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Powder Diffraction

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Abstract

The importance of x-ray powder diffraction as an analytical tool for phase identification of materials was first pointed out by Debye and Scherrer (1,2) in Germany and, quite independently, by Hull (3,4) in the United States of America.

Three distinct periods of evolution lead to ubiquitous application in many fields of science and technology. In the first period, until the mid-1940's, applications were and developed covering broad categories of materials including inorganic materials, minerals, ceramics, metals, alloys, organic materials and polymers. During this formative period, the concept of quantitative phase analysis was demonstrated (5).

In the second period there followed the blossoming of technology and commercial instruments became widely used. The history is well summarized by Parrish (6) and by Langford and Louër (7). By 1980 there were probably 10,000 powder diffractometers in routine use, making it the most widely used of all x-ray crystallographic instruments.

In the third, present, period data bases became firmly established and sophisticated pattern fitting and recognition software made many aspects of powder diffraction analysis routine. High resolution, tunable powder diffractometers were developed at sources of synchrotron radiation (8,9,10). The tunability of the spectrum made it possible to exploit all the subtleties of x-ray spectroscopy in diffraction experiments (11).

Introduction

The first design of an x-ray powder camera, by Debye and Scherrer (1), has remained essentially unchanged until the present day. The sample, in the form of a cylindrical rod, is located at the center of a strip of photographic film which is bent into a cylinder and held in place inside a light tight container. More recently, the film has been replaced by a position sensitive electronic detector.

When a narrow monochromatic beam of x-rays strikes a powdered sample of crystalline material grains which are oriented at the correct angle, given by Bragg's Law, $2d \sin \theta = \lambda$, diffract x-rays at an angle 2θ to the incident beam. For a perfectly random collection of powder crystallites all such diffracted rays lie on the surface of a cone with semi-vertex angle θ. Thus, the powder diffraction pattern on a flat film is a set of concentric circles with the primary incident beam at the center. The radii are determined by the distance from the sample to the film and the diffraction cone angles $2\theta_{hkl}$ given by Bragg's Law with d_{hkl} being the Bragg spacing of the hkl planes. A pattern obtained at Daresbury Laboratory using synchrotron radiation and an imaging plate is shown in Figure 1. The pattern is from orthorhombic InSb-II at a pressure of about 4GPa in a diamond anvil cell at an x-ray wavelength of 0.48 Å. On the flat image plate, which is normal to the incident beam and intercepts radiation diffracted at forward angles, can be seen the circular intersections of the diffracted cones of x-rays. In this case the sample volume is only a few tens of micrometers cubed!

Although this geometry had been explored in Hull's early experiments it is not widely used in laboratory experiments because intensities are too low. Such high quality patterns are simply not possible with conventional laboratory sources of x-rays but can be obtained in just a few minutes or hours with synchrotron radiation sources. In film cameras the only parameter to be

determined was the powder ring diameter. To increase the intensity, Debye and Scherrer therefore used a slit and cylindrical sample rather than a pinhole and flat sample and recorded just one diameter of the complete pattern on their cylindrical film. Hull used both flat and cylindrical films in his early experiments. In those early days, Debye and Scherrer and Hull solved the structures of several elements, metals, diamond and graphite and simple compounds such as lithium fluoride. Hull defined many of the important parameters of the new method; the importance of using small particle sizes and the use of specimen rotation so as to randomize the orientation. In his 1919 paper, Hull recognized and pointed out the potential importance of x-ray powder diffraction patterns as a means of identifying materials. As I will outline later, during the following 25 years this application of powder diffraction became an established and important analytical tool.

A *Personal Reminiscence* of this era by Paul Scherrer and an *Autobiography* by Albert W. Hull appeared in the book celebrating 50 years of x-ray diffraction which was edited by P.P. Ewald and published by the International Union for Crystallography in 1950.

The Powder Diffraction File

The application of x-ray powder diffraction patterns to the identification and analysis of materials initially developed locally in many laboratories. But it was, throughout the 1930s, a topic of increasing importance and a subject of intense discussion at conferences in the USA, Europe and the USSR. In 1938 Hanawalt, Rinn and Frevel (5) published the x-ray diffraction data for 1000 common inorganic compounds and illustrated a system for the identification of the components of a mixture. In the same year, Boldyev, Mikheev, Dubinina and Kovalev at the Bureau of Mines in Leningrad showed how minerals could be identified by the retrieval of patterns from a similar but smaller data base. By 1941, the American Society for Testing and Materials (ASTM) had arranged to provide the data on standard file cards and during the next few years the

future was assured by the formation of a Joint Committee for Diffraction Standards (JCPDS) which still exists, albeit in a modified and updated form as the International Center for Diffraction Data (ICDD), providing on a commercial basis the Powder Diffraction File and courses of instruction on its use and application.

