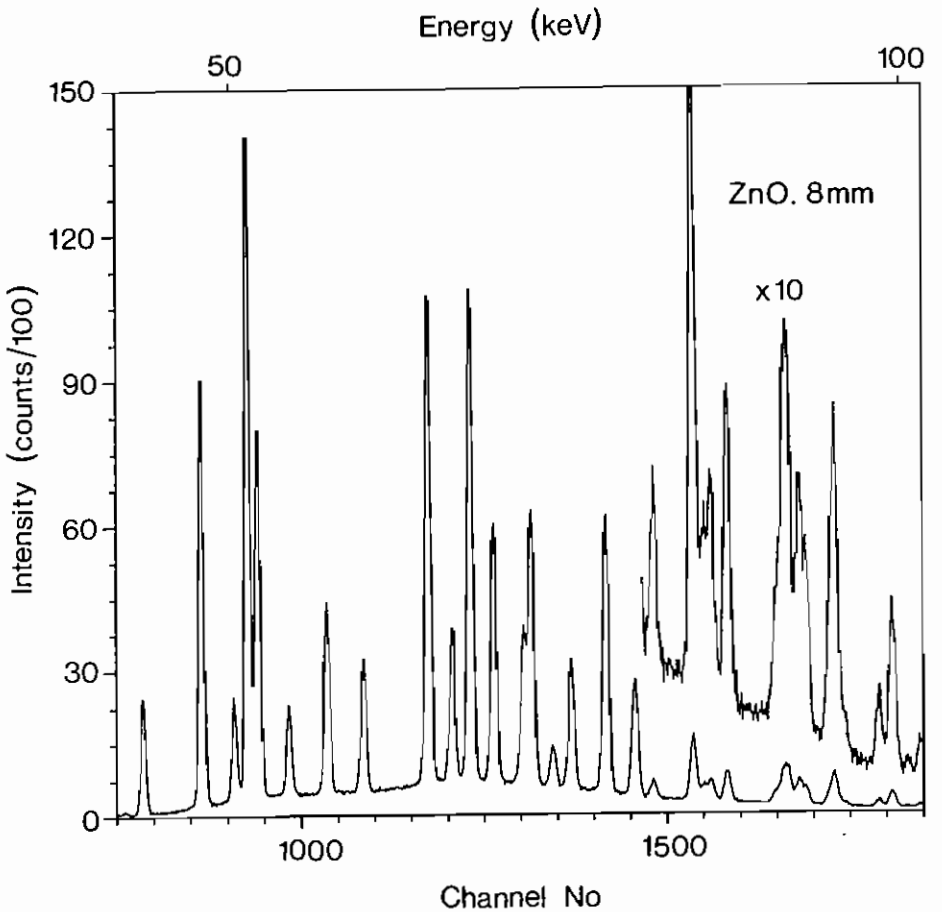
80
150
120
90
60
30
0
Intensity (counts/1000)
TiO_2. 8mm
x20
500
1000
1500
Channel No
Energy (keV)
80
100
100
50
0
Intensity counts/10
CeO_2. 4mm
150
2000
Channel No

Fig 7(b)


Energy (keV)
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100
150
120
90
60
30
0
Intensity (counts/100)
ZnO. 8mm
x10
1000
1500
Channel No

