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DL/SCI/TM76E

A PROPOSAL FOR STATION 16.4 TO BECOME A CONSORTIUM-LED ENERGY-DISPERSIVE DIFFRACTION STATION FOR HIGH PRESSURE AND KINETICS STUDIES

by

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PREFACE

This proposal was endorsed by Daresbury Laboratory and approved by the SRFC in December 1990, and is now going to be implemented: this action will be able to draw on a consortium of experienced workers in synchrotron radiation and high pressure applications (a list is included) who will be able to help and advise in acquiring the technology required for this project.

ABSTRACT

The proposal can be summarised as follows:

1. The station would be run in energy-dispersive mode with minimal or zero pre-sample X-ray optics (i.e. no monochromator/focussing optics);
2. The station would house state-of-the-art diamond anvil cell (DAC) and multi-anvil press (MAP) high pressure devices;
3. The project would, in particular, concentrate on developing combined high pressure plus high/low temperature devices;
4. The station would also house a state-of-the-art system for studying the kinetics of rapid transformations;
5. The overall project would be consortium-led in collaboration with Daresbury Laboratory (DL).

SUMMARY OF THE MAIN ARGUMENTS FOR THE PROPOSAL

1. The proposed facility could not be developed on any other DL beamline.

2. In particular the proposed facility would rely on:
   a) the increased intensity at high X-ray photon energies from the new wiggler;
   b) the accesible space, within the station, around the 16.4 beam port.

3. The station would feed scientific endeavour in the areas of materials science and minerals physics: these are subject areas of importance recognised by research councils in UK and elsewhere (Japan, USA).

4. The SRFC has already invested considerable financial resources into the high pressure and kinetics areas(1), yet this very same community is in effect starved of appropriate beam-time as a consequence of station-sharing (station 9.7) with one of the highest over-bidding ratios on the SRS.

5. The driving force behind this proposal would be an impressive consortium of academic users in collaboration with DL. A similar consortium (with many of the same academics) was responsible for activating the present station 9.7 which then become one of the most successful and over-bid stations.

6. An essential ingredient of this proposal is the inclusion of several highly-rated mineral-geologists within the consortium. They would seek major NERC-funding for

   a) a DAC high pressure/laser heating system;
   b) an appropriate multi-anvil press (MAP)

   to be housed in station 16.4. There is currently no MAP-facility planned on other European synchrotrons, including the ESRF. No doubt DAC- and MAP-support would have to involve high level discussions between SERC and NERC to agree on a suitable quid pro quo for both communities.

7. The relative simplicity of the ED-optics and inclusion of the NERC element would greatly reduce the SRFC- and DL- cost component of the whole operation.

MAIN SCIENTIFIC OBJECTIVES

It should be first noted that the following arguments are based on the current general scientific scene: by the time we would use station 16.4, this scene would inevitably have shifted, and with it our precise directions of study. The scientific endeavours divide into two broad areas:

(a) High Pressure/Temperature Studies

X-ray diffraction is the primary experimental method for the determination of equations of state and the characterisation of structural phase transitions at ultra-high pressures. Such fundamental information on physical and chemical properties is essential within materials science generally and also for advancing our understanding of the nature of the interiors of the Earth and other planets. Pressures close to 5 Mbar (500 GPa) have been reported with the diamond anvil cell (DAC) and powder diffraction measurements have been performed up to ~2 Mbar. Characteristic of these experiments at ultra-high pressure is the significant decrease in the volume of sample that can be confined at the peak pressure (~0.1 pl or 10^{-7} mm^3) and the large pressure gradients generated across the sample perpendicular to the load axis. Use of an incident X-ray beam that is collimated to widths in the microns size range is therefore required to provide the necessary spatial resolution at the sample. Also the oxides and silicates (that form the bulk of the Earth's lower mantle) and molecular solids (which are important for planetary research) have low atomic scattering factors ($Z<14$) for X-rays. Hence the diffracted intensities are intrinsically weak from this class of materials, especially from low-symmetry structures, and this adds to the difficulty of detection of diffracted radiation from pico-litre sample volumes.

A synchrotron is the only X-ray source with sufficient intensity and collimation to permit the ultimate design required for such experiments, and energy-dispersive diffraction is the most suitable method for rapid acquisition of basic phase information. Part and parcel of an SRS-based ultra-high pressure powder programme would be complementary single crystal studies at lower pressures (<200 kbar) by white beam (Laue) and monochromatic (4-circle) diffractometry using both synchrotron(2) and laboratory(3) sources.