A detailed history of these developments up to 1983 is given by Hanawalt (12). Since then several other data bases have become available and are widely used (7). In essence, the early developments showed that searches based on just the d_{hkl} for the four strongest diffraction lines were quite definitive. Since the beginning of the computer era more powerful algorithms have come into use. Search-match programs depend upon pattern recognition procedures in various forms and many programs are currently in use for that purpose (13).

Electronic detectors; the diffractometer

A major change in the practice of powder diffraction came when electronic x-ray detectors became commercially available and the automation of laboratory apparatus started in the 1950s. In the previous decades many contributing developments had been made and the so-called para-focussing geometry, first explored by Bragg (14) and Brentano (15), was adopted by Lindemann and Trost (16), by Friedman (17) and in a design specifically optimized for use with electronic counters (18). In this design the x-ray source and the detector are constrained to lie on the circumference of a circle at the center of which is the flat powder sample. The angle of incidence and the angle of scattering are constrained so that they are in a $\theta : 2\theta$ relationship and divergent rays leaving the source are all refocussed at the detector. Now, with a large flat plate of sample and with the efficient collection of divergent radiation, both the quality of the patterns and the intensity were improved. 10,000 instruments had been sold by 1983 (6).

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More recently still, many detectors which are more sensitive to x-rays than Geiger counters and which have additional features such as position sensitivity in one or two dimensions, or energy resolution, have spawned a wide range of specialized designs which are beyond the scope of this historical review (7).

By the early 1980s x-ray powder diffraction had become an indispensable analytical tool for:

- the identification of crystalline phases;

- qualitative and quantitative analysis of mixtures;

- the determination of phase diagrams;

- and for following solid state reactions.

In addition, a wide variety of other features in the diffraction patterns, such as systematic peak shifts and variations in peak shape, had been developed as measures of sample attributes such as:

- strain;

- grain size;

- thermal expansion;

- preferred orientation;

- impurity and dopant concentration;

- dislocation and stacking fault density.

Synchrotron Radiation

Starting in the early 1980s x-ray synchrotron radiation became available. This delivered very high intensity beams and at the same time bright beams of variable wavelength; the restrictions of the past were instantly removed! On the one hand the extraordinary intensity could be used to speed up conventional measurements or it might be exploited in novel x-ray optical

designs to make for the first time aberration free diffractometers with ideally symmetric instrument functions or with convenient x-ray beam attributes. In addition, the whole x-ray physics of spectroscopy could be incorporated into a new degree of experimental freedom within diffraction and scattering experiments.

Figure 2 shows schematically some typical experimental arrangements. A monochromatic plane wave x-ray beam is selected from the white beam of synchrotron radiation by the doubly reflecting channel cut silicon monochromator CM (Figure 2a,b). The beam diffracted by the flat powder sample S is then analyzed either with a multiple set of parallel slits HPS (Figure 2a), (9,10) or by a single crystal analyzer A (Figure 2b) (8) or by a simple receiving slit RS (Figure 2c) as commonly used in laboratory experiments for cylindrical fibre or powder samples FS. In all cases the vertical divergence--i.e., the experimental means for controlling the angular integration around the arc of the diffraction cone--must be defined by the Soller slits VPS. With synchrotron radiation sources the wavelength can be independently set by tuning the channel-cut monochromator Bragg angle θ_M.

Using the relatively low resolution [0.05° 2θ] multiple slit system shown in Figure 2a the powder pattern from quartz at 1.28 Å shows perfectly symmetric peaks on a flat background even out to very high scattering angles. The triplet of peaks at about 55° 2θ in Figure 3 is shown in enlarged detail in the right hand part of Figure 4. Here they are measured at 1.54 Å wavelength and so appear at about 68° 2θ. For comparison, the left hand part of Figure 4 (19) shows the same peaks taken with copper Kα radiation, also 1.54 Å, where the resolution and shape are inferior and the pattern is further complicated by the presence of the copper Kα doublet. The improved quality of these ten year old synchrotron radiation patterns is obvious. With perfect crystal analyzers, as in Figure 2b, even narrower peaks are obtained and the resolution can be as

high as desired (in principle) by simply selecting monochromators and analyzers with narrower Darwin widths (20). The ultimate resolution is set in practice not by the x-ray optical system but by the sample perfection and particle size.

High speed powder diffraction

An alternative application for the high intensity is simply to speed up the exposure time. This is not a trivial extension to the technique since it makes possible experiments which determine complete phase diagrams in a reasonably short time, perhaps just a few hours, or to follow phase changes while they occur on the timescale of practical industrial processes.

The advantages which result from speeding up the timescale of data collection to match the inherent time-constants of the chemical process are decisive; one can determine the

- kinetics of phase transformation and crystallization;

- existence of intermediate phases;

- parameters for optimizing synthesis conditions;

- temperature/time relations for the process.

