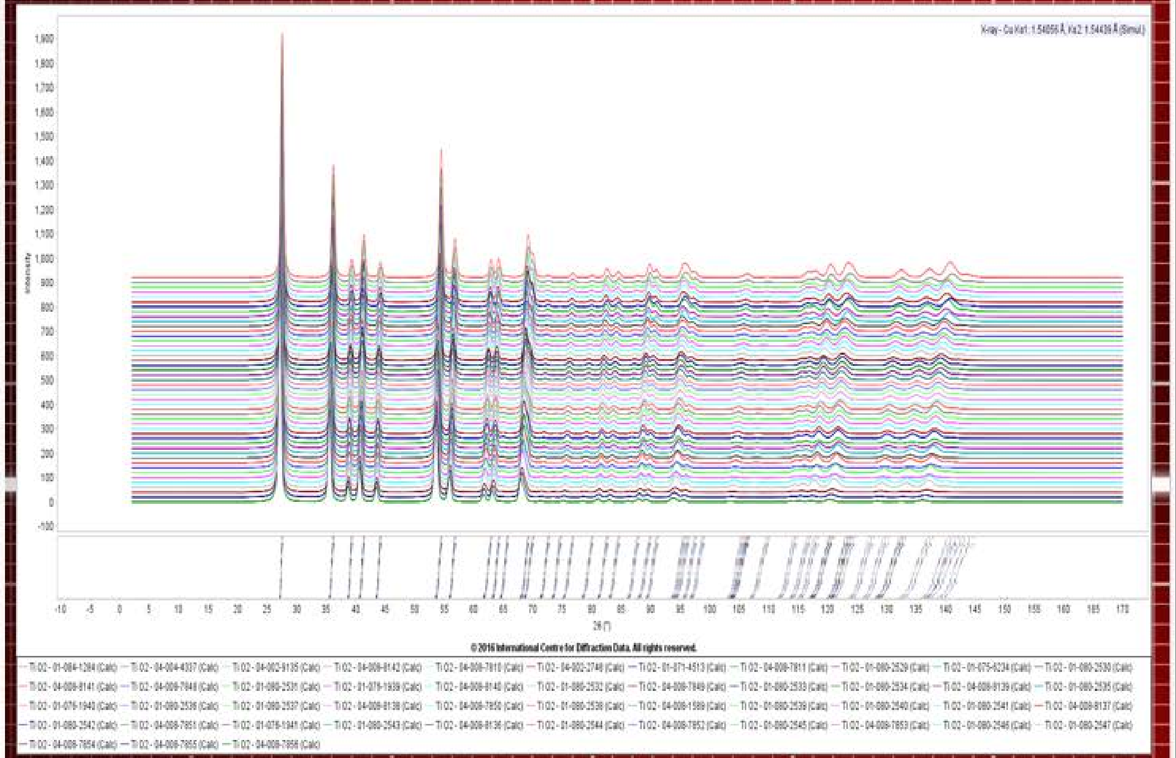
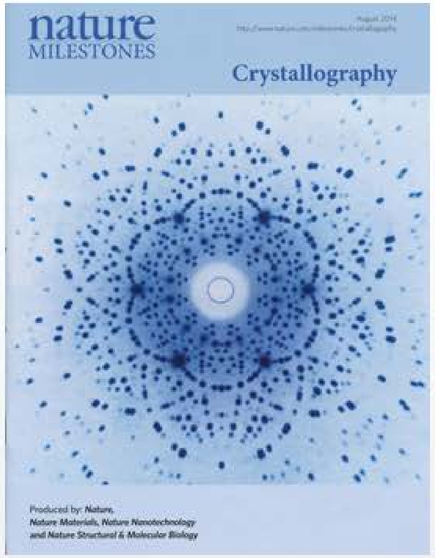
100 Years of X-ray Powder Diffraction

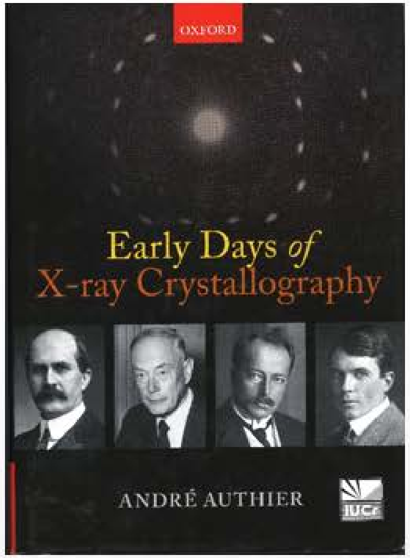
1916-2016



Tim Fawcett
Executive Director, ICDD

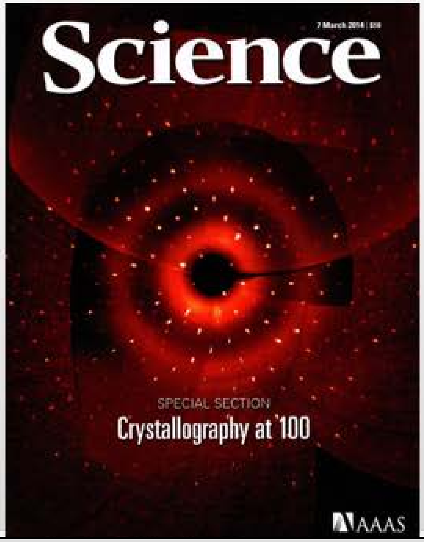
This presentation was originally given at the plenary session of the 65th Denver X-ray Conference, August 3rd, 2016.





100 Years of
Crystallography

1914-2014



Isaac Newton, 1676

“If I have seen a little further it is by standing on the shoulders of Giants.“

There have been several reviews of the history of crystallography. These include anniversary publications in Nature and Science as well as an excellent detailed historical account written by Andre Authier. These publications outline the works of thousand of scientists who contributed to the field.

This presentation is just one of many stories about these historic developments. (One branch of many)

100 Years of Powder Diffraction

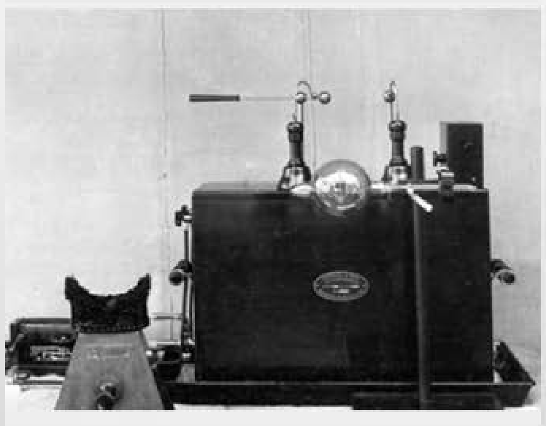
History of Powder Diffraction

..........Discovery

...........Invention

................Innovation

Most historical accounts focus on discovery and invention. I have tried to focus on the process of innovation, where ideas are developed into practical usage for the benefits of society. The innovation process encompasses the original idea but usually includes additional breakthroughs and inventions to bring the idea to practice.



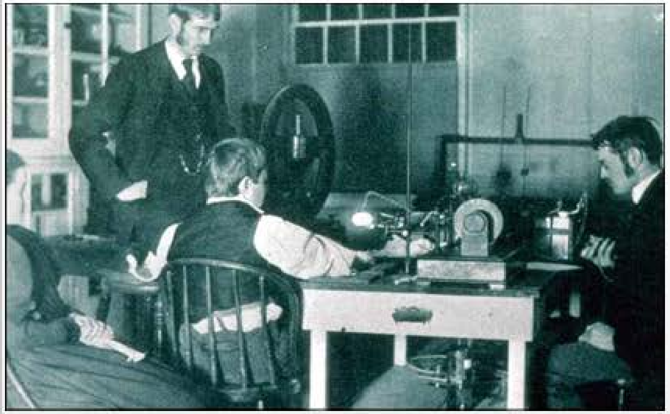
1895
Wilhelm Conrad Roentgen

Discovery of X-rays

Experiment in November
Published
28 December 1895

Nobel Prize in Physics, 1901

We actually start over 120 year ago, with the amazing discovery of X-rays by Wilhelm Conrad Roentgen. A reproduction of the original image of his wife's hand is shown above – you could actually see human bones, the implications to the field of medicine were staggering. We are told by historians that >200 hospitals had reproduced this experiment within a year of publication.



X-RAY VISION: Frank Austin, class of 1895, x-rayed his own hand. Photograph courtesy of New Hampshire Profiles magazine.

X-ray image
of the broken wrist
of Eddie McCarthy

January 1896
Frank Austin, Dartmouth
Physics assistant, reproduces
Roentgen experiment using
his own hand

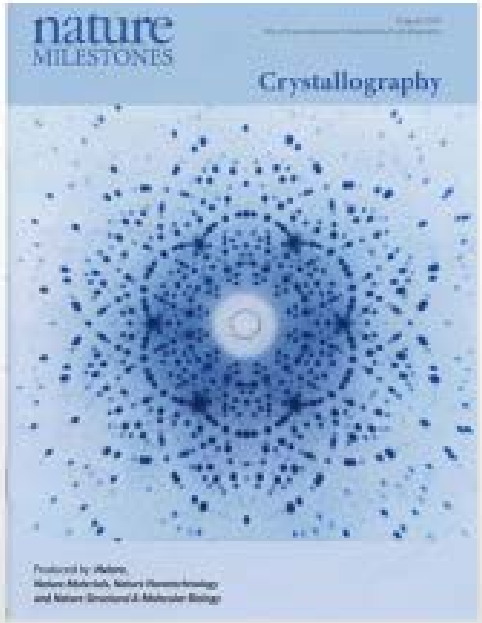
February 3rd, 1896

Edwin and Gilman Frost, professors of medicine and physics

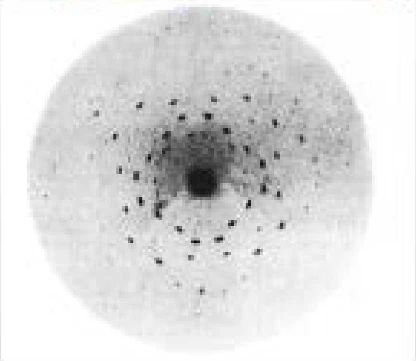
First Medical X-ray in the United States
Dartmouth College

Photo's courtesy of
Mary Hitchcock Hospital
Dartmouth, NH

Within weeks, Roentgens experiment was duplicated by Frank Austin at Dartmouth College in New Hampshire, USA. Weeks later the experiment was duplicated again by Edwin and Gilman Frost to image the broken wrist of Eddie McCarthy who had slipped on the ice in the nearby Connecticut River. Above are the remarkable photographs of the experiment and results. Notice the "glowing" Crookes tube, producing X-rays, in the photograph on the left.