As stated, a significant section of the high pressure/temperature studies would be pitched at the interface of minerals physics and materials science. Here we are primarily thinking of:
1) model chemical systems (e.g. $MgSiO_3$);
2) more complex systems representative of the Earth's mantle (e.g. Ca-, Na-, K-bearing aluminosilicates);
3) solid molecular systems(4) (i.e. condensed gases) typical of larger planetary interiors.

Suitable samples, particularly those of more complex chemistry, can be synthesised:

1) off-beam using the MAP's at UC, Bristol;
2) by in-situ direct laser heating of charges within DAC's;
3) in-situ using an on-beam MAP.

The DAC cells would provide the front line approach, identifying stability regimes, equations of state (at ambient temperatures), determining melting regimes. DAC experiments at combined high pressure/temperature are then envisaged to determine second-derivative effects on unit cell volumes (i.e. variation of thermal expansion with pressure, compressibility with temperature) for determining phase stabilities. Combined high pressure/temperature regimes in DAC's by laser flash heating (up to 3000°C and 400 kbar) would be developed by the experienced Oxford and Leicester groups respectively. The MAP would be used for work requiring larger sample volumes (several mm^3), temperature stability above 1500°C, and reduced temperature and pressure gradients without the use of a near-hydrostatic pressure medium. These characteristics have enabled a variety of important and innovative high pressure/temperature studies to be carried out, primarily in Japan, including:

1) rapid in-situ phase equilibria determinations;
2) equations of state;
3) kinetics of phase transitions in polycrystalline aggregates;
4) viscosity of silicate liquids at high pressure by monitoring a falling sphere with an X-ray shadow graph.

In addition to the mineral aspects there is the great need for high pressure/temperature measurements in materials science. The range of studies is too diverse and extensive to be summarised here: topics include super-hard materials, superconductors, synthetic minerals, polytype structues, solid lubricants, catalysts etc: Appendix I lists the relevant researchers (and topics) who have expressed their desire to be involved in this part of the programme.

(b) Kinetics Studies

This field overlaps partly with (a) since the kinetics of phase transitions and in-situ synthesis is also an important aspect of MAP-work. Monochromatic techniques currently available at the SRS (including the new imaging plate system) will never compete with ED-diffraction for rapid data collection on transformations and chemical reactions(5), or indeed for small powder samples required for pressures >200 kbar. The experiences gained with station 9.7 have already given valuable indications of what can be achieved here. In terms of rapid data capture the 9.7 ED-system has shown(5c) that sub-second diffraction patterns can be routinely collected and, in certain cases, analysed to yield quantitative kinetic data (transformation rates, Arrhenius plots, activation energies) on the transformation processes.

The other notable feature of ED-diffraction, that is not always so fully appreciated, is the relative ease of subjecting the materials of study to the chosen conditions of temperature/pressure/gas-environment due to the fixed scattering angle (2θ) and consequently restricted entrance/exit X-ray window regions. A number of novel high temperature and in-situ hydration/synthesis cells have been designed jointly by DL and Birkbeck College. These have been well exploited in dynamic studies on station 9.7 using 1 sec. to 3 min. pattern collection times. These have produced a number of notable "firsts" including the only full dynamic study(5b) on the synthesis of monoclinic/tetragonal zirconia; the early hydration of portland cements(5a) and rapid hydration of high alumina cement systems(5e,f) which show lattice parameter changes on a 10-20 second time scale; the in-situ hydrothermal synthesis of basic zeolites(5f). There is clearly enormous scope here for innovative SRS-based studies on the synthesis and in-service performance of materials generally. The increased 9.7 wiggler flux at high energies has already been a key factor in many of these studies allowing in some cases the sample sizes to approach those commonly used in neutron studies (i.e. diameters of ~10 mm). Increased penetration on 16.4 at high energies would enable more ambitious studies such as in-situ synthesis in autoclave cells etc to be undertaken. We also see increased oppurtunities for industrial (repayment) work in this area.