Two different examples suffice to indicate the range of applications which are becoming *almost* routine. Both use the so-called Debye-Scherrer geometry with a cylindrical capillary containing the sample. Either a position sensitive detector shaped to lie on an arc of the circle or an image plate mounted on a slide unit which translates it between exposures replace the original film. The sample is illuminated by a narrow beam of monochromatic x-rays from a standard channel cut silicon crystal monochromator. In such a diffractometer, high resolution patterns are obtained over a limited angular range, typically up to 120°, in just a few minutes. Multiple patterns covering a wide range of sample status can be measured in a matter of hours.

Cement is ubiquitous as a building material and yet a detailed account of the hydration process is not complete. The nature of the process means that it cannot be easily followed by electron microscopy and it cannot be studied as bulk material at all. Since these reactions take place at atmospheric pressure and close to room temperature the experimental arrangement is not too complicated but the reaction times involve phase transformations in minutes or hours at most. The high-speed of the synchrotron radiation data collection is therefore crucial and the high resolution essential since multiple phases of low symmetry materials must be analyzed (21,22). For example, in the reaction system MgO - $MgCl_2$- H_2O over the temperature range 0 - 175° C, in addition to $Mg(OH)_2$, there are five magnesium chloride hydroxide hydrates produced depending on the temperature and concentrations of the starting components.

Zeolites are an important catalytic component in many industrial processes. They have been studied over many years by powder diffraction on samples extracted from reaction chambers during synthesis or application. Since the processes work at high temperature and pressure, *in situ* studies provide essential information for detailed understanding and analysis. Figure 5 shows an example from the National Synchrotron Light Source [NSLS] at Brookhaven National Laboratory (23). Hydrothermal conversion of zeolite LTA at temperatures below 350°C results in the formation of zeolite Li - A(BW), $LiAlSiO_4$ H_2O (24). Under the normal transformation conditions, the reaction also results in the production of cancrinite. As the reaction proceeds, from front to back in this graph, the intensities of individual lines change and the final phases appear about one third of the way through the data set. The reaction takes place at 260°C and at 45 atmospheres pressure--no other method can give such comprehensive and quantitative information on the appropriate reaction time scale. The quantitative detection and analysis of extra phases is an important benefit of the method.

X-ray spectroscopy; anomalous dispersion

A most important second attribute of synchrotron radiation sources for powder diffraction is the energy tunability of the synchrotron radiation x-ray beams. The photon energy can be selected at will so that atom specific scattering can be utilized in the analysis of powder diffraction patterns and, in suitable situations, the scattering amplitudes can be chemical state specific!

In laboratory-based powder diffraction experiments there is no scope for altering the scattering power of individual elements by changing the x-ray energy; intensities are simply too low from conventional x-ray sources. The first demonstration that powder diffraction intensities could be systematicaly altered by tuning the x-ray energy around characteristic absorption edges was provided by Will, et al., in 1987 (25). In some ways the result was surprising because the practical single crystal diffraction experience at that time dictated that the common observation of anomalous dispersion was that so-called Friedel pairs of Bragg reflections had different intensities. In powder diffraction patterns, the Friedel pairs overlap since they have identical d-spacings. The use of energy tuning near absorption edges in powder diffraction is now well established as a means of achieving element specific contrast. For example, the Y/Zr site occupancy in yttrium stabilized cubic zirconia was determined by resonant scattering powder diffraction by Moroney, Thompson, and Cox (26). Howland, et al. (27) have used anomalous dispersion to selectively influence the scattering powers of Fe, Co, Ni and Zn dopants which partially replaced Cu in $YBa_2Cu_3O_{7-\delta}$ so as to determine their partial site occupancies. Perkins and Attfield (28) worked close to the Fe K-edge to achieve elemental contrast in the determination of Fe and Ni occupancies in the structure of $FeNi_2(BO_3)O_2$. Warner, et al. (29) used resonant powder diffraction analysis to differentiate the distribution of cobalt and iron in $Fe_2Co(PO_4)$ with a precision which is comparable with that achieved previously only by neutron diffraction where contrast between

elements and isotopes is widely utilized. The inability to differentiate neighboring elements, such as the exceptionally important triplet of iron, cobalt and nickel, has in the past been a crucial handicap of the laboratory based powder method. A particularly interesting application of elemental contrast is for the identification of superlattices and slightly distorted phases, for example at high pressure in III-V semiconducting compounds (30). Some difference scattering amplitudes in cubic InSb are almost zero because the indium and antimony atoms scatter in anti-phase. Similar reflection conditions are also found in the orthorhombic high pressure phases, some of which also involve subtle superstructures. The presence of super cells is signaled by the appearance of Bragg peaks with double or triple etc. spacings compared with the starting structure, but symmetry conditions may dictate that they give rise only to very weak peaks. Such a situation is seen in Figure 6 where superlattice peaks occur near 7° 2θ scattering angle. In the inset are shown two patterns for that angular region, one (n) at an energy close to the indium K-edge and the other (f) far from the indium K-edge. The inset triangles indicate where superstructure peaks are expected and it can be clearly seen that some are only visible in the near edge (n) data when the contrast between the indium and antimony is maximized. This pattern leads to the correct identification of the phase. This sophisticated example is related to the classical example of KCl. In that case K^+ and Cl^- ions have identical scattering powers so that the difference Bragg reflections vanish (in apparent violation of the space group extinction conditions). Although the 200 Bragg reflections are allowed by the fcc space group extinction rules they are virtually absent in potassium chloride (31).