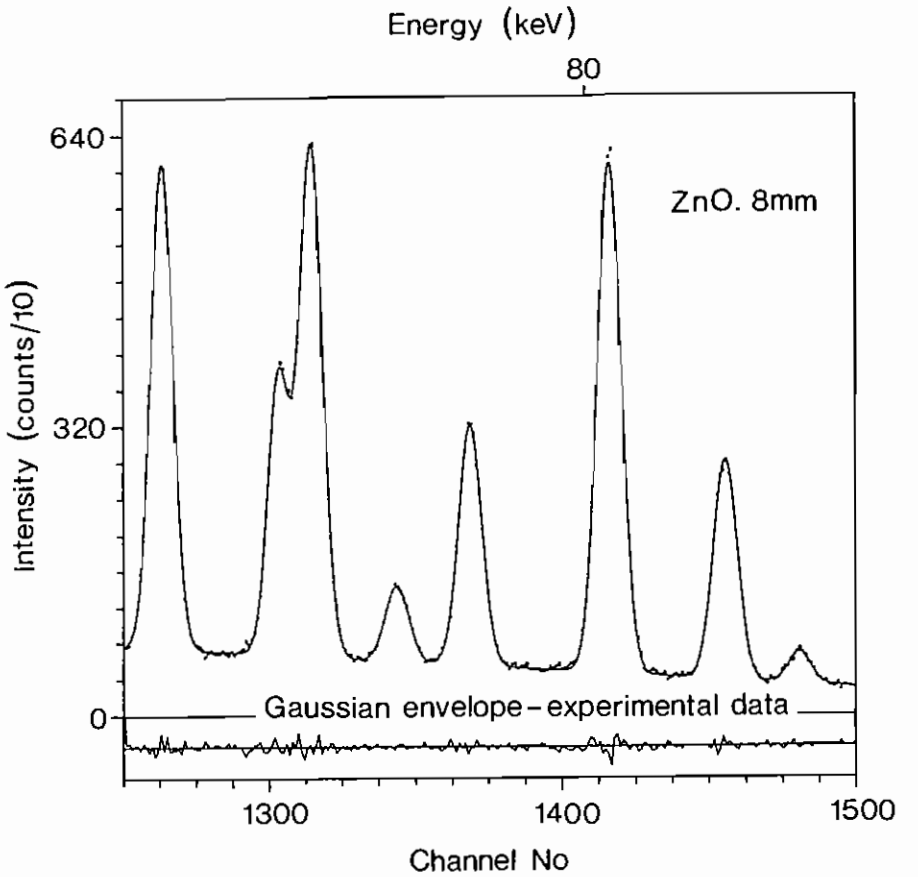
Energy (keV)
80
640
320
0
Intensity (counts/10)
ZnO. 8mm
Gaussian envelope - experimental data
1300
1400
1500
Channel No

Fig 7(c)

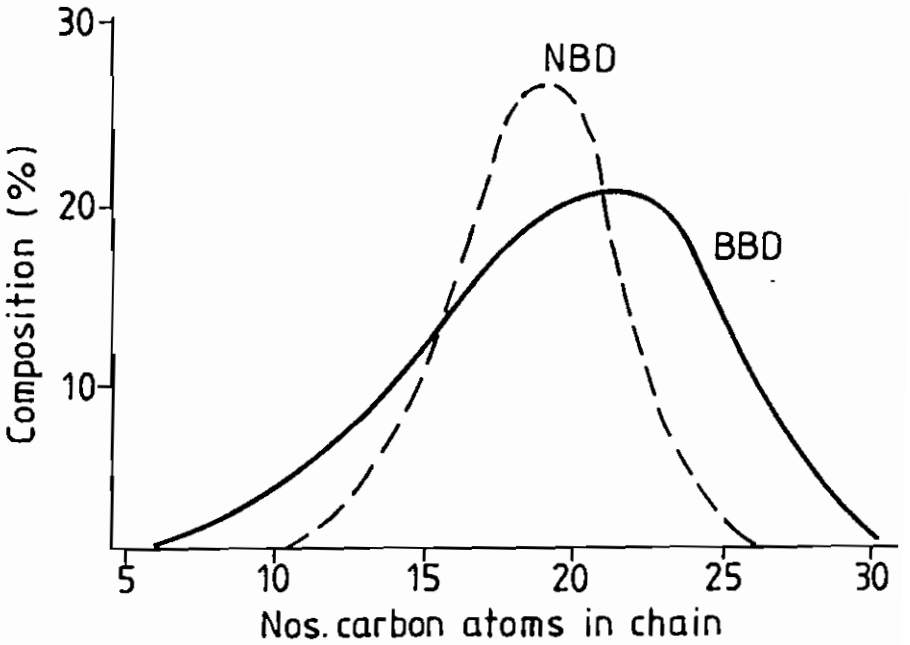
30
20
10
Composition (%)
NBD
BBD
5
10
15
20
25
30
Nos. carbon atoms in chain