MAIN TECHNICAL FEATURES AND ADVANTAGES OF A 16.4 SYSTEM

(a) High Pressure Systems

The main technically advantageous features of station 16.4 would be the increased flux above ~45 keV (Fig.2c) and useful available floor space (Fig.1). The latter feature is particularly pertinent in the case of the high pressure part of the proposal. For example, the space in station 9.7 is so restrictive as to make the high pressure programme quite impossible. The plans for the proposed DAC-system (Fig.1) are for diffraction in the vertical or horizontal plane with laser heating mount and laser-ruby-callibration systems. The laser systems should not be casually moved in a serious dedicated high pressure research programme and thus the station plan (Fig.1) is to accomodate these features on a semi-permanent basis. Similarly it would be quite unacceptable to have to move the MAP set-up in and out of the station on mode changeovers. There is however a clear solution to thess problems: MAP-systems are now being designed on a significantly smaller scale to those currently used in Japan. For example the "Walker" model MAP reduces the load cell to approximately one cubic foot, and the essential load frame to floor space of approximately one square metre. Prof.D.Walker (Lamont) is interested in collaborating with the UK-MAP-consortium (Henderson-Manchester; Woods-Bristol; Jones-UC, London) to design his MAP around the 16.4 configuration. This could be fitted in effect in tandem with the DAC/kinetics system, with the load frame straddling the continuation beam-pipe to station 16.3 (Fig.1). Together with the detector systems this would result in a total length of nearly 4 m for the combined MAP and DAC/kinetics set-up. While this combination fits easily breadth-wise, it is too long for easy operation in the currently planned station area and so an excavation hole of ~1 metre into the existing concrete outer wall would be the preferred option as indicated.

The increased flux at higher energy is particularly relevant for both DAC- and MAP-work because of the larger sample sizes involved and, consequently, increased X-ray absorption. To illustrate this Fig.3a,b shows ED-patterns obtained on station 9.7 for MoS_2, a solid lubricant which would be studied on 16.4 under industrial working conditions of combined high pressure and temperature. The DAC and Drickamer high pressure cell (the latter in effect simulates the absorption of a MAP set-up) spectra show markedly the need for an increased intensity above ~50 keV where much information is currently missing.

(b) Kinetics Systems

For rapid (ED-diffraction) data capture studies on materials synthesis and performance, there are many factors which can be optimised: scattering angle 2θ, beam geometry, sample geometry and electronics. One of the most important factors to consider is the resolution/count rate statistics of the technique since this is detector limited. To see this one notes that for ED-diffraction the net relative resolution ΔE/E improves (i.e. decreases) with energy E:

$$\Delta E/E = (k_1/E^2 + k_2/E + k_3)^{1/2}, \qquad \begin{array}{l} k_1,k_2 = \text{detector constants,} \\ k_3 = \text{geometrical factor,} \end{array}$$

which is illustrated in Fig.2a,b. Thus ΔE/E can be improved somewhat by reducing the fixed angle, 2θ, since this will have the effect of shifting a given ED-diffraction pattern to higher energies (Edsinθ = constant). This cannot however be pursued indefinitely because eventually the geometrical factor, k_3, will increase suddenly at low angles (the cotθ effect) and dominate. Buras(7) has shown that for typical cases the optimum 2θ-angle is in the 6-12° range: In fact at the SRS with state-of-the-art detectors, 2θ~8° and d-spacings of 0.5 → 3 Å, the energy range for optimum resolution would be ~30 → 90 keV. Fig.3 illustrates this point using data previously obtained on station 9.7 for MoS_2 under high pressure and during the high temperature synthesis of zirconia: the need for improved intensity in the higher keV range is clear. Fig.2c then gives a prediction as to how the flux from station 16.4 would exceed that of station 9.7 above ~45 keV.

In addition to the improved flux >45keV there are other ways in which we would plan to move rapid ED-diffraction forward on station 16.4. One of these would be to use geometrical integratation around the Debye-Scherrer cone to improve the grain sampling and intensity statistics. We know, from the current image plate work(1e), that grain sampling and preferred orientation problems can be greatly improved in this way. For ED-methods, this would involve a short precision conical collimation system for the diffracted beam. This would typically require a 5cm long conical slit of 10 μm, or alternatively a 20 cm by 1/3-conical slit of 50 μm onto a bank of crystal detectors.

There are yet further avenues, but which are less well defined at the present, for keeping up with developments in detector and beam optics technology; a bank of crystal detectors, analagous to the EXAFS Canberra detector, has already been referred to with regard to conical integration optics. Any improvements in detector performance at high count rates (currengly being developed at DL) will also be exploited. For cases where only the high energy part of the ED-patterns are required, low energy absorbers can be used to effectively improve the useful detector performance; when an improved high <u>and</u> low energy intensity profile is required (e.g. for the synthesis of some materials like autoclaved cements where a wide range of d-spacings is involved) attention would be paid to developments in straight or tapered capillaries(8) to enhance radiation intensities up to 30 keV with an acceptable loss of beam parallelism at low energy. The existing station 9.7 facilities would then logically be used for those rarer cases when only low energies are require required.