Just above the energy of the absorption edges the so-called XANES features in the x-ray absorption result from chemistry specific variations in atomic scattering amplitude. Thus, for example, at particular energies the x-ray scattering amplitude for Fe^{2+} can differ significantly from

that for Fe^{3+}. Warner, et al. (32) exploited this effect to determine that the Fe^{2+} and Fe^{3+} ions in

the mixed valence compound α-Fe_2PO_5 were on different crystallographic sites. The value of the

method has been very quickly recognized since it presents unique opportunities for analysis. More

recent examples include:

- the separate location of Cu^+, Cu^{2+} and Cu^{3+} sites in the high temperature

  superconductor YBCO by diffraction near the copper K-edge; (33)

- the identification of Eu^+ and Eu^{3+} sites in Eu_3O_4 by diffraction near the L_{III}- edge of

  europium; (34)

- studies of Ga^+ and Ga^{3+} in $Ga^+Ga^{3+}Cl_4$ near the gallium K-edge. (35)

It is quite clear that the sensitivity to atomic number and to chemical state adds a powerful

tool to the study of materials structure by powder diffraction. Of course, similar developments

are under way to exploit x-ray spectroscopy within diffraction and scattering experiments whether

on single crystals, powders or less ordered materials.

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Figure Captions

1. Powder diffraction pattern of a high pressure phase of InSb at 0.48 Å wavelength obtained at the Synchrotron Radiation Source [SRS] at Daresbury Laboratory. Courtesy of R.J. Nelmes and M. I. McMahon.

2. General purpose synchrotron radiation powder diffractometers for flat sample and cylindrical capillary samples. Beam steering is accomplished with slits C1, C2 and ES. Detectors SC1 and SC2 record the intensity of the primary beam and scattered beam respectively.

3. Powder diffraction pattern of quartz obtained at the Stanford Synchrotron Radiation Laboratory [SSRL] with 0.05° resolution.

4. Comparison between patterns obtained with a laboratory source of copper Kα radiation and a conventional para-focussing diffractometer and the corresponding peaks from Figure 3.

5. Powder diffraction profiles obtained during the hydrothermal conversion of zeolite LTA with aqueous LiCl at 260° C using the National Synchrotron Light Source [NSLS] at Brookhaven National Laboratory. Abscissa, scattering angle; ordinate, intensity and time varies from front to back data sets. Recorded on a moving image plate.