Fig. 8

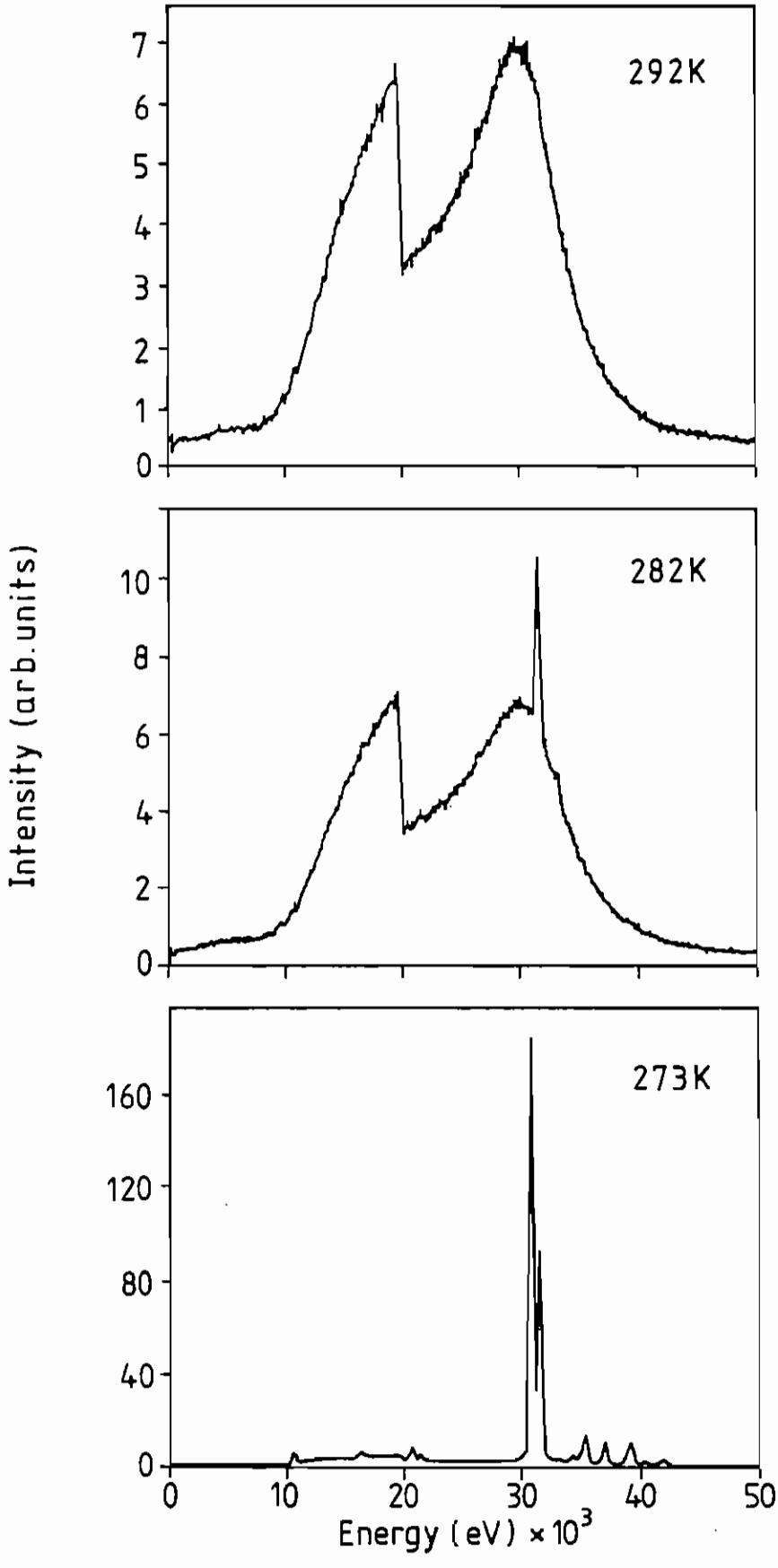
292K
282K
273K
Intensity (arb.units)
Energy (eV) × 10³
0
10
20
30
40
50

Fig. 9