(c) General

Fig.1 illustrates the preferred layout. The philosophy would be towards heavy fixed table mounts with the majority of components (particularly the laser systems) remaining permanently fixed in place. The first table activity would alternate between the horizontal DAC and vertical kinetics ED-diffractometers: these two could co-exist easily so that only the specimen cells and ED-detector would need reconfiguration on changeover. The first table activities would in turn alternate with the MAP set-up by means of an extendable beam pipe system. A small excavation into the existing concrete wall would ease the congestion considerably. Approximately equal splits between the 3 modes (DAC, kinetics, MAP) is envisaged with continuous periods (~2 months) on each to minimise change-over and setting up time. The consortium split with regard to development responsibility would be:

1. General infrastructure, front-end, mounts - Daresbury Laboratory

2. Kinetics system - Dr.D.Hausermann, Dr.P.Barnes (Birkbeck).

2. Diamond anvil cell/laser systems - Dr.A.Jephcoat (Oxford), Dr.R.Angel (UC,London), Dr.D.Adams (Leicester).

4. Multi-anvil press - Prof.M.Henderson (Man'), Dr.B.Woods (Bristol), Dr.A.Jones (UC,London).

5. Other high pressure/temperature systems - Prof.W.Sherman (King's), Dr.D.Hausermann (Birk').

FINAL CONCLUSIONS

This proposal is to exploit the increased flux at high energies and conveniently available floor space in station 16.4 to set up a high pressure/temperature and kinetics project in materials/minerals science that would compete for the forseeable future with world leaders in these fields. To do this the project would break new ground at both the political level (i.e. the proposed SERC/NERC link) and the developmental side (multi-anvil press, combined high pressure/temperature cells, novel kinetics set-up etc.). In this document we have concentrated on outlining the general feasibility of the proposal in terms of what is currently known on the world scene in relation to what would be available on station 16.4. If the proposal were accepted we would then wish to make use of the considerable expertise of our "inner consortium" (see D(c) above), initially for making the appropriate grant applications to NERC for the high pressure items (valued at many thousands of pounds), and then also in the design and implementation stages. The eventual concept would be for this station then to serve a large potential user community (see App.I for a list of groups who have already expressed their needs) in the materials science area.

APPENDIX I PRESENT USER GROUP COMMUNITY FOR PROPOSED STATION 16.4

Prof.C.R.A.Catlow et al. The Royal Institution, London.	High pressure studies on ternary ceramics (high Tc superconductors); in-situ kinetic studies on zeolites undergoing activity.
Prof.C.M.B.Henderson, Dr.S.Redfern; Dept. Geology, Manchester University.	DAC high pressure studies on transitions in solid solutions (leucite group, Cu-Zn tungstates) model systems; MAP-work on glass/melt systems, displacive/martensitic/ferroelastic transitions.
Dr.D.M.Adams et al. Dept. Chemistry, Leicester University.	Phase transitions in inorganic solids(9) over T,P-space (hafnia, zirconia, silicate analogues, model systems); spin-parity transitions.
Mr.C.Cousins et al. Dept. Physics, Exeter University.	Complementary studies, using DAC and image plate systems, on methods of measurement of internal strain (Fe_2O_3, quartz, corundum, related oxides).
Prof.W.F.Sherman et al. Dept. Physics, King's College, London.	Studies on structural stability at high pressure and medium temperatures; development of DAC, Drickamer and other high pressure cells.
Dr.B.Wood Dept.Geology, Bristol University.	Investigation into equations os state of Mantle minerals linking seismic data with high pressure unit cell parameters on MAP at 250kbar & 1500°C.
Drs.Barnes/Hausermann, Dept. Crystallography, Birkbeck College, London.	Kinetic studies on dynamic processes (synthesis of ceramics, cements, zeolites); high pressure studies on wide range of industrial materials.
Dr.R.J.Angel et al. Dept. Geology, UC, London.	DAC studies on model silicates, Ca,Na,K-bearing aluminosilicates to determine stability regimes, equations of state (combined T + P).
Dr.A.P.Jephcoat et al. Dept.Earth Sciences, Oxford University.	Development of DAC systems + laser calibration and flash heating; use to study minerals and molecular solids typical of planetary interiors.
Prof.R.Nelmes/P.D.Hatton Dept. Physics, Edinburgh University.	Complementary single crystal and powder high pressure studies using both image plate and energy-dispersive methods.
Dr.P.Farr et al. Dept. Materials etc. Birmingham University.	Behaviour of solid lubricants and frictional surfaces under working conditions (e.g. 100kbar, 600°C);

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FIGURE LEGENDS

Fig.1. Schematic of hutch layout for proposed station 16.4:

1) Front-end shielding;
2) beam collimation and slit system;
3) YAG/CO_2 heating laser (note 2m cavity length is possible, and one estimates 3m is needed along beam for apparatus);
4) 1st. axis/sample position (diamond-anvil and other cells);
5) energy-dispersive detector (horizontal scattering geometry), vertical scattering possible only with additional axis hardware;
6) optical table;
7) microscope alignment optics, ruby fluorescence collection optics, spectrometer and detector;
8) ruby fluorescence laser;
9) Multi-Anvil-Press (MAP) with load frame straddled around continuation beam pipe to station 16.3;
10) collimation and detector system;
11) excavated outer wall.