6. The profile integrated around the entire powder diffraction ring of an image similar to that in Figure 1, in this case InSb - IV at 5.1 GPa (30). The near indium K-edge (n) data was recorded at 0.4445Å while the far-from-the-edge data (f) was obtained at 0.4635Å.
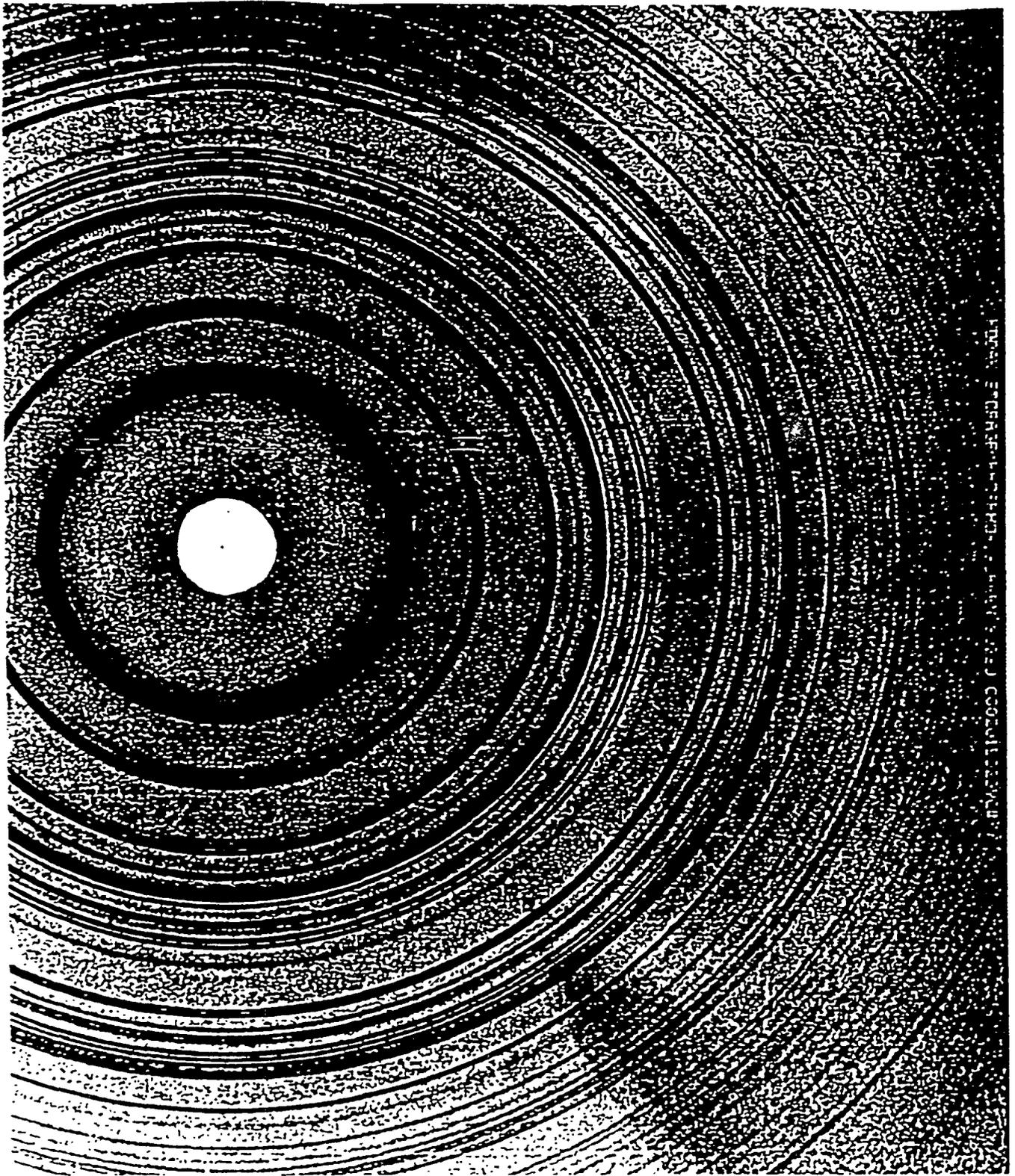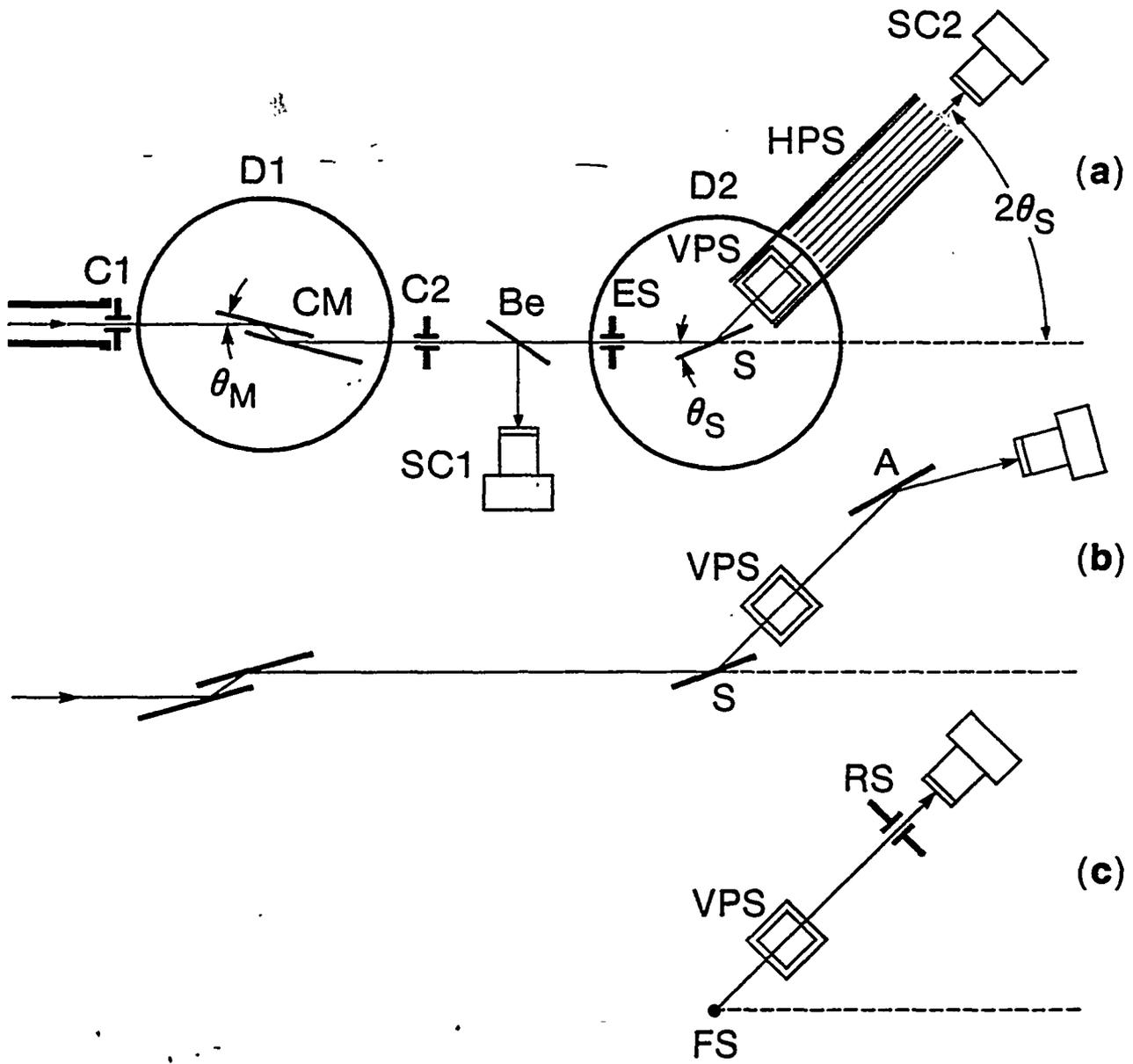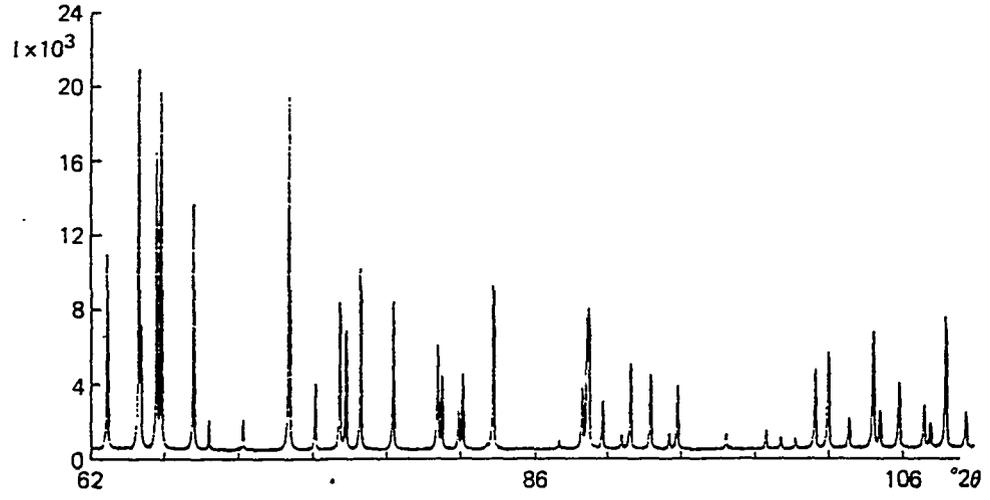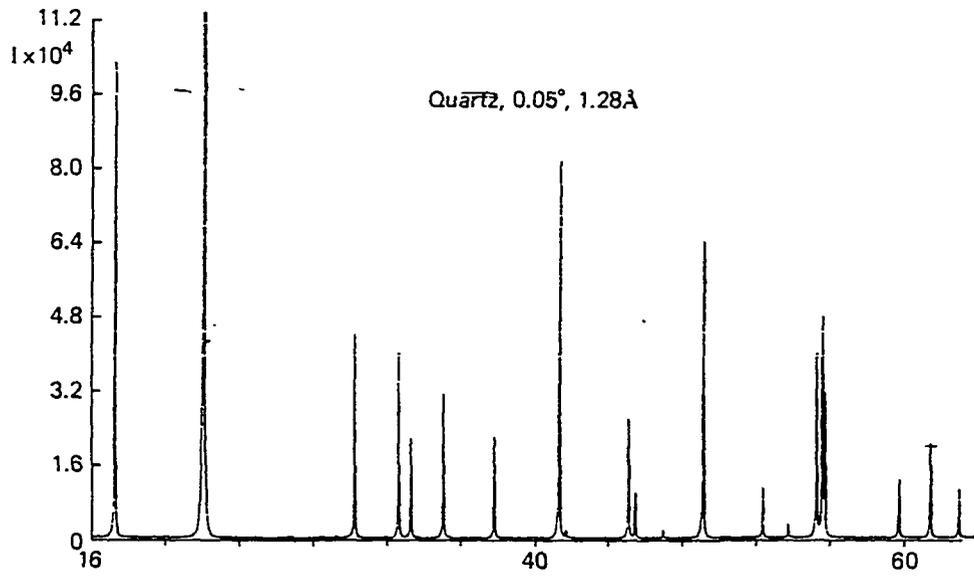
Feb. 1995   Figure 1