$Be_3Al_2Si_6O_{18}$



ZnS - 1912

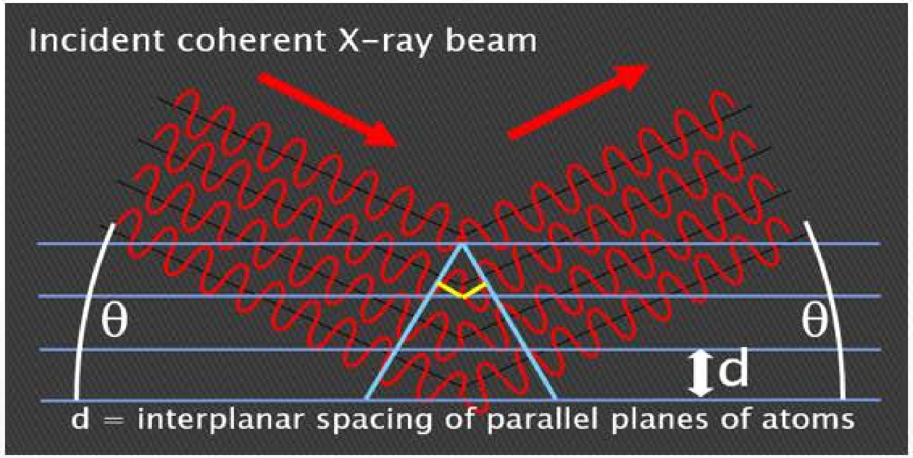
Friedrich, W., Knipping, P., and Laue, M., (1912), "Interferenz-Erscheinungen bei Röntgenstrahlen", Bayerische Akad. d. Wissenshaften zu Munchen, Sitzungsberichte, math.-phys. Kl, p. 303-322.

1912
Max Von Laue

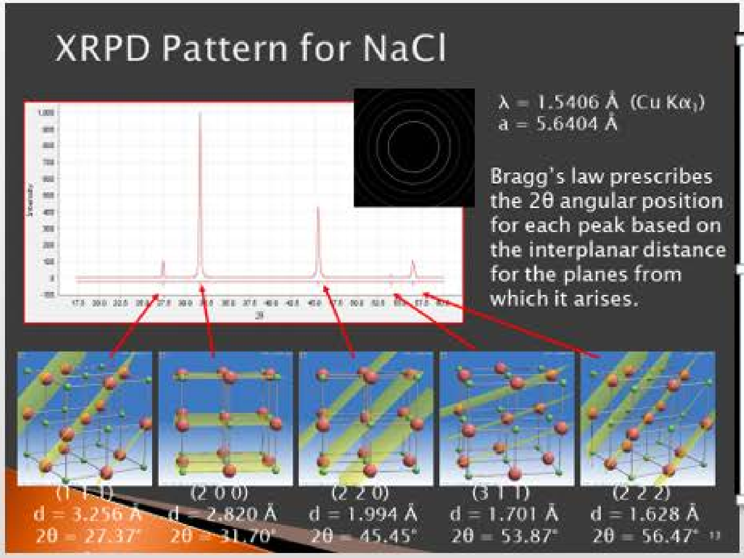
"Diffraction of X-rays from Crystals"

Nobel Prize in 1914

The discovery of X-rays (or Roentgen rays) excited scientists from around the world. Fierce scientific debates centered around members of the leading Universities in Munich, Germany. It was Max Von Laue who suggested the critical experiment, working with Friedrich and Knipping, that lead to the discovery of diffraction. Von Laue was also able to explain the physics of the resulting diffraction patterns for which he won the Nobel Prize in 1914



$$n\lambda = 2d \sin\theta$$



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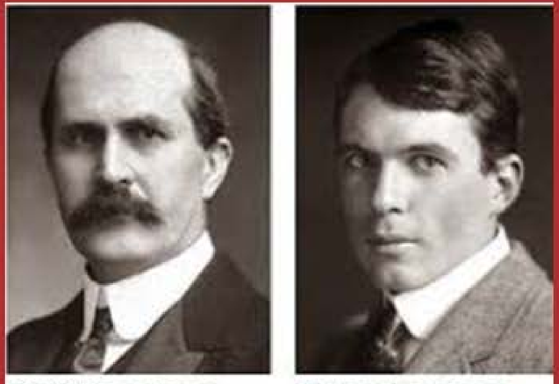
The X-ray spectrometer built by W. H. Bragg.



Sir William Henry Bragg | William Lawrence Bragg

1912
Sir William and William Lawrence Bragg

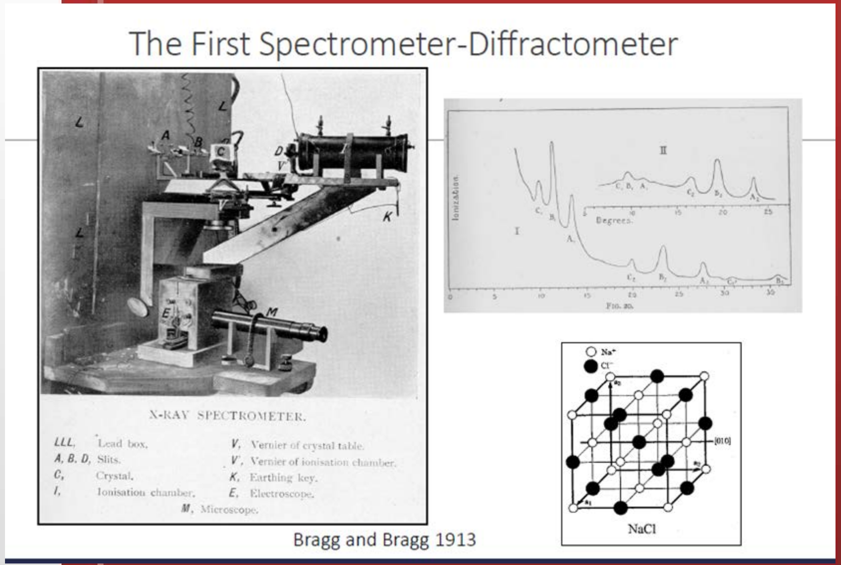
X-ray Diffraction

Nobel Prize 1915 in Physics

Use of X-rays to determine crystal structures

The father and son team of Sir William and William Lawrence Bragg were also working on the nature of X-rays. It was William Lawrence who suggested that diffraction was occurring from parallel plans of atoms in an atomic structure. The Braggs went on to prove this using their single crystal X-ray spectrometer, developing the relationships between angle of diffraction, wavelength, and interplanar spacings, "The Bragg Equation".

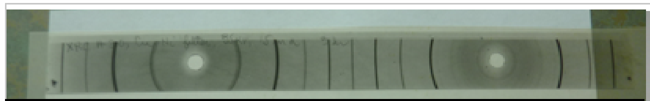
- Bragg, W. L. The specular reflection of X-rays. Nature 90, 410 (1912)
- Bragg, W. L. The structure of crystals as indicated by their diffraction of X-rays. Proc. Royal. Soc. Lond. A 89, 248–77 (1913)
- Bragg, W. H. & Bragg, W. L. The structure of the diamond. Nature 91, 557 (1913)
- Bragg, W. H. & Bragg, W. L. The X-ray spectrometer. Nature 94, 199–200 (1914)

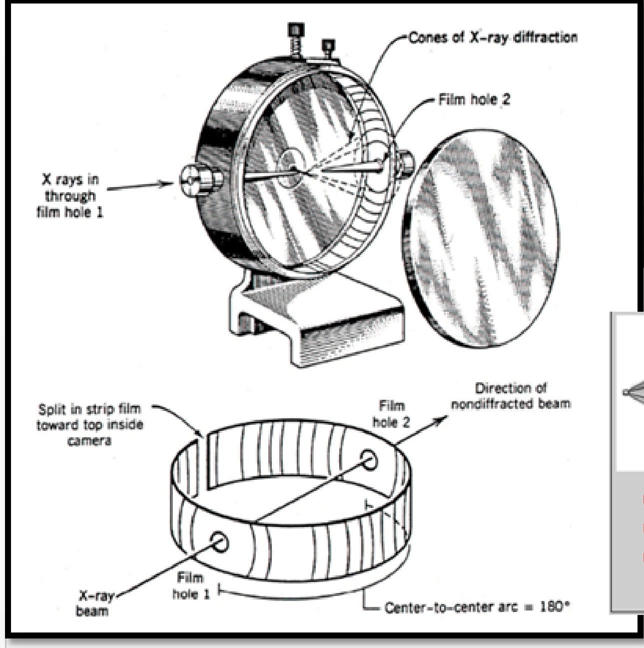


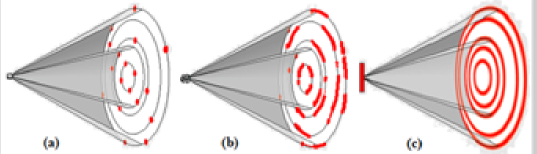
With their spectrometer and knowing the interplanar distances exhibited by diffraction patterns and crystalline lattices the Bragg's successfully determined the structure of diamond and several other materials.

1916

Up to now, the discovery of diffraction and diffraction analyses were done using large single crystals.
Diffraction was a method primarily used to determine crystal structures.
1916 marked the beginning of Powder Diffraction and a new era in materials analysis.







- (a) Single crystal pattern
- (c) Ideal powder diffraction pattern
- (b) Polycrystalline samples with poor grain sampling statistics (large grain size, thin film, inhomogeneous structure, micro area, small amount of sample)

PDF #	Compound Name	Year - PR	Journal - PR	Author - PR	Title - PR
01-071-4681	Lithium Fluoride	1916	Phys. Z.	Debye, P., Scherrer, P.	Crystal structure of lithium halides
01-073-5918	Carbon	1916	Phys. Z.	Debye, P., Scherrer, P.	Interferenzen an regellos orientierten Teilchen im Roentgenlicht
01-073-6978	Silicon	1916	Phys. Z.	Debye, P., Scherrer, P.	Interferenzen an regellos orientierten Teilchen im Roentgenlicht
01-071-4682	Sodium Fluoride	1918	Phys. Z.	Debye, P., Scherrer, P.	Crystal structure of lithium halides

“Interferences in irregularly oriented particles in Roentgen light” Physik. Z. 17, 277–283 (1916)

Peter Debye and Paul Scherrer University of Goettingen, Germany

“The Debye-Scherrer Powder Method”

Peter Debye was Paul Scherrer’s thesis advisor

1916 Diffraction of powders
(Milestone #4 – Nature Magazine 100 Years

INNOVATION……………..In 1916, Peter Debye and Paul Scherrer published the Debye-Scherrer powder method. Debye was the professor and thesis advisor for Paul Scherrer at the University of Goettingen, Germany. They were both inventors and innovators in that they described the method, applied the physics, and developed instrumentation for powder measurements.

Peter Debye

Debye scattering function - 1915

$$I_P(s) = \frac{A(\theta)P(\theta)}{R^2}\sum_m\sum_n f_m(s)f_n^*(s)\frac{\sin(2\pi s d_{mn})}{2\pi s d_{mn}}$$

Diffraction from amorphous solids and liquid crystals

Effect of temperature on diffraction Patterns (Debye-Waller)

Small angle scattering

Debye, P. (1915). "Zerstreuung von Röntgenstrahlen," Ann. Phys. (Berlin, Ger.), 351, 809–823.

Paul Scherrer

$$\beta = \frac{\int I(2\Theta)d2\Theta}{I(2\Theta_B)} = \frac{\lambda}{L\cos\Theta}$$

Scherrer equation for crystallite size - 1918

Study of colloidal particles

Helped build first cyclotron at ETH, Zurich - 1940

Scherrer, P., (1918). "Determination of the size and internal structure of colloidal particles using X-rays," Göttinger Nachrichten Gesell., 2, 98.

Like many innovators and pioneers, Debye and Scherrer were men of extraordinary ability and multiple talents. Debye contributed to the theory of diffraction from amorphous materials and liquids. Scherrer did the first microstructural investigations using powder diffraction with his study of colloidal particles.

The early years were an exciting time. However there were many obstacles, high voltages were needed to produce X-rays and the power supplies were unreliable, vacuum tube technology was in its infancy, and X-ray tubes were short-lived with irregular output. This put practical limits on experimentation and slowed the rate of discovery.

General Electric – 1917........

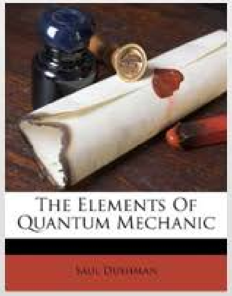
William Coolidge
- Tungsten filaments (light bulbs)
- X-ray Tubes
- Rotating anodes

Albert Hull
- Magnetron
- Materials analysis using X-rays
- Microwaves

Irving Langmuir
- Atomic theory with electrons
- Surface Chemistry
- Incandescent lamps
- Hydrogen welding

Wheeler Davey
- Atomic packing
- Dielectrics
- Materials analysis using X-rays

Coolidge hot cathode X-ray tube



Saul Dushman
- Quantum mechanics
- Atomic structure
- Vacuum Techniques
- Rectifier

INNOVATION !....... Thomas Edison realized the potential impact of X-rays on the medical community. Shortly after William Coolidge's discovery of the tungsten filament for light bulbs, Edison directed him to work on X-ray Tubes. An incredible environment was created at the General Electric laboratories in Schenectady, New York where a group of amazing scientists were put together. Coolidge developed the hot cathode X-ray tube, Dushman invented a rectifier, and Hull was able to assemble a high voltage generator ! The group also had experts in atomic theory, electronic structure, and quantum mechanics.

Albert Hull – memoirs

When I came to the Laboratory in 1914, Langmuir had discovered the law of electron space-charge, and Coolidge, following closely Langmuir's discoveries, had utilized the unique electron emission of tungsten to invent his hot-cathode 'Coolidge' X-ray tube. It was appropriate that Coolidge should make this invention, for he was one of the first in this country, while at M.I.T., to experiment with the original Crookes' X-ray tube, and he still bears the scars of the burns from those pioneer experiments.

At this point something fortuitous happened. Sir William Bragg visited our laboratory and spoke at our colloquium, telling us about the X-ray crystal analysis work which he and his son were doing. In the discussion I asked if he had found the crystal structure of iron, which I though might be a clue to its magnetism. He might have answered, 'no, but I think we shall have it soon', and that would have ended it. But he replied, 'no, we have tried but haven't succeeded.' That was a challenge, and I decided to find the crystal structure of iron.

Langmuir

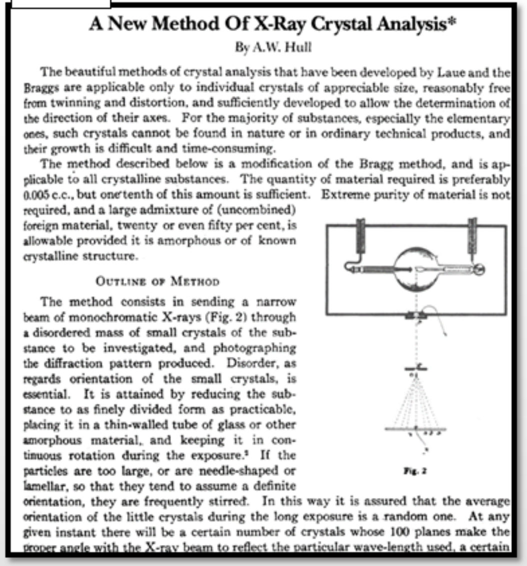
Coolidge

Bragg

Sir William Bragg made a famous visit to the GE Laboraties in 1914. His lecture inspired Albert Hull to investigate powder diffraction as a means for determining the structure of iron

Published structures of Al, Si and Fe

1917



A New Method Of X-Ray Crystal Analysis*

By A.W. Hull

The beautiful methods of crystal analysis that have been developed by Laue and the Braggs are applicable only to individual crystals of appreciable size, reasonably free from twinning and distortion, and sufficiently developed to allow the determination of the direction of their axes. For the majority of substances, especially the elementary ones, such crystals cannot be found in nature or in ordinary technical products, and their growth is difficult and time-consuming.

The method described below is a modification of the Bragg method, and is applicable to all crystalline substances. The quantity of material required is preferably 0.005 c.c., but one tenth of this amount is sufficient. Extreme purity of material is not required, and a large admixture of (uncombined) foreign material, twenty or even fifty per cent, is allowable provided it is amorphous or of known crystalline structure.

Outline of Method

The method consists in sending a narrow beam of monochromatic X-rays (Fig. 2) through a disordered mass of small crystals of the substance to be investigated, and photographing the diffraction pattern produced. Disorder, as regards orientation of the small crystals, is essential. It is attained by reducing the substance to as finely divided form as practicable, placing it in a thin-walled tube of glass or other amorphous material, and keeping it in continuous rotation during the exposure.[3] If the particles are too large, or are needle-shaped or lamellar, so that they tend to assume a definite orientation, they are frequently stirred. In this way it is assured that the average orientation of the little crystals during the long exposure is a random one. At any given instant there will be a certain number of crystals whose 100 planes make the proper angle with the X-ray beam to reflect the particular wave-length used, a certain

Fig. 2

Exposure
9 Hours, 60 KeV, 37 mA

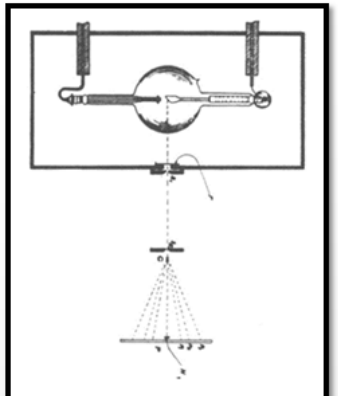


Fig. 2

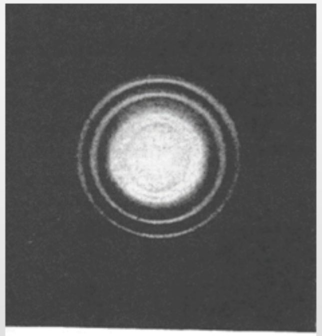


Fig. 1. Aluminium

Albert Hull

X-ray Diffraction Analysis - 1917
X-ray Fluorescence Analysis 1919

1919
"A New Method of Chemical Analysis" (XRF)

Using the equipment invented by the GE team, Hull developed a powder diffraction method and tackled the structures of Al, Si and Fe. He wrote two amazing publications in 1917 and 1919, on X-ray powder diffraction and X-ray fluorescence as new analytical methods. Hull's diffraction work was originally presented at a conference in 1916 with subsequent publication in 1917. Hull, Debye and Scherrer were unaware of each others research due to communication interruptions during World War I. In subsequent years Hull, working with colleague Wheeler Davey, determined the structure of dozens of metals and alloys and developed the Hull-Davey indexing method. Wheeler Davey became the first Chairman of the Board for the Joint Committee of Powder Diffraction Standards, 1941-1956.

1934 Dow Chemical Company

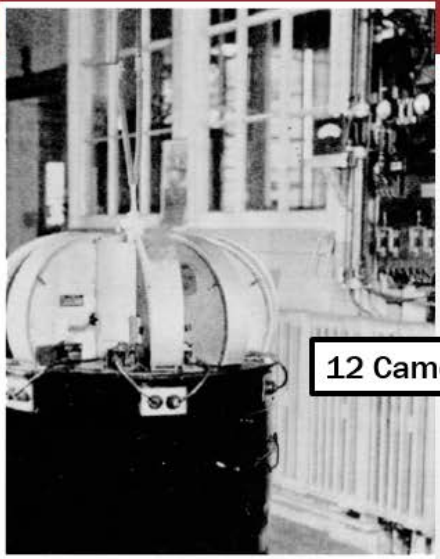


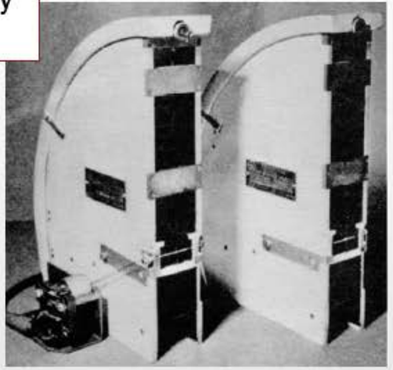
Figure 4. Use of loading box for substances which take up water in air.

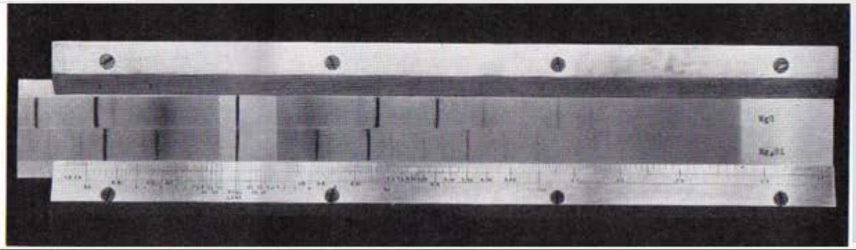
12 Cameras

GE X-ray Generator
Hull Camera
GE X-ray Tubes

Theories and experiments of
the Braggs, Debye, Scherrer, Hull, Davey
and Pauling

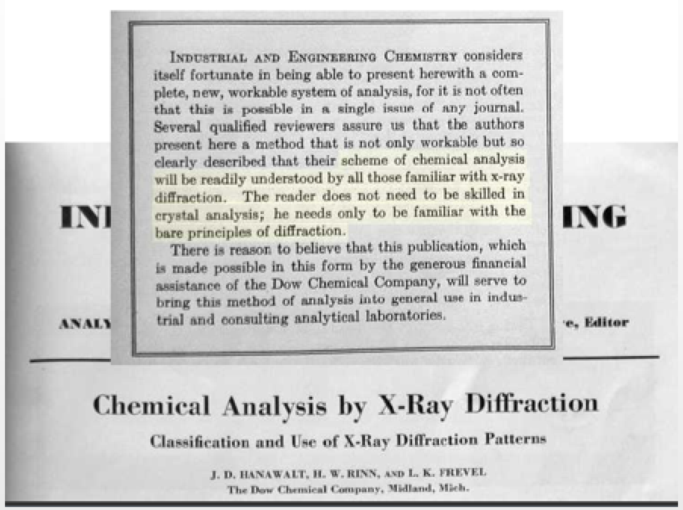
Rotating capillary
for powder specimens





During the 1920's the structure of many metals and alloys were determined by powder diffraction methods. Hull introduced the concept that powder diffraction could be used for materials analysis. A team of scientists in the Physics Laboratory at The Dow Chemical Company were looking for methods to identify materials that they encountered in an industrial environment. The laboratory was equipped with a GE generator, GE X-ray tube and Hull cameras. Just as important, the Dow team, led by Don Hanawalt, frequently corresponded with other leading scientists in the field. Ludo Frevel joined the group after he did his post doctoral work with Linus Pauling at Cal. Tech.

Innovation ! – *"Complete, new workable system of analysis"*



INDUSTRIAL AND ENGINEERING CHEMISTRY considers itself fortunate in being able to present herewith a complete, new, workable system of analysis, for it is not often that this is possible in a single issue of any journal. Several qualified reviewers assure us that the authors present here a method that is not only workable but so clearly described that their scheme of chemical analysis will be readily understood by all those familiar with x-ray diffraction. The reader does not need to be skilled in crystal analysis; he needs only to be familiar with the bare principles of diffraction.

There is reason to believe that this publication, which is made possible in this form by the generous financial assistance of the Dow Chemical Company, will serve to bring this method of analysis into general use in industrial and consulting analytical laboratories.

Chemical Analysis by X-Ray Diffraction

Classification and Use of X-Ray Diffraction Patterns

J. D. HANAWALT, H. W. RINN, AND L. K. FREVEL

The Dow Chemical Company, Midland, Mich.

Identification of Crystalline Materials, Classification and Use of X-ray Diffraction Patterns, JD Hanawalt, HW Rinn, Industrial & Engineering Chemistry, **1936** – ACS Publications

Chemical Analysis by X-ray Diffraction
JD Hanawalt, HW Rinn, LK Frevel – Industrial & Engineering Chemistry, **1938** – ACS Publications

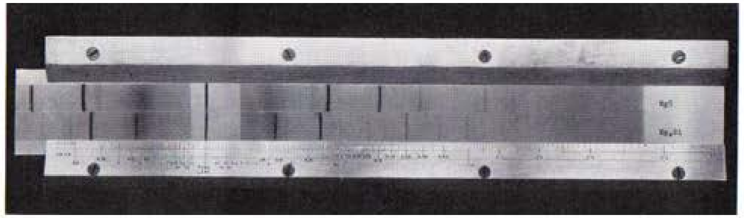
Chemical Analysis by Powder Diffraction
LK Frevel – Industrial & Engineering Chemistry Analytical Edition, **1944** – ACS Publications

Innovation – Identification of materials with powder patterns *without* knowing the crystal structure !

Published 1,054 reference diffraction patterns

INNOVATION !..............A series of publications by Don Hanawalt, Ludo Frevel and Sid Rinn, outlined a new analytical method for the analysis of unknowns by X-ray diffraction. While they also published 1,054 reference patterns, the development of standardized data and indexes led to a process that defined practical materials analysis.
The editors of Industrial and Engineering magazine were impressed and wrote an insert about the "complete, new workable system of analysis....... without knowing the crystal structure".

Phase Identification



Name: Lanthanum Nitrate · Reg. No. 84963
Formula
46A

d(hkl)	I	I/I(o)	1	
9.8	15	75	2	
7.9	10	50	3	
6.6	8	40		
5.9	10	58	4	
5.35	20	100	1	
4.80	4	20		
4.60	6	30		
4.38	8	40		
4.10	8	40		
3.92	6	30		
3.79	4	20		
3.38	8	40		
3.20	6	30		
3.01	2	10		
2.87	8	40		
2.675	10	50		
2.51	8	40		
2.365	4	20		
2.275	4	20		
2.20	8	40		
2.12	8	40		
2.03	4	20		
1.98	4	20		
1.926	4	20		
1.85	4	20		
1.78	2	10		

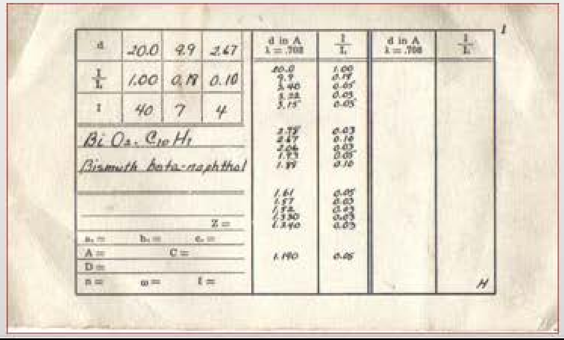
Hanawalt Method

Collect powder patterns

Reduced data to d-spacings (peaks) and Intensities (series of number pairs)

Use the strongest 3 lines and permute their order in an index

Match unknowns with the index then match the full pattern



d	20.0	9.9	2.67
I/I1	1.00	0.18	0.10
I	40	7	4

Bi O2 . C10 H7
Bismuth beta-naphthol

Z =
a0 = b0 = c0 =
A = C =
D =
n = ω = t =

d in A λ = .708	I/I1	d in A λ = .708	I/I1
20.0	1.00		
9.9	0.18		
3.40	0.05		
3.32	0.03		
3.15	0.05		
2.79	0.03		
2.67	0.10		
2.06	0.03		
1.93	0.05		
1.89	0.10		
1.61	0.05		
1.57	0.03		
1.52	0.03		
1.330	0.03		
1.340	0.03		
1.190	0.05		

1938
Ludo Frevel, Don Hanawalt and Sid Rinn

Chemical Analysis by X-ray Diffraction

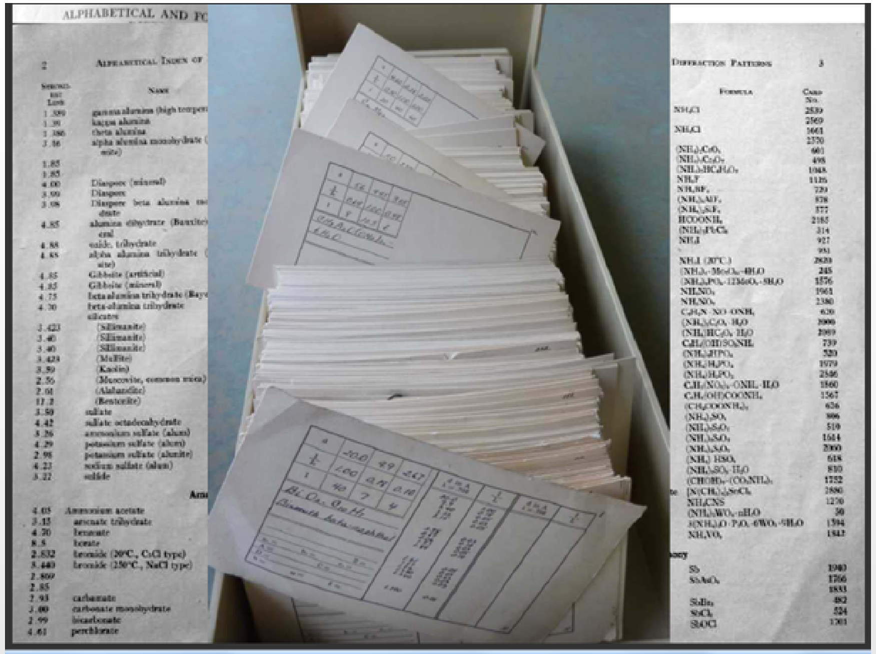
Hanawalt – Vice President Mg metals
Frevel – 446 publications, 60 patents

Don Hanawalt Award named in 1983

Ludo Frevel receives first Hanawalt Award in 1983

The phase identification method is outlined above and named the "Hanawalt Method". It is still used today. Hanawalt, Frevel and Rinn also made significant contributions to other fields of science. All three eventually became a chairman of the board for the JCPDS-ICDD.

1941



Card Files and Indexes transported from Midland, Michigan to ASTM headquarters in Philadelphia in Don Hanawalt's car, copied by hand – Set # 1 of the Powder Diffraction File

Joint Committee on Powder Diffraction Standard (JCPDS) –

1941, 1945

(ASTM Committee on X-ray and Electron Diffraction, British Institute of Physics, National Research Council)

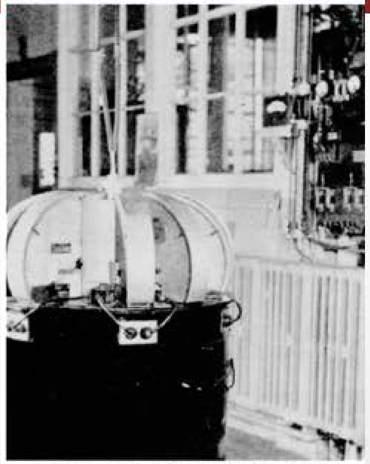
Davey (Hull)	General Electric (then Penn State)
Pickett, Wyman	General Electric
Hanawalt	The Dow Chemical Co. (Mg)
Wilson, Lawrence Bragg	British Institute of Physics
Barton	Institute of Physics (USA)
Fink	Aluminum Company of America
Fuller	New Jersey Zinc
Bannister	British Museum, Cambridge University
Huggins	Eastman Kodak Co.
Boldyrev	Institute of Mines, Leningrad, Russia
Harcourt	American Mineralogist
Kerr	Columbia University
Nelson	Battelle
Magos	Crane Co.
Richmond	US War Department

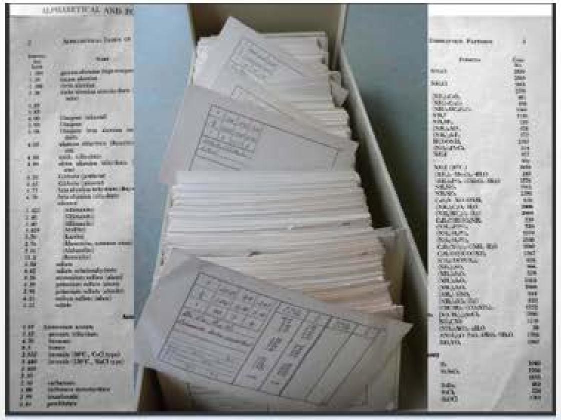
The Powder Diffraction File

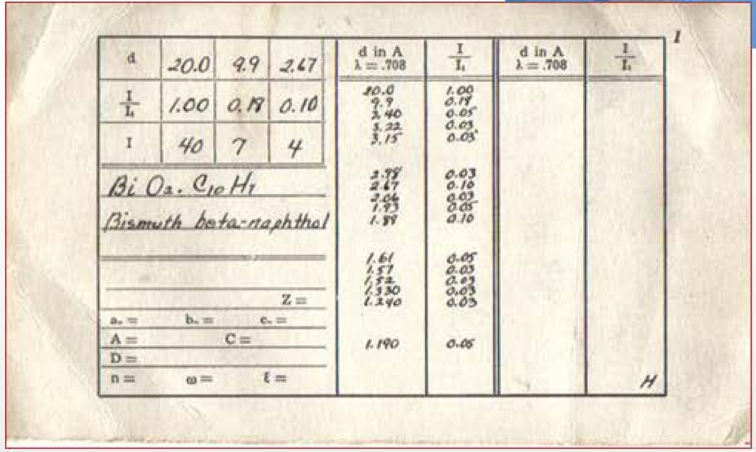
Powder diffraction well established as the method for the analysis of metals and alloys

In 1937, ASTM created a Joint Committee on Powder Diffraction Standards (JCPDS). By then powder diffraction was well established as a method for the analysis of metals and alloys. The committee brought together many leaders in the production of basic metals and chemicals (Dow, Alcoa, Kodak, New Jersey Zinc), fabricators (GE, Crane, Batelle) and leading academic and government scientists. The committee included scientists from the US, Canada, Britain and Russia. In 1941, the Dow records were duplicated by hand and became the first records of the Powder Diffraction File and the first commercial products were introduced. 2016 celebrates the 75th anniversary of the JCPDS – International Centre for Diffraction and the Powder Diffraction File™.

The early years 1916-1941







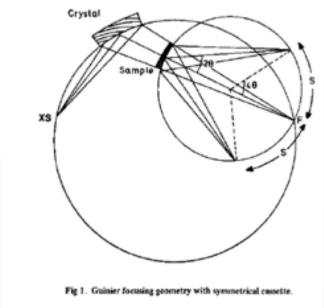
All work done on film
High resolution required fine grain films
Required methods for film development and processing
Intensity measurements required comparator strips of film
or an optical densitometer

Result

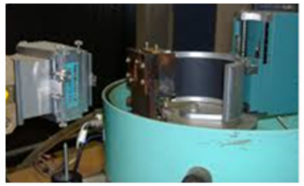
Most d-spacings were to 3 significant figures at best

Most intensities were visually estimated

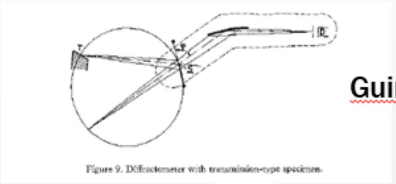
In the first 25 years, tremendous progress had been made. However all work was done with photographic film, high resolution work required a dark room, fine grained films, and an optical densitometer to measure peaks and intensities. The fine grain (~1um) film and densitometers were not readily available so much of the early work involved visual estimation of intensities and manual d-spacing measurement to 3 significant figures.



Guinier 1937

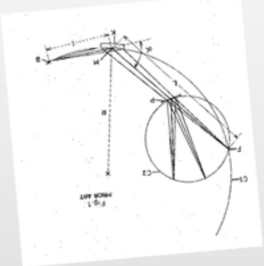


Huber Camera

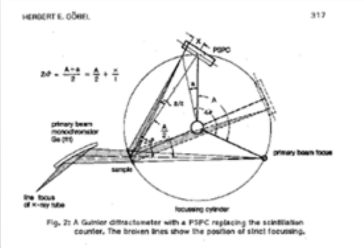


Guinier-DeWolfe 1962

Norelco



Guinier-Hagg 1971



Goebel 1981 with Position Sensitive Detector

André Guinier
University of Paris

Focusing monochromators for precision measurements

Also worked on small angle scattering and The electron microprobe

1985 Aminoff Prize

A. Guinier, 'X-ray Diffraction, In Crystals, Imperfect Crystals and Amorphous Bodies", Dover Publications, Inc., New York (1994)

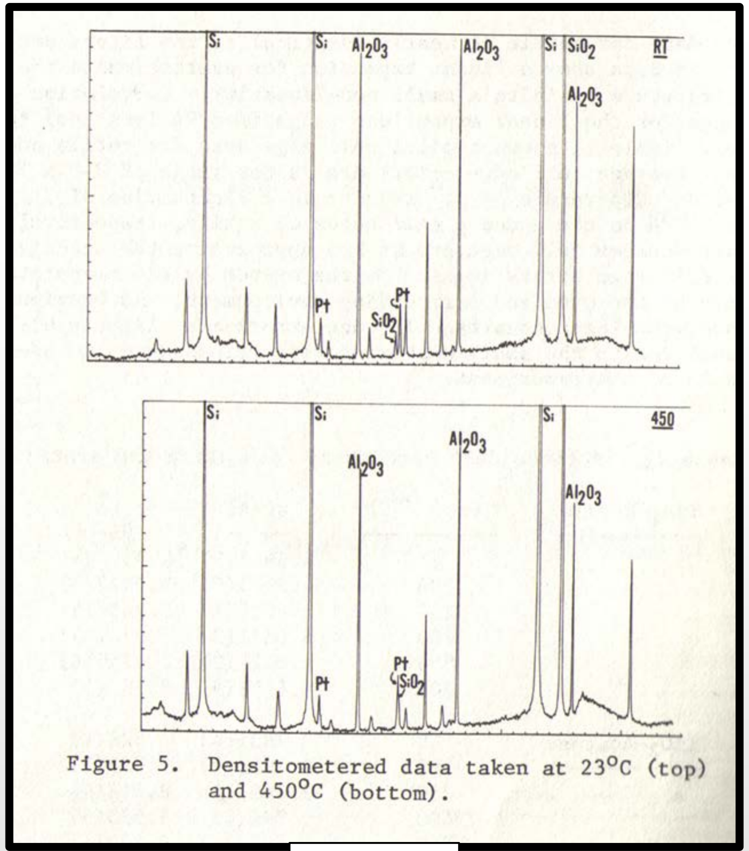
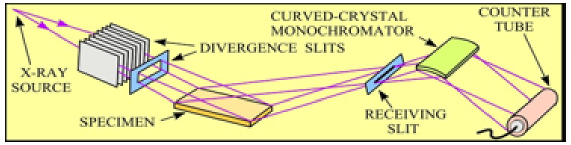


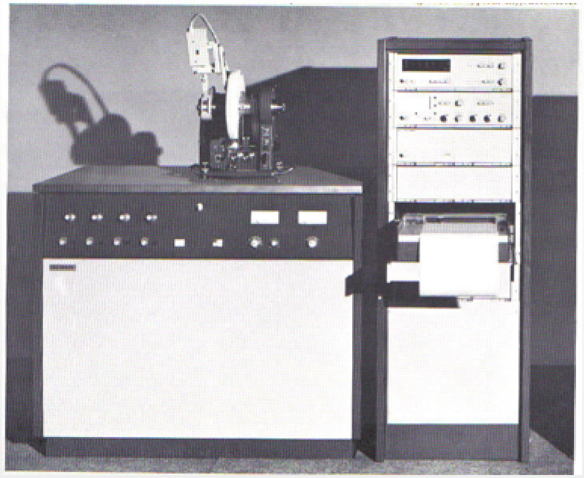
Figure 5. Densitometered data taken at 23°C (top) and 450°C (bottom).

Insert.

INNOVATION !................ Andre Guinier recognized the need to improve resolution in diffraction measurements. In 1937 he developed a focusing system that used a curved incident beam crystal. However, manufacture of high quality, curved crystals with the appropriate mosaic structure was very difficult and resulted in large loses in incident beam intensity.

Improvements in the crystal manufacturing process directly contributed to new focusing camera designs in 1962, 1971 and 1981. The data shown in the insert was taken on a Huber camera (top right) in 1982 at The Dow Chemical Co., demonstrating the remarkable resolution even at elevated temperatures. These data was used for measuring thermal expansion another application of powder diffraction.





Scintillation and proportional counter detectors with pulse height discrimination –

digital intensities !

Fundamental contributions to line profile analysis (microstructure), qualitative and quantitative phase analysis

Advances in X-ray Analysis

Accuracy and Precision of Intensities in X-ray Polycrystalline Diffraction
W. Parrish and T. C. Huang, Vol. 26, pp. 35-44 (1982).

William Parrish

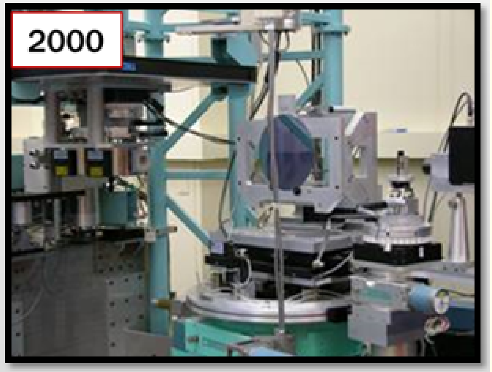
Penn St/Philips/IBM

Vertical powder goniometer and diffractometer

Philips (Norelco) goniometer and
Philips powder diffractometer
– patented by Parrish in 1947

Hanawalt Award, 1986

Bill Parrish developed the vertical powder goniometer and diffractometer, patented in 1947. Bill personally worked on almost every aspect of this instrument and this because the dominant powder diffractometer used in much of the world in the 60's through the 80's. Later improvements included stepping motors and improved detectors that resulted in digital positions and intensities. The latter were required for microstructural studies and quantitative analysis.



Methods for the production of high quality powder patterns –

- specimen preparation,
- data collection,
- data analysis and
- methods to identify and quantify

Development of NBSAIDS83 for the analysis of powder patterns, including crystallography and chemistry

Development of certified standard reference materials for powder diffraction techniques

Published 2,098 high quality reference patterns

Howard McMurdie

National Bureau of Standards

Established ICDD NBS Research Associateship 1948-1986

Methods for the production of high quality powder patterns

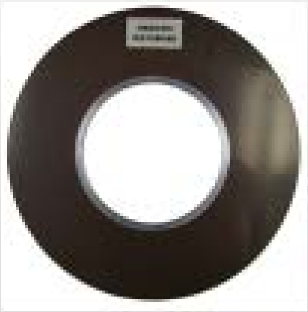
Barrett Award 1999

McMurdie Award established in 2000

With the birth of the JCPDS-ICDD and Powder Diffraction File in 1941, there was a need for high quality references and methods of analysis. The JCPDS-NBS Research Associateship was developed in 1941 and continued to 1986. The associateship developed methods, references and certified reference standards. The work on certified standards continues today at NIST. For most of its lifetime the Associateship was directed by Howard McMurdie and many notable scientists worked at the Associateship or collaborated with the efforts.

Innovation ! – 1986-87
CD-ROM

1971
Ferrite disk
2.5 MB
~ 7,025 entries



1986
Cards

46,000 entries

1987
CD-ROM
<1GB
46,000 Entries

2016
DVD
28 GB
9 GB
Inorganic
19 GB
Organic
952,957 Entries

As with many fields of science, the introduction of personal computers with fast processors and large storage capacities (CD-ROM) dramatically changed our ability to analyze materials. Early data disks (left) and computers of the 1970's were very limited. By 1986 the Powder Diffraction File™ contained 46,000 entries that needed to be put in a large file cabinet. In 1987, with the introduction of CD-ROM technology, the database fit on a small disk. Today, databases with 952,957 entries and hundreds of millions of d-spacings can be put on a memory stick.

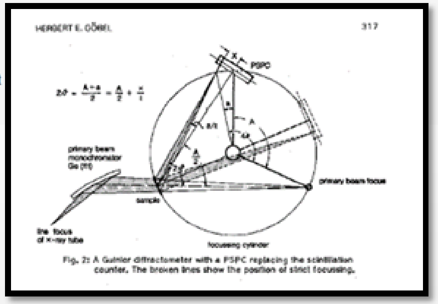
1980

X-Ray diffractometer with high time resolution

Patent number: 4301364

Abstract: An x-ray diffractometer is disclosed having a position-sensitive detector which is quasi-continuously movable in stepped fashion around a sample by a stepping motor. Output signals triggered by x-ray quanta are output from the position-sensitive detector and converted by an electronic evaluation unit into a time duration corresponding to a position of a particular x-ray quantum in the detector. The time-digital converter connected to the evaluation unit converts the time duration to a digital signal. A digital adder is provided having three inputs. The first input connects to an output of the time-digital converter, the second input connects to receive a digital value generated by a counter associated with the stepping motor, and a third input connects with a digital region selector. An output of the adder connects to a multi-channel analyzer having a plurality of regions therein for analyzing various desired measurement applications.

Type: Grant
Filed: February 21, 1980
Issued: November 17, 1981
Assignee: Siemens Aktiengesellschaft
Inventor: Herbert Goebel



1999

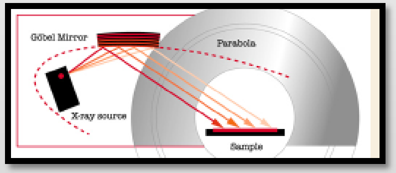
X-ray analysis apparatus with a graded multilayer mirror

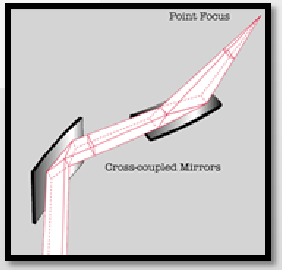
Patent number: 6226349

Abstract: An X-ray analysis apparatus having a curved paraboloid-shaped curved graded multilayer Bragg reflector (5) is characterized in that the layers of the reflector (5) are directly introduced onto a concave curved surface of a paraboloid-shaped hollow substrate and a maximum allowable shape deviation for the concave substrate surface facing the reflector is &Dgr;p={square root over (2px)} &Dgr;&thgr;R, and having a maximum allowable waviness Δ y Δ x = 1 2 Δθ R and a maximum allowable roughness &Dgr;y=d/2&pgr;, preferentially &Dgr;y≦0.

Type: Grant
Filed: July 19, 1999
Issued: May 1, 2001
Assignee: Bruker AXS Analytical X-Ray Systems GmbH
Inventors: Manfred Schuster, Herbert Goebel, Carsten Michaelsen, Ruediger Bormann

Bruker-AXS



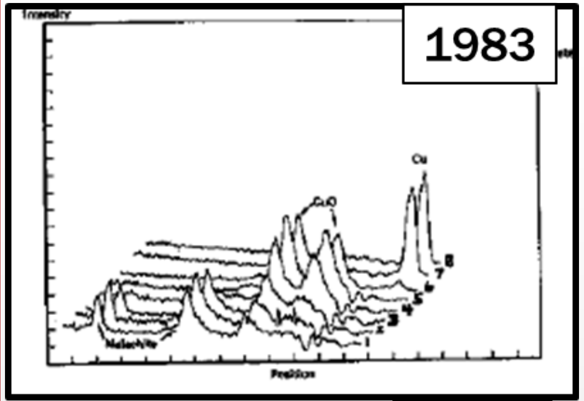


Herb Goebel
Siemens R&D Laboratories

Fast and time resolved diffraction
X-ray diffractometer with position sensitive detectors

Graded-Multilayer Mirror Optics (Goebel Mirrors)

Hanawalt Award 1998



Insert

In-situ catalyst analysis conducted at The Dow Chemical Company using the Goebel optic design in 1983.

INNOVATION…….A major development in the late 1970's and early 1980's was the use and application of position sensitive detectors. Herb Goebel helped develop the first commercial systems for time resolved diffraction. Nearly two decades later he made another major contribution with the development of high photon efficiency graded multilayer optics.

The development of high speed detectors opened up new areas of analysis capability – this included dynamic solid state chemistry investigations, in-situ experiments, and on-line production analyses, all of which were rapidly developed in the 1980's.

Pattern Indexing

Runge - 1917
Hull and Davey - 1921
Ito - 1949
automated indexing
de Wolff - 1963
de Wolff and Visser – 1966
Ishida and Watanable - 1967
Visser – 1969
Louër and Louër – 1972
Werner - 1985

ICDD Grantees 1949-2000

P. M. de Wolff – 243 references
J. Visser – 346 references
D. Louër – 344 references

Louër, D., and Louër, M., 1972."Méthode d'essais et erreurs pour l'indexation automatique des diagrammes de poudre" [Trial and error method for automated indexing of powder patterns]. J. Appl. Crystallogr. 5, 271-275.

Louër, D., Auffrédic, J.-P., Langford, J. I., Ciosmak, D., and Niepce, J.-C., 1983. "A precise determination of the shape, size and distribution of size of crystallites in zinc oxide by X-ray line-broadening analysis." J. Appl. Crystallogr. 16, 183-191.

Louër, D., and Langford, J.I., 1988. "Peak shape and resolution in conventional diffractometry with monochromatic X-rays, J. Appl. Crystallogr., 21, 430-437.

Louër, D., Louër, M., and Touboul, M., 1992. "Crystal structure determination of lithium diborate hydrate, LiB2O3(OH).H2O, from X-ray powder diffraction data collected with a curved position-sensitive detector." J. Appl. Crystallogr. 25, 617-623.

Langford, J. I., Boultif, A., Auffrédic, J.-P., and Louër, D., 1993. "The use of pattern decomposition to study the combined X-ray diffraction effects of crystallite size and stacking faults in ex-oxalate zinc oxide." J. Appl. Crystallogr. 26, 22-33.

A. Boultif and D. Louër "Powder pattern indexing with the dichotomy method", J. Appl. Crystallogr. (2004). 37, 724-731

Daniel Louër
University of Rennes, France

Automated indexing, structure determination, and line profile analysis

>200 Publications

1992 Hanawalt Award

2013 EPDIC Award for Outstanding Research

In the early years, scientists could manually index high symmetry materials (cubic metals and salts) to help solve crystal structures. The process was much more intensive for low symmetry systems. Mainframe computers, minicomputers and finally PC's greatly enriched our ability to index materials. Several notable scientists contributed to this effort through decades of hard work. We and others have noted the work of Daniel Louer, who developed the dichotomy method. Daniel not only developed the method, but taught scientists areound the world how to index materials.

1941-1985

Precision d-spacings (5-6 significant figures)

NBS/NIST Standards for accuracy and precision, instrument calibration

Digital intensities and profiles

Time resolved diffraction

Automated pattern indexing

Improved phase identification

Quantitative Analysis

Microstructural Analysis

By the 70th anniversary of the powder diffraction method, we could now determine precision d-spacings. Intensities and profiles were digitally recorded. There was time resolved diffraction and computer automated indexing methods. Commercial standards available through NIST could be used to calibrate and normalize an enormous variety of instruments and opitical configurations. These developments led to improved phase identification, quantitative analysis and microstructural analyses.

FREVEL, L. K. (1965). Computational aids for identifying crystalline phases by powder diffraction. Anal. Chem. 37, 471-482.

NICHOLS, M. C. (1966). A Fortran II program for the identification of X-ray powder diffraction patterns. Report UCRL-70078. Lawrence Livermore Laboratory, CA, USA.

JOHNSON, G. G. JR & VAND, V. (1967). A computerized powder diffraction identification system. Ind. Eng. Chem. 59, 19-26.

FREVEL, L. K., ADAMS, C. E. & RUHBERO, L. (1976). A fast search-match program for powder diffraction analysis. J. Appl. Cryst. 9, 199-204.

MARQUARDT, R. G., KATSNELSON, I., MILNE, G. W. A., HELLER, S. R., JOHNSON, G. G. JR & JENKINS. R. (1979). Search-match system for X-ray powder data. *J. Appl. Cryst.* 12,629–634.

EDMONDS, J. W. (1980). Generalization of the *ZRDSEARCH- MATCH* program for powder diffraction. J. *Appl. Crystallogr.* 13,191-192.

FREVEL, L. K. (1982). Structure-sensitive search-match procedure for powder diffraction. *Anal. Chem.* 54,691-697.

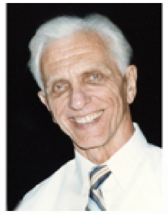
CHERUKURI, S. C. & SYNDER, R. L. (1983). Comparison of the Hanawalt and Johnson-Vand computer search/match strategies. *Adv. X-ray Anal.* 26, 99-104.

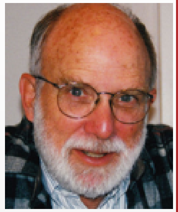
GOEHNER, R. P. & GARBAUSKES, M. F. (1983). Computer-aided qualitative X-ray powder diffraction phase analysis. *Adv. X-ray Anal.* 26, 81-86.

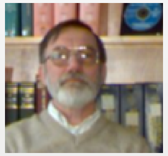
MARQUART, R. G. (1986). *]~PDSM:* mainframe search/match on IBM PC. *Powder Diffr.* 1, 34-39.

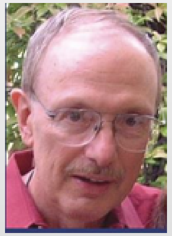
JENKINS, R. & HOLOMANY, M. (1987). *PC-PDF:* a search/display system utilizing the CD-ROM and the complete Powder Diffraction File. *Powder Diffr.* 2, 215-219.

CAUSSIN, P., NUSINOVICI, J., BEARD (1988) D.W., Using Digitized X-ray Powder Diffraction Scans as Input for a New PC-AT Search/Match Program, Adv. X-ray Anal., 31, 423-430









Robert Snyder and Ron Jenkins

Automated Phase Identification
(mainframes to PC)

Concepts of

- **Full pattern analysis**
- **Identification by peak location *and* by their absence using full patterns**

While dozens of experts contributed to automated phase identification we highlighted Ron Jenkins and Bob Snyder, both of whom, lectured globally and frequently published. They developed, taught and promoted methods of analysis

The availability of computers attracted many scientists to develop automated methods of material analyses. Early work with mainframe computers in the 1960's by Frevel, Nichols and Johnson transitioned to VAX computers and then to personal computers. As the CPU and storage capability increased, algorithms increased in sophistication. In this 40 year development two important concepts arose, the use of whole patterns (requiring more CPU) and identification using both peak locations and peak absence. These concepts are now embedded in nearly all modern search/match algorithms.

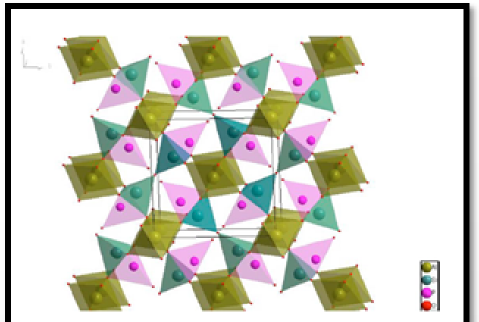
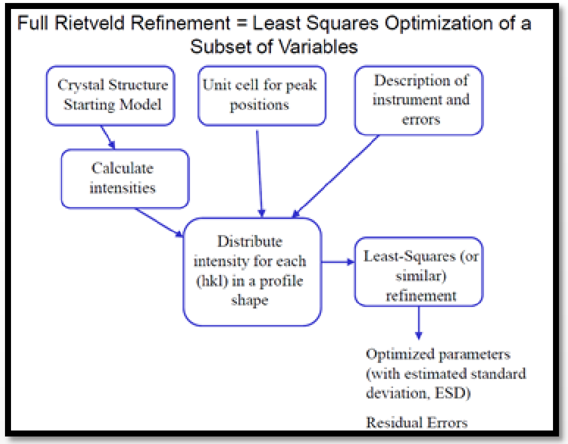


Figure 1. (Color online) The crystal structure of mullite viewed approximately down the *c* axis. The partially occupied Al4 site is designated "P" to permit plotting in a different color.



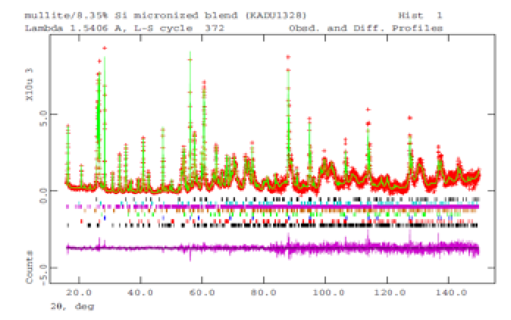


TABLE III. Quantitative phase analysis.

Phase	Raw wt %	Scaled wt %	True wt %
Mullite ($Al_{4.85}Si_{1.18}O_{9.77}$)	72.90(7)	71.11	77.60(7)
Quartz (SiO_2)	8.46(4)	8.25	9.00(4)
Silicon (Si)	8.57(3)	8.36	-
Rutile (TiO_2)	1.14(3)	1.11	1.20(3)
Cristobalite (SiO_2)	0.42(3)	0.41	0.45(3)
Kyanite (Al_2SiO_5)	3.81(10)	3.72	4.06(10)
Zircon ($ZrSiO_4$)	0.04(1)	0.04	0.04(1)
Corundum (Al_2O_3)	4.63(9)	-	-
Amorphous		7.00	7.65(14)

Structure Refinement

Quantitative Analysis !

"Line Profiles of Neutron Powder-diffraction Peaks for Structure Refinement." (Rietveld, H.M.(1967). Acta Crystallogr., 22,151-2

"A Rietveld Tutorial" J. Kaduk Powder Diffraction 24, 4, December 2009, pp 351-361

Hugo Rietveld

The Rietveld Method

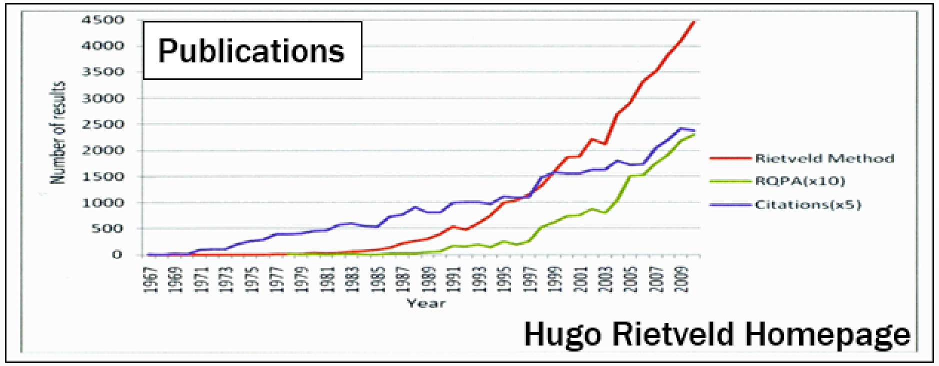
Barrett Award 2003

EPDIC Outstanding Researcher 2010

Aminoff Award 1995

1969 Rietveld structure refinement
(milestone #15 – Nature Magazine, 100 Years

The Rietveld Method, utilizing line profile analysis, automated structure refinement, quantitative analysis of mixtures, and many microstructural analyses. This is a common tool used in modern powder diffraction facilities. Hugo Rietveld originally developed the method for neutron diffraction but it was quickly adapted for laboratory X-ray and synchrotron applications.



J. Rodriguez-Carvajal, "Fullprof Program," Physica B, Vol. 192, No. 1-2, (1993), pp. 55-69.

A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (1994).

T. Roisnel, J. Rodriguez-Carvajal, "WinPLOTR: a Windows tool for powder diffraction patterns analysis", Materials Science Forum, Proceedings of the Seventh European Powder Diffraction Conference, EPDIC 7, (2000), p.118-123

A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (2000).

B. H. Toby, EXPGUI, a graphical user interface for GSAS, J. Appl. Cryst. 34, 210-213 (2001)

J. Cui, Q. Huang and B. H. Toby "Magnetic structure refinement with neutron powder diffraction data using GSAS: A tutorial" (2006) Powder Diffraction, 21(1), pp 71-79

Robert Von Dreele, Juan Rodriguez-Carvajal and Brian Toby

Applications of The Rietveld Method

Laboratory, Neutron and Synchrotron Analyses

Magnetic Structures
Protein Structures

Von Dreele -Barrett Award 2009

Rodriguez-Carvajal – Barrett Award 2011

Toby – Barrett Award 2013

INNOVATION !.................. The power and applicability of the Rietveld method to several types of analysis spurred further innovation and development. Robert Von Dreele, Juan Rodrigues and Brian Toby have improved the technique and broadened the scope to include more types of materials and more types of analyses. They continue to incorporate new improvements so that the GSAS and Fullprof programs now handle a wide variety of radiation types, instrument designs and optical configurations. These programs are available worldwide.

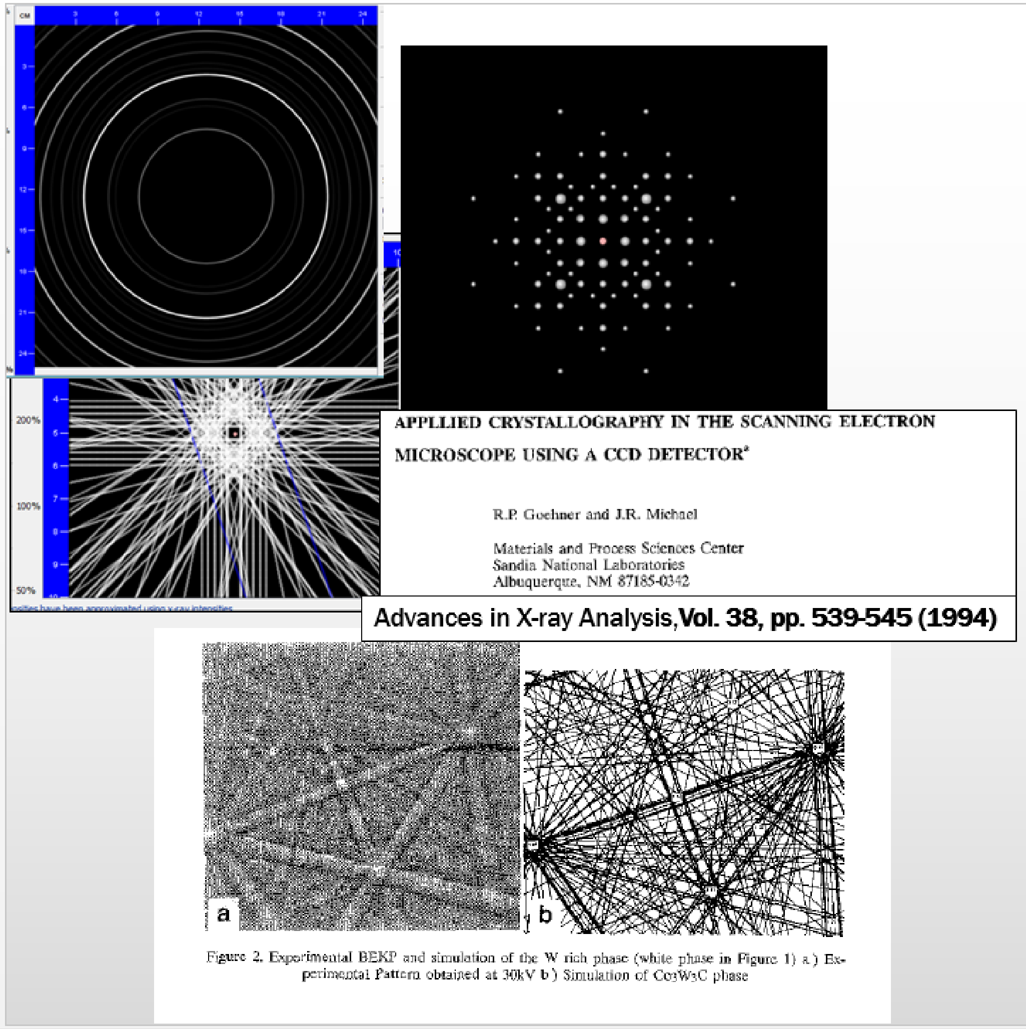
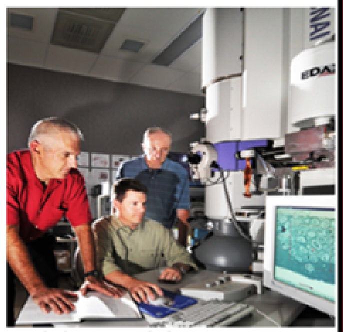


Figure 2. Experimental BEKP and simulation of the W rich phase (white phase in Figure 1) a) Experimental Pattern obtained at 30kV b) Simulation of Co_3W_3C phase



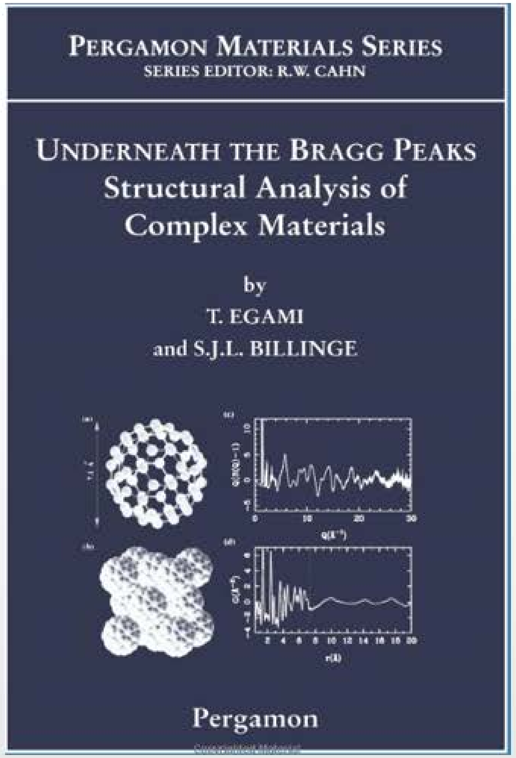
Sandia's material characterization analysts (from left to right) Joseph Michael, Paul Kotula, and manager Ray Goehner (photo by Randy Montoya).

Joe Michael and Ray Goehner

Electron Diffraction Analyses

Hanawalt Award 2001

Diffraction in a microscope ! Joe Michael and Ray Goehner led the way and automated both conventional methods with high resolution electron microscopy (spot and ring patterns – single and multigrain diffraction) and with electron backscatter patterns (EBSD). This expanded upon the early work of Guinier (electron microprobe) and the electron diffraction work of groups at Sandia, IBM, NBS and the JCPDS-ICDD (i.e. Stalick, Carr, Anderson et. al.).



Cover illustration is taken from Billinge, S. J. L., Petkov, V., Proffen, Th., "Structure on different length scales from powder diffraction: the real-space pair distribution function (PDF) technique", Commission on Powder Diffraction of the International Union of Crystallography Newsletter, number 24 (2000).

Simon Billinge, Tom Blanton, Takeshi Egami

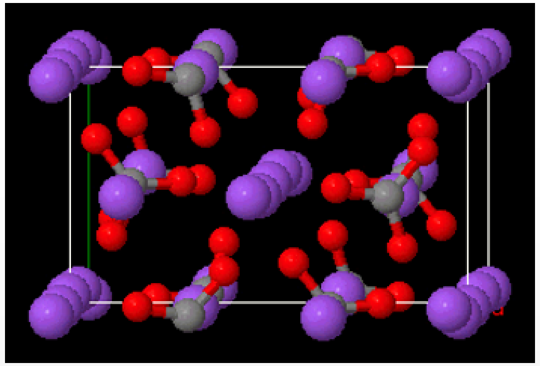
Simon Billinge and Takeshi Egami

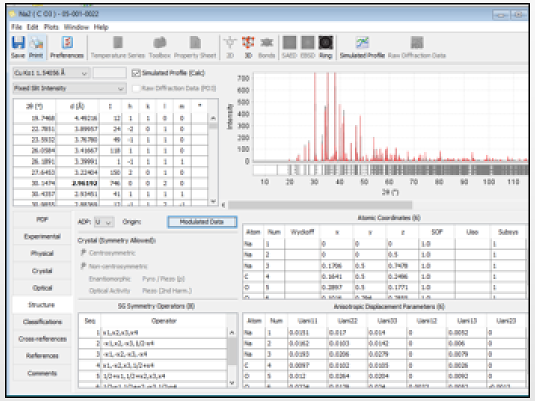
Pair Distribution Function Analysis

2010 Hanawalt Award

Similar to some of the other developments, the theory of Pair Distribution Function Analysis was developed in the 60's but the practice has now come to fruition with commercial equipment and automated analyses. Takeshi Egami and Simon Billinge were innovators in developing the theory and then putting the theory to practice. Development continues as PDF analysis gets combined with synchrotron analyses of non crystalline systems, in-situ analyses of dynamic systems, and electron diffraction analyses in a microscope

"Sodium carbonate revisited". Michael Dusek, Gervais Chapuis, Mathias Meyer and Vaclav Petricek Acta Crystallogr., Sec. B: Struct. Crystallogr. Cryst. Chem. 59, 337 (2003).





4,5,6 dimensional indexing
Superspace groups

Na2 (C O3) - 05-001-0022

Positional Displacement Parameters (8)

Atom	Axis	WV ID	Cos	Sin
C	y	1	0.0009(7)	0.0589(6)
Na1	y	1	0	0.0567(4)
Na2	y	1	0	0.0656(4)
Na3	y	1	-0.0057(4)	0.0687(3)
O13	x	1	-0.0184(3)	-0.0275(2)
O13	y	1	0.007(5)	0.077(4)

"The modulated structure of gamma-Na_2CO_3 in a harmonic approximation." van Aalst W., den Hollander J., Peterse W. J. A. M. and de Wolff P. M. Acta Crystallogr., Sec. B: Struct. Crystallogr. Cryst. Chem. 32, 47 (1976)

Vaclav Petricek

Modulated Structures

Barrett Award 2013

Modulated structures were first described in the 1950's, where modulations in an atomic structure are caused by factors such as atom displacement, vacancies and thermal motions. Superspace groups and 4,5 or 6 dimensional indexing were required to describe modulated systems. Vaclav Petricek developed the mathematics and an analytical program, JANA, to identify and classify new modulated materials. This works has led to a basic understanding of the unusual physical properties demonstrated by these materials, such as ion conductivity and superconductivity.

Scardi, P. and Leoni, M. (2001). "Diffraction line profiles from polydisperse crystalline systems," Acta Crystallogr. A57, 604–613.

Scardi, P. and Leoni, M. (2002). "Whole powder pattern modeling," Acta Crystallogr. 58, 190–200.

Scardi, P. and Leoni, M. (2004). "Whole Powder Pattern Modelling: theory and applications," in Diffraction Analysis of the Microstructure of Materials, edited by E. J. Mittemeijer and P. Scardi, Springer Series in Materials Science, Vol. 68, Springer-Verlag, Berlin, pp. 51–92.

Scardi, P., Leoni, M., and Delhez, R. (2004). "Line broadening analysis using integral breadth methods: a critical review," J. Appl. Crystallogr. 37, 381–390.

Scardi, P. and Leoni, M. (2006). "Line profile analysis: pattern modelling versus profile fitting," J. Appl. Crystallogr. 39, 24–31.

Grain size distribution of nanocrystalline systems Journal

Paolo Scardi, Matteo Leoni, Diego G. Lamas and Edgardo D. Cabanillas

Powder Diffraction / Volume 20 / Issue 04 / December 2005, pp 353 - 358
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DOI: http://dx.doi.org/10.1154/1.2135309 (About DOI), Published online: 01 March 2012

Diffraction line profile from a disperse system: A simple alternative to Voigtian profiles Journal

P. Scardi, M. Leoni and J. Faber

Powder Diffraction / Volume 21 / Issue 04 / December 2006, pp 270 - 277
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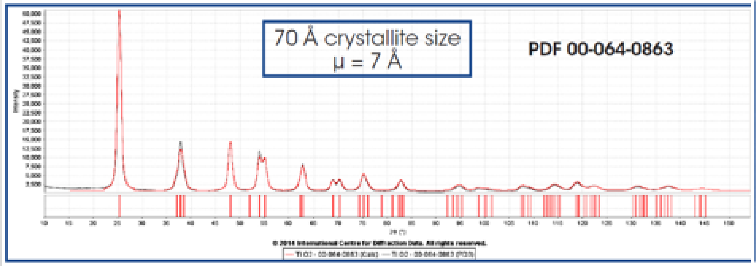
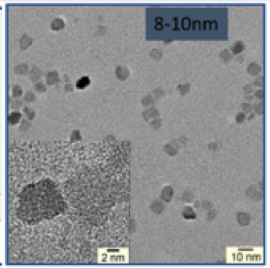
DOI: http://dx.doi.org/10.1154/1.2358359 (About DOI), Published online: 01 March 2012





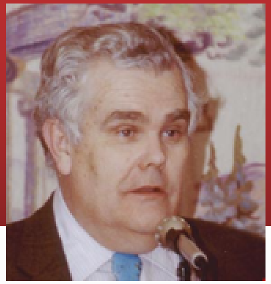
Paolo Scardi and Matteo Leoni

Nanocrystalline Systems

Hanawalt Award 2016

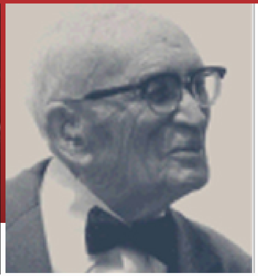
Paolo Scardi and Matteo Leoni have the development of whole pattern analysis methods used to study the microstructure of materials. They deepened our knowledge of nanomaterial systems.

Notable Developments

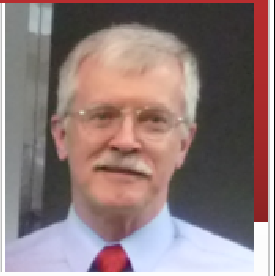


Deane Smith

Harold Klug



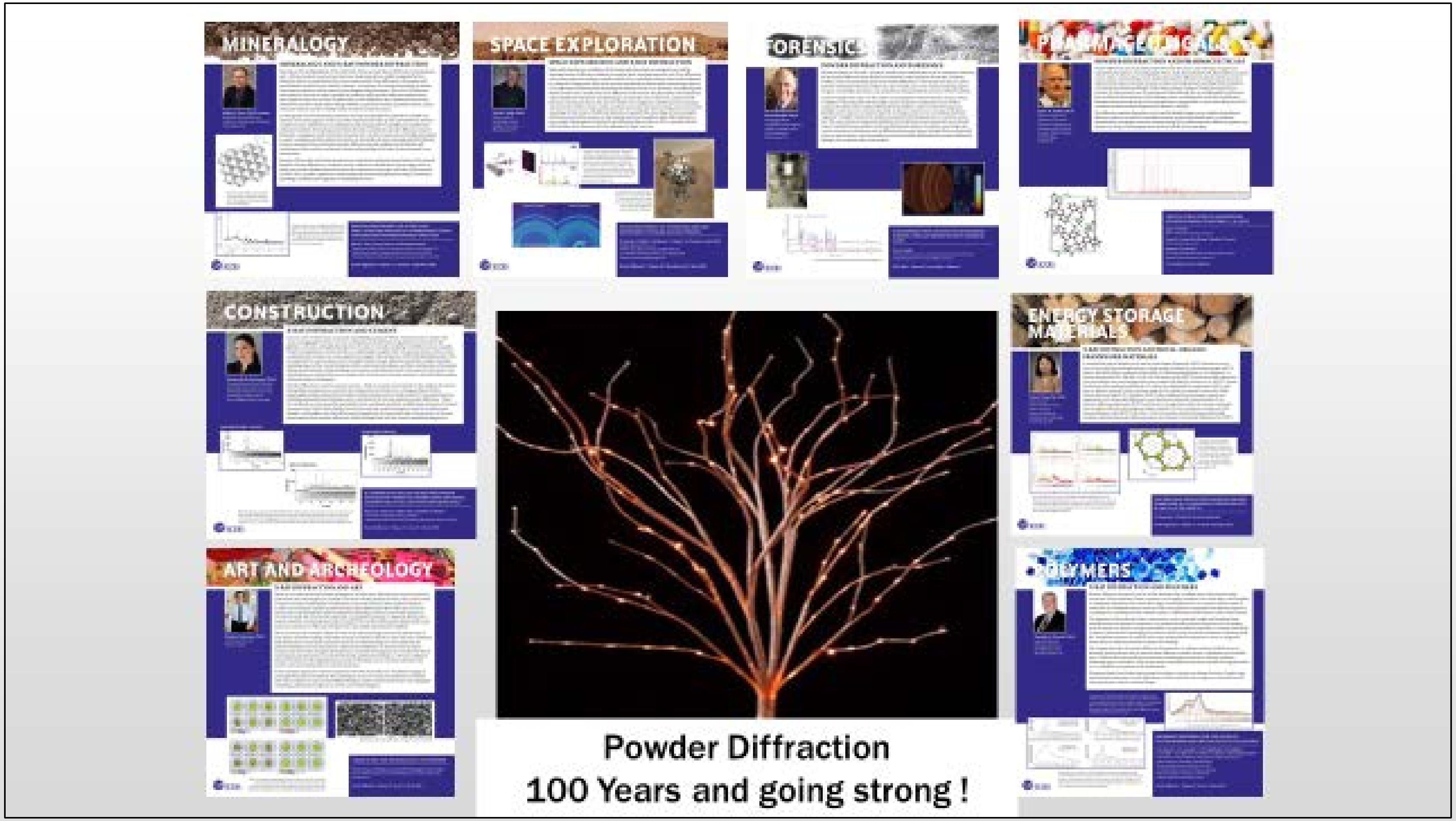
Charles Barrett



Dave Bish

Year	Author	Development
1927	F. Zernicke and J.A. Prins	The diffraction of x-rays in liquids, pair distribution function
1927	C.J. Davisson, L.H. Germer	Observation of electron diffraction
1936	D.P. Mitchell, P.N. Powers, H. von Halban, P. Preiswerk	Observation of neutron diffraction
1942	C. S. Barrett	Structure of Metals
1948, 1974	H. P. Klug and L.E. Alexander	X-ray Diffraction Procedures
1966	D. K. Smith	Powd: Calculation of powder patterns
1977	C. O. Ruud	Stress Measurements with a PSD
1988	A. LeBail	Pattern deconvolution/matching methods
2000	R.B. Von Dreele, P.W. Stephens, G.D. Smith, R.H. Blessing	First protein structure from powder diffraction
2005	P. Sarrazin, D. Blake, S. Feldman, S. Chipera, D. Vaniman and D. Bish	MARS Rover XRD/XRF

The field of powder diffraction has had thousands of contributors, only a few of which have been highlighted in this presentation. The above works have been cited by many scientists as significant contributions.



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100 Years and Still Going Strong !

Powder Diffraction is used to analyze materials throughout the world.
The next 100 years should be amazing.

About this presentation

Dr. Tim Fawcett has been the Executive Director of the International Centre for Diffraction Data since 2001. As Executive Director, he has directed and participated in the dramatic growth of the Powder Diffraction File to >950,000 entries, which is now used by scientists in over 120 countries. He is a frequent international guest lecturer on diffraction methods. In 2009, he received the Jenkins Award for Lifetime Achievement in the advancement and use of X-rays for materials analysis. Prior to the ICDD, Dr. Fawcett worked 22 years in the analytical and corporate research laboratories of The Dow Chemical Company. In 1987 he was part of a Dow team that won an IR-100 Award for the invention of the DSC/XRD/MS instrument.

Authors note: By working at both The Dow Chemical Company and the ICDD, I have been fortunate to personally meet many of the scientists mentioned in this presentation. As a young scientist in the late 70's I joined The Dow Chemical Company and was quickly encouraged to join the International Centre for Diffraction Data. At Dow, some of the original hardware, index books, data records and film archives established since the 1930's were still in use. As a member of the ICDD, I met many of the international scientists and innovators who defined and grew the field of powder diffraction.

About the International Centre for Diffraction Data (ICDD)…… The full name of the ICDD is JCPDS-International Centre for Diffraction Data as amended in 1978. The organization was previously called JCPDS (Joint Committee for Powder Diffraction Standards) from the 1969 articles of incorporation as a non-profit organization. Prior to 1969 the organization was ASTM – JCPDS, where the JCPDS was operated as a commercial arm of ASTM (American Society of Testing Materials). JCPDS was the producer of the Powder Diffraction File in 1941 (slide 19). Wheeler Davey was the first chairman, 1941-1956.