

microscopy), A. V. Crewe (high-intensity electron guns and scanning microscopy), U. Valdré and M. J. Goringe (special stages) and K.-H. Hermann *et al.* (image recording). Septier's contribution is particularly clear and informative, containing a number of worked examples, and that of A. V. Crewe is timely in view of the great interest in field-emission electron guns.

The middle section of the book is introduced by accounts of the interaction of the beam with crystalline material by A. Howie and R. Gevers. This is followed by contributions from L. M. Brown (metallurgical information) and M. J. Makin (radiation damage studies) which demonstrate their fields of application. M. J. Goringe discusses computing methods. The final contribution to this section by Goringe and C. R. Hall contains 22 problems which range over the preceding material and enhance the value of the whole section.

In the final part of the book are lectures by F. A. Lenz (transfer of image information), F. Thorn (phase contrast) A. C. van Doorsten (amorphous and macromolecular objects), C. R. Hall (small clusters), R. H. Wade (Lorentz microscopy) and D. Wohlleben (magnetic phase contrast).

Thus the book presents a comprehensive survey of the power of the electron microscope as a tool in Materials Science. The Organizers of the School and the lecturers are to be congratulated on presenting the material in a way that will stimulate use of the power rather than reverence of it. The book is handsomely produced and strongly bound, which is well, for it will surely get the use it deserves.

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Book Received

The following book has been received by the Editor. Brief and generally uncritical notices are given of works of marginal crystallographic interest; occasionally a book of fundamental interest is included under this heading because of difficulty in finding a suitable reviewer without great delay.

Handbook of Geochemistry.
Vol. II/3. Editorial board: C. W. CORRENS, D. M. SHAW, K. K. TUREKIAN, J. ZEMANN. Executive editor: K. H. WEDEPOHL. New York: Pp.

600 approx. Springer-Verlag, 1972. Price (Looseleaf binder) DM 258, U.S. \$ 81.80 (Subscription, price DM 206,40, U.S. \$65.50).

This work is in loose-leaf form and is issued in instalments. Each section of Volume II deals with either a single element, or sometimes a group of related elements. The sections are written by different authors and are issued as they are received by the publishers so that they must be rearranged in correct sequence by the reader. For each element there is a chemical and physical description, an account of the natural occurrence in minerals and a reference section.

Meeting Report

Conference on Phase Analysis: Identification and Quantitative Determination. Hull, 5-7 April 1972.

The Crystallography Group of the Institute of Physics devoted its 1972 Spring Conference to Phase Analysis: Identification and Quantitative Determination. The meeting, held in the Physics Department of the University of Hull from 5-7 April, covered in four sessions the following topics: phase identification and characterization, quantitative determination and data processing, instrumentation and indexing. There were 125 participants - several from abroad - drawn from industry, research laboratories and Universities.

The first session opened with an invited paper by Professor H. P. Rooksby (University of Leeds) and Dr E. A. Kellert (The General Electric Company Limited). Professor Rooksby described the unique role played by X-ray diffraction as part of an analytical partnership. The importance of the photographic method, in particular the Debye-Scherrer technique, was stressed, since in an industrial environment many specimens are not amenable to powder diffractometry. The non-destructive aspect of the Debye-Scherrer method was emphasized together with the possibilities of examination *in situ* and the importance of the additional information which may be recorded on a film.

The power of the X-ray technique when used in conjunction with other analytical methods such as microprobe analysis, emission spectroscopy, infrared absorption and even Curie-temperature

measurements was illustrated by a variety of applications ranging from the non-destructive identification of small inclusions to more complex problems involving thin-film composition and semiconducting devices. It was shown that although X-ray powder methods can identify the presence of various phases, other techniques such as X-ray spectrochemical or microprobe analysis are required to obtain the atomic composition of each phase. The importance of correct characterization was stressed by Dr G. F. Claringbull (British Museum) in his introductory address and illustrated by Dr J. H. C. Hogg and Dr H. H. Sutherland (University of Hull) in their paper on the indium-sulphur/selenium/tellurium systems, in which they showed by X-ray single-crystal studies that four reported phases previously identified by X-ray powder methods had been assigned incorrect formulae.

An investigation of the cadmium-copper-zinc ternary system, undertaken by Mr R. D. Nicholson, Dr P. H. Spriggs and Mr K. A. Stubbs (University of Manchester) showed that the previously reported Laves phase quoted for the equi-atomic alloy Cu-Cd-Zn was an f.c.c. phase obtained during investigation of the pseudo-binary system γ -CuCd and γ -CuZn. The attempted preparation of the equi-atomic alloy resulted in two cubic phases one of which was related to δ -CuZn₃ by the ordered substitution of cadmium.