SC2

HPS

$2\theta_S$

D1

D2

C1

CM

C2

Be

VPS

ES

θ_M

S

(a)

θ_S

SC1

A

VPS

(b)

S

RS

VPS

(c)

FS

Hart 1995 Figure 2

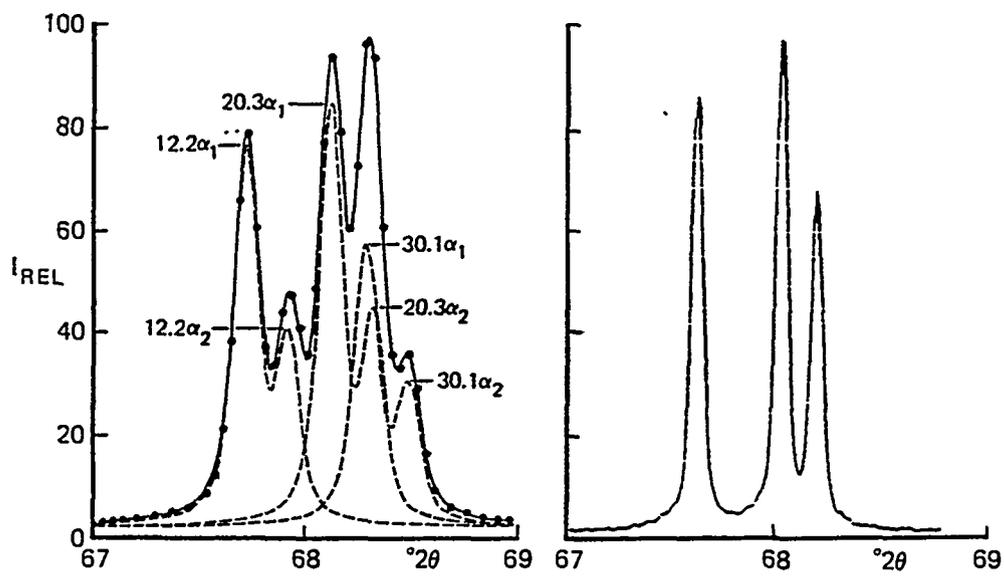Quartz, 0.05°, 1.28Å
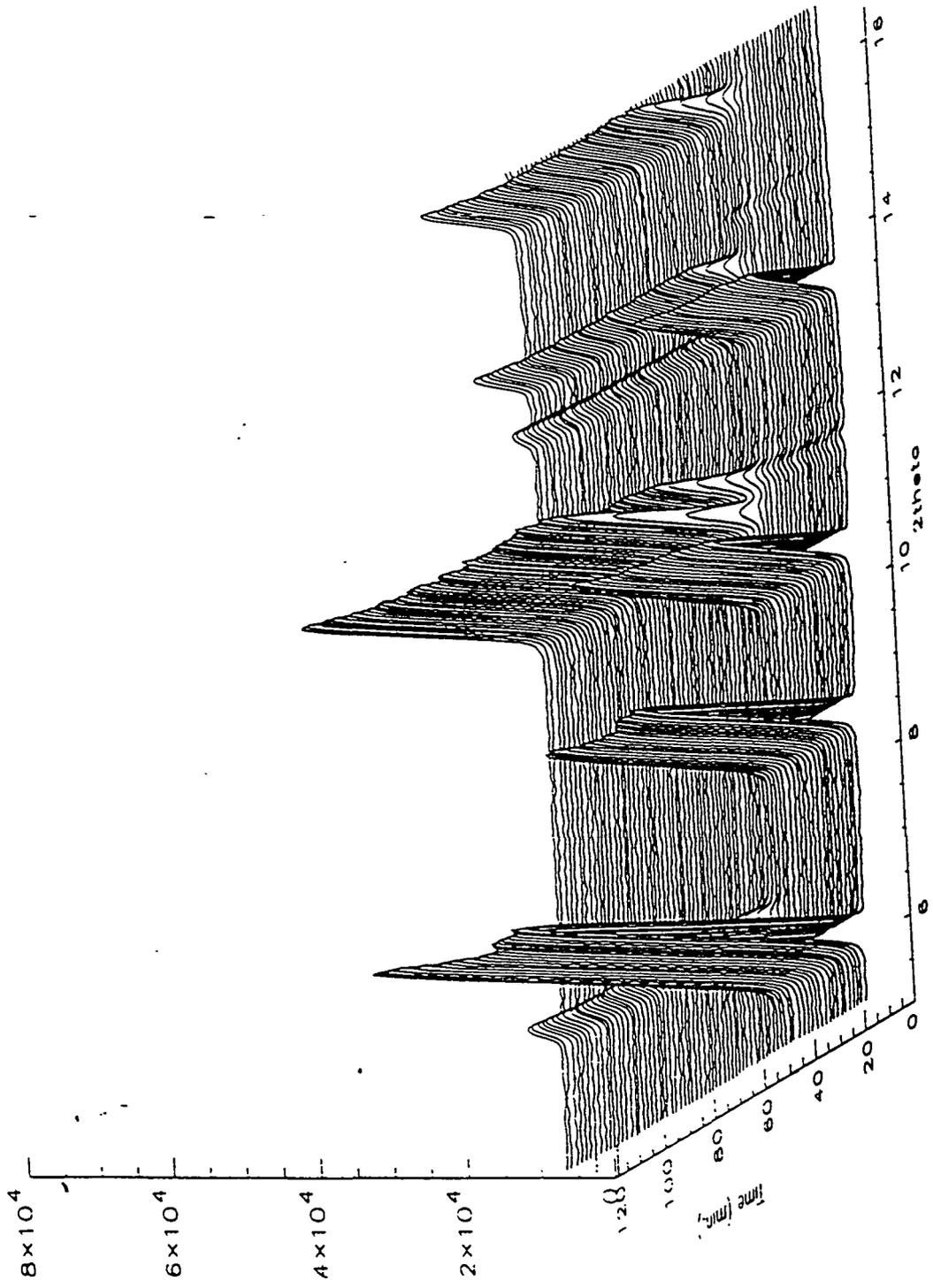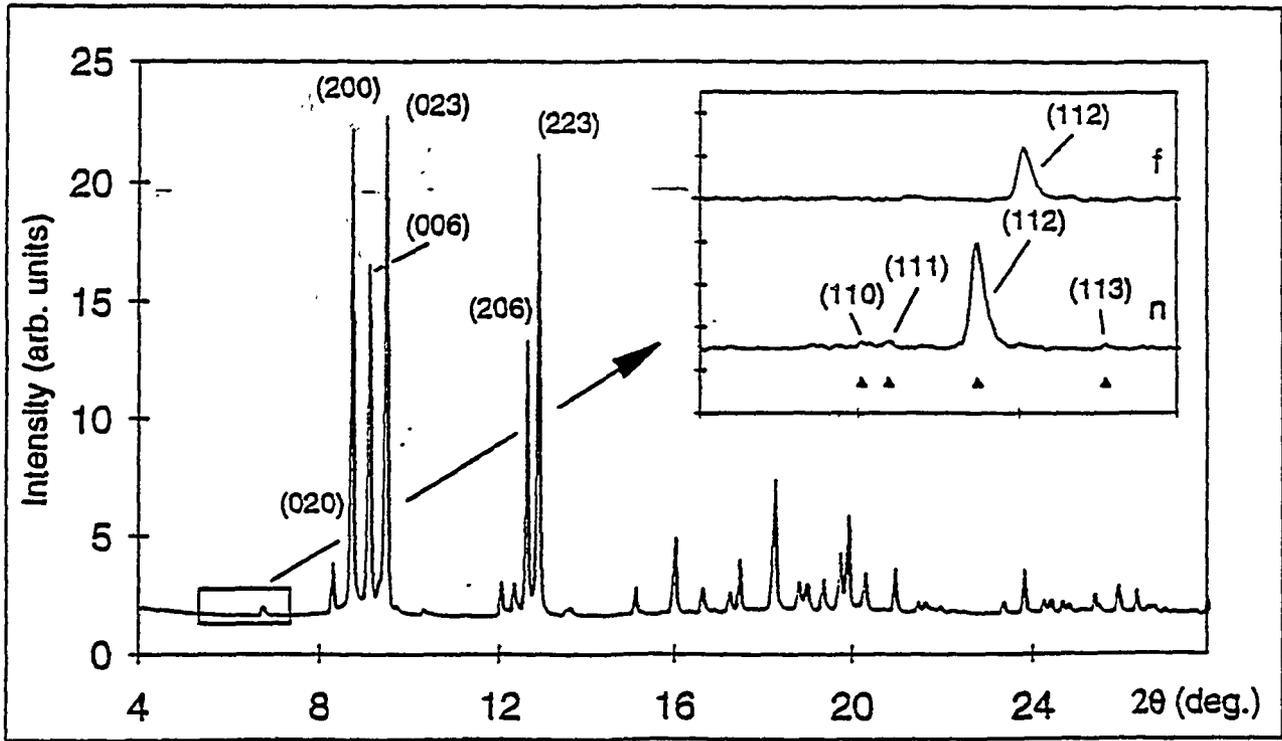
Hart 1995   Figure 3

Hart 1995   Figure 4

Hart 1995   Figure 5

Hart 1995   Figure 6