Fig.2. a) Measured total resolution {E/E in EDXRD at the optimum scattering angle of $2\theta = 8°$. {E is the peak width and E the energy of the main peaks in a spectrum of alumina collected on station 9.7. This figure shows that as long as the divergence of the diffracted beam (2.4 & 4.0 x 10^{-4} rad.) is kept small the geometrical contribution to the total resolution is minimal. In this case the overall resolution is essentially detector limited and hence improves with higher photon energies.

b) The ratio of the separation to mean width for the (214),(300) doublet in alumina (d-spacings of 1.40 & 1.37 Å respectively). These data illustrate clearly that the maximum resolving power occurs at low scattering angles and hence when the reflections occur at high photon energies (values given next to each point). On station 9.7 the optimum angle lies approximately in the range 6 to 12°.

c) Calculated flux (photons/s in a 0.1% bandwith) incident on $1mm^2$ of sample for SRS stations 9.7 and 16.4 (15 and 22 m from tangent point respectively). In EDXRD a better performance is obtained if higher intensity high energy photons are available.

Fig.3. a) Spectrum collected at $2\theta=8°$ during a high pressure study of molybdenite using a Drickamer-type cell (station 9.7, Cu as a pressure calibrant). In such a cell a disc of sample 2.5 mm in diameter, surrounded by 12mm of gasket material, is compressed between two tungsten carbide anvils, hence the absorption is similar to that in a Multi-Anvil-Press: very little transmission exists below 40 keV.

b) Spectrum collected at $2\theta=9°$ during a high pressure study of molybdenite using a diamond anvil cell (station 9.7, Ag as pressure calibrant). Here the absorption is lower as the X-ray beams travel through the diamonds and a very thin sample, but much information is lost due to the low intensities above 50 keV. The peaks labelled "F" are fluorescence lines from the sample and calibrant.

c) Energy-dispersive patterns obtained during a high temperature synthesis of tetragonal/monoclinic zirconia(5b). The blow-ups show the calcination from amorphous hydroxide to tetragonal zirconia, and the transformation from tetragonal to monoclinic zirconia. However it is clear that information above 50 keV, particularly in the intermediate tetragonal phase, is severely depressed by loss of beam intensity.

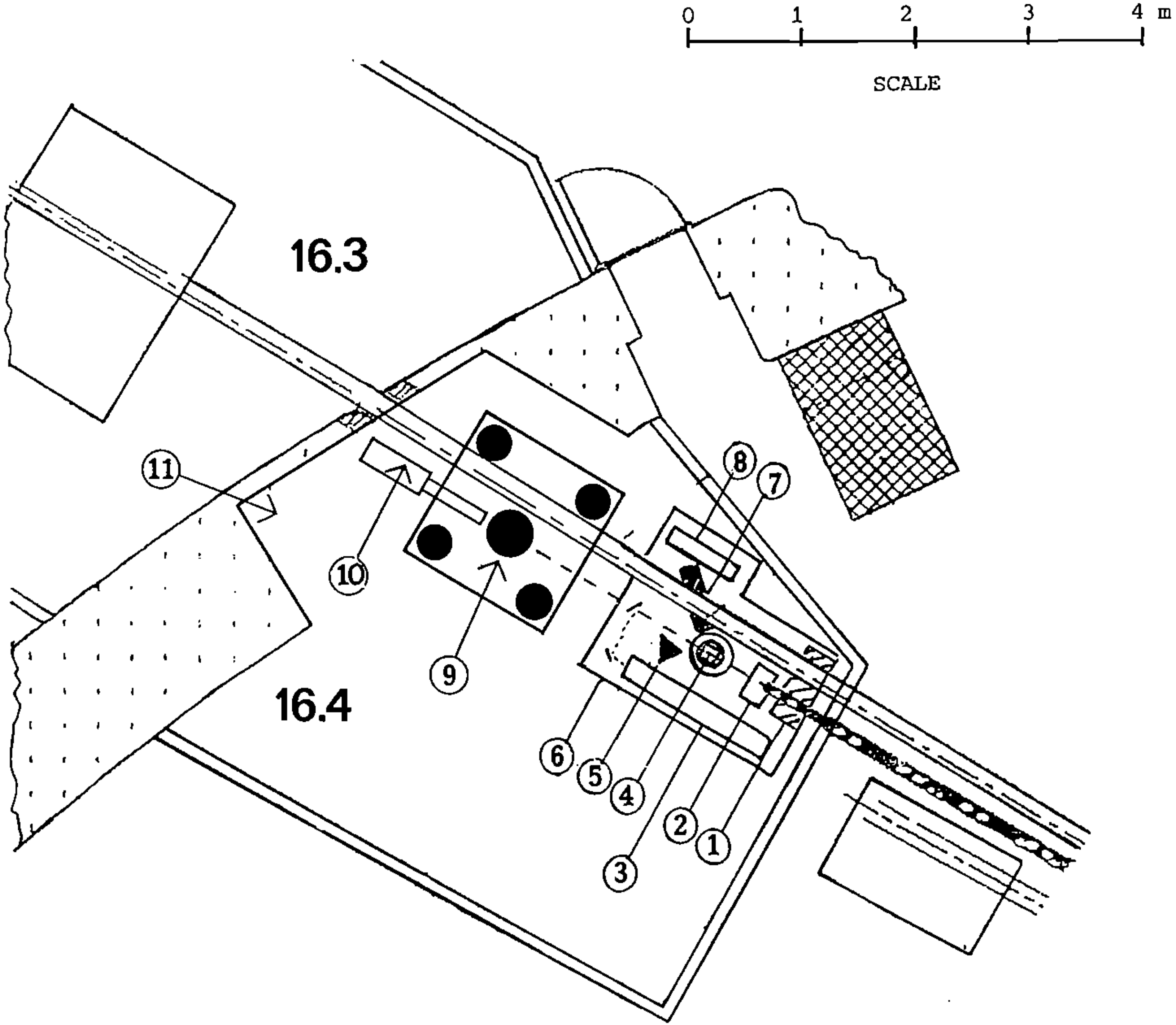

Fig.1

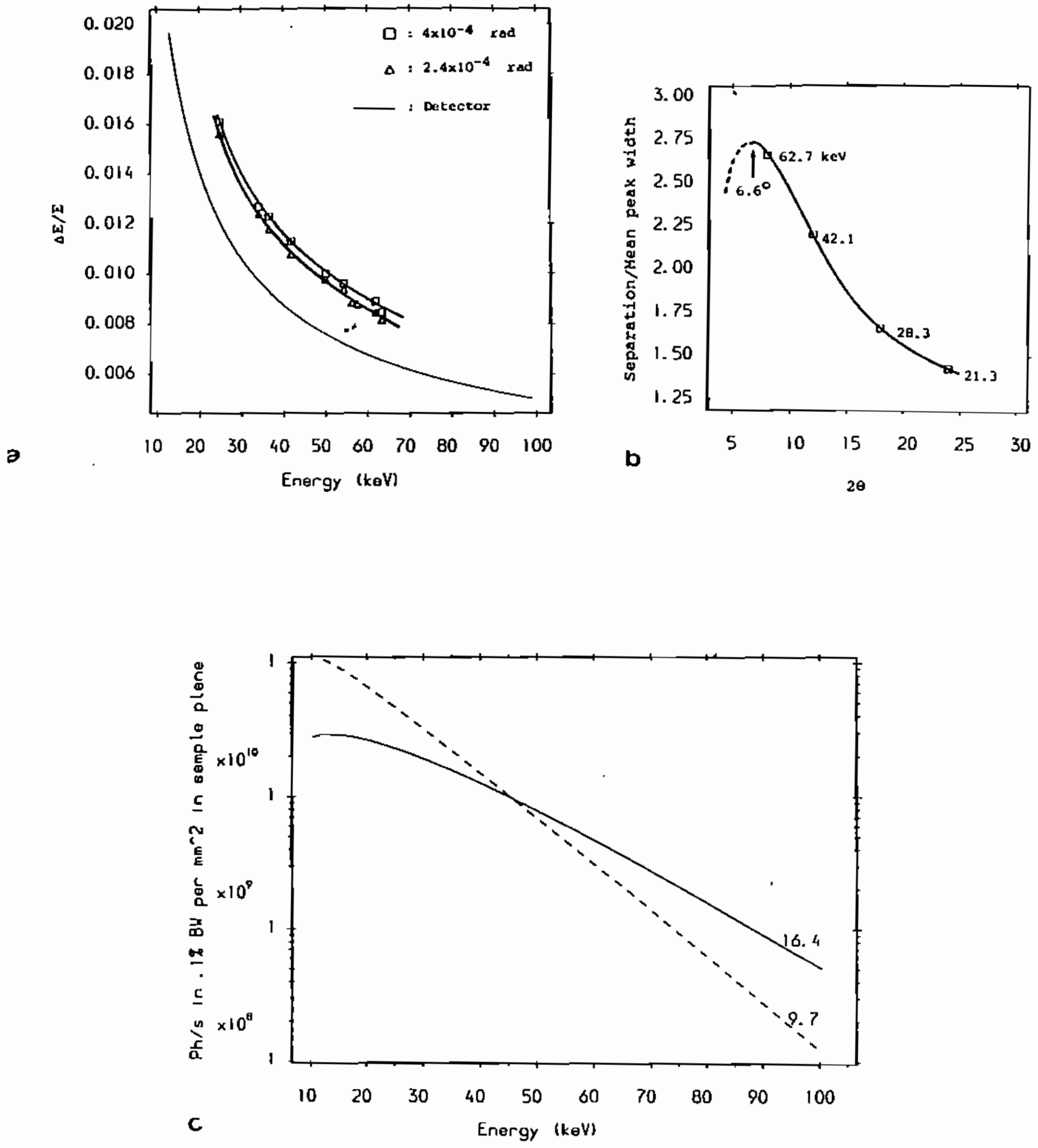
a
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
ΔE/E
□ : 4x10^{-4} rad
Δ : 2.4x10^{-4} rad
: Detector
10 20 30 40 50 60 70 80 90 100
Energy (keV)
b
3.00
2.75
2.50
2.25
2.00
1.75
1.50
1.25
Separation/Mean peak width
62.7 keV
6.6°
42.1
28.3
21.3
5 10 15 20 25 30
2θ
c
Ph/s in .1% BW per mm^2 in sample plane
1
x10^{10}
1
x10^{9}
1
x10^{8}
1
16.4
9.7
10 20 30 40 50 60 70 80 90 100
Energy (keV)

Fig.2

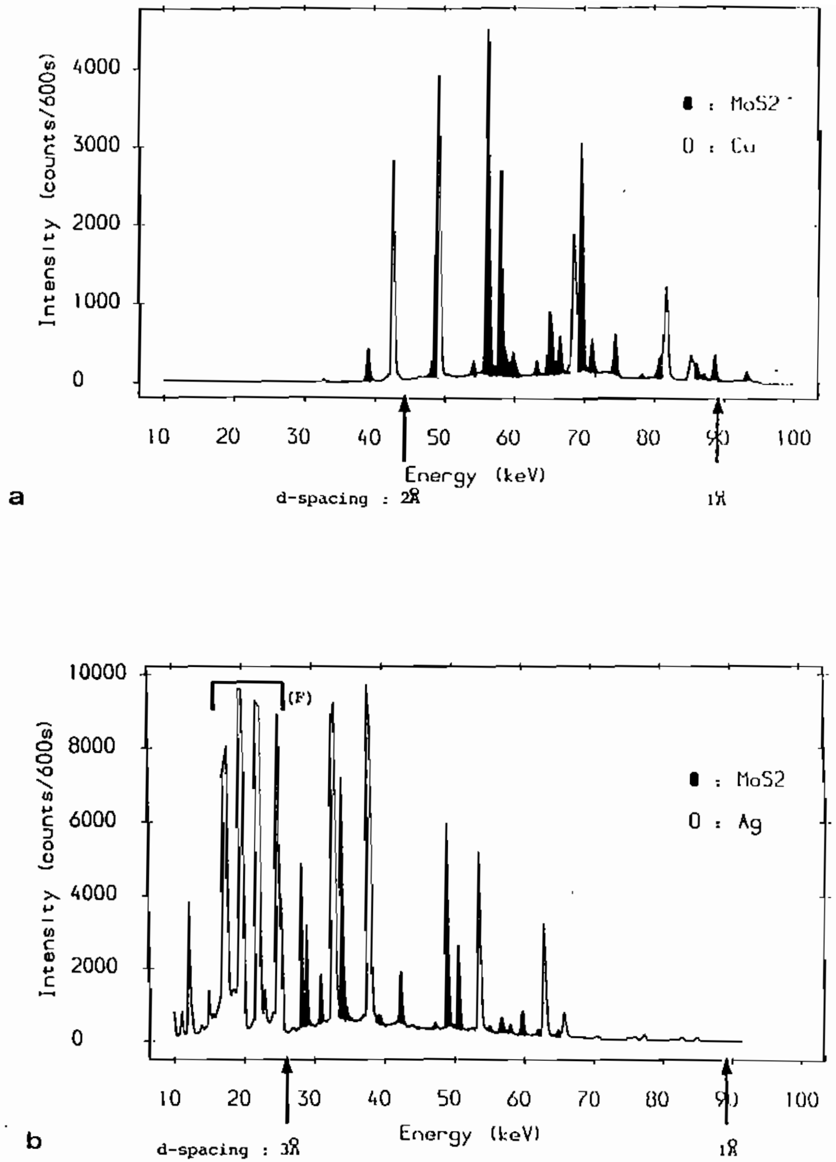
a
Intensity (counts/600s)
4000
3000
2000
1000
0
● : MoS2
0 : Cu
10 20 30 40 50 60 70 80 90 100
Energy (keV)
d-spacing : 2Å
1Å
b
10000
8000
6000
4000
2000
0
Intensity (counts/600s)
(F)
● : MoS2
0 : Ag
10 20 30 40 50 60 70 80 90 100
Energy (keV)
d-spacing : 3Å
1Å

Fig.3

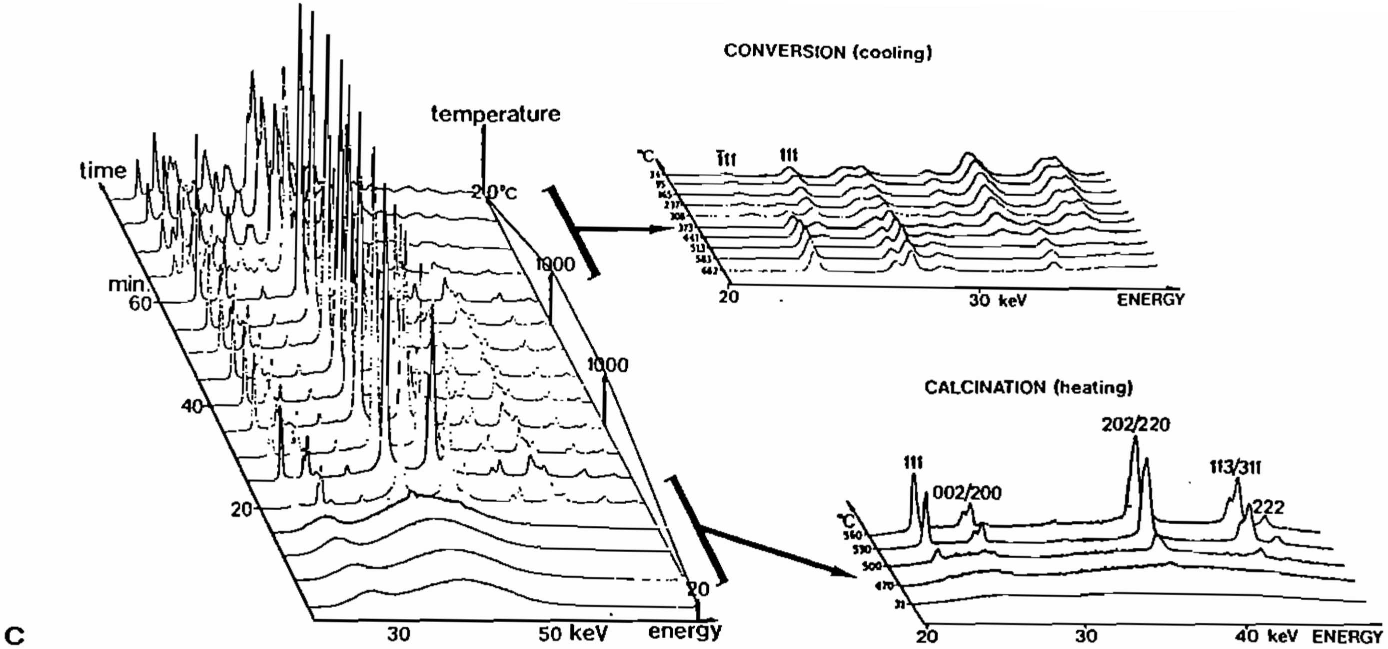
C
time
min.
60
40
20
temperature
200°C
1000
1000
20
30
50 keV
energy
CONVERSION (cooling)
°C
T11
111
20
30 keV
ENERGY
CALCINATION (heating)
111
002/200
202/220
113/311
222
°C
560
530
500
470
31
20
30
40 keV
ENERGY

Fig.3