At a time when the uncertainty in lattice parameters is one part in 10⁵ or 10⁶, Mr L. Zwell (Joint Committee on Powder Diffraction Studies, Swarthmore) pointed out that often the chemical characterization and homogeneity of the materials are not known to one part in 10⁴. Inaccurate data, from poorly prepared or inadequately characterized specimens, inevitably cause failure in efforts to relate various properties of materials to either the presence and quantitative distribution of phases, or the electronic structure and relative sizes of the atoms in solid solutions. He described the change in the lattice parameter of α -iron by the addition of titanium and manganese, showing how this is related to density. This work was further coordinated with Curie temperature measurements and results from shear-stress experiments. Mr Zwell made the plea for more accurate density determinations as an aid to specimen characterization - a point which was frequently made by other speakers including Dr Shirley and Professor Lipson.

The analytical partnership mentioned by Professor Rooksby was illustrated specifically in six subsequent papers and appeared as one of the main themes throughout the conference.

Dr I. F. Ferguson (United Kingdom Atomic Energy Authority) utilizing both X-ray diffraction and scanning electron microscopy examined the coatings of silicon carbide on nuclear-fuel granules prepared in a fluidized bed to obtain information on the phases present and on crystallite size, shape and strain: evidence for the existence of disordered α -SiC was obtained. In an investigation of the action of lead compounds as stabilizers against thermal decomposition during the blending and fabrication of PVC, Mr E. W. J. Mitchell (Associated Lead Manufacturers) described how X-ray Guinier and diffractometer measurements had been used together with optical microscopy. It has been shown that the inhibition of decomposition depends upon the milling lubricant together with the amount of plasticizer used in the PVC blend. The complex lead salts formed as a result of the reaction between the basic lead stabilizer and the milling lubricant were shown to be soluble and mobile in the plasticizer by the appearance of a crystalline phase formed at nucleation sites away from the sites of the basic lead stabilizer crystals. This product phase was thought to be a new and unidentified form of lead chloride.

The use of X-ray diffraction, electron-probe microscopy and optical microscopy in the analysis and identification of an unusual clinopyroxene occurring as a minor phase in iron ore sinters was described by Mr D. J. Dyson (British Steel Corporation). The material consisted of more than 90% of the hypothetical Tschermaks molecule, whereas synthetic pyroxenes contain 30–50% and naturally occurring pyroxenes even less.

An interesting application of optical and X-ray analysis was given by Dr G. J. L. Griffin and Mr D. K. Majumdar (Brunel University) who inserted needle, plate and lath-shaped crystals in polymer melts to monitor the flow occurring during extrusion processes. They investigated the effects of crystallite growth occurring during the cooling of the melts and derived approximate quantitative relationships between the aspect ratio of the needles and laths and the degree of perfection of X-ray diffraction patterns. Total orientation of lath-like crystals dispersed in a polyethylene melt extruded through a rectangular orifice

has been observed, the resultant polymer ribbon being to all crystallographic purposes a mosaic single crystal.

A situation where field ion microscopy proved more useful than X-ray diffraction was described by Mr R. Sinclair and Dr J. A. Leake (University of Cambridge) who investigated the mechanism of the decomposition of a supersaturated nickel–titanium solid solution showing that the formation of γ' -Ni₃Ti did not proceed in a classical manner *via* an intermediate pre-precipitate stage. γ' -Ni₃Ti was shown by field ion microscopy to be formed from a continuous ordering process concurrent with the spinodal decomposition of the nickel–titanium solid solution. The two phases, γ' and the depleted solid solution, were clearly identified and characterized by field ion microscopy at a much earlier stage in the aging sequence than by X-ray diffraction.

Opening the second session on quantitative determination Professor P. M. de Wolff (Technische Hogeschool, Delft) outlined the theoretical basis for the principle that the volume fraction of a crystalline compound in a mixture is proportional to the intensity of its diffraction lines; the various methods of quantitative determination depend on the measurement of the proportionality constant. The two main methods of analysis described were the internal-standard technique, in which a fixed proportion of a known material is admixed with the unknown sample, and the absolute reflexion measurement using a powder diffractometer, where a pure reference sample of the unknown phase is required to calibrate the diffractometer. In order to place all published powder data on the same relative intensity scale it was suggested that authors should make a 1:1 mix with some standard such as α -Al₂O₃ (corundum) and report the relative intensity of the strongest line for each pattern as proposed by the JCPDS. Professor de Wolff went on to discuss the detection and attempted elimination of preferred orientation, together with the problems of particle absorption.

The quantitative analysis of Portland cement poses many difficulties which were outlined by Dr W. A. Gutteridge. He described the various X-ray methods which have been devised for this analysis, amplifying and extending Professor de Wolff's paper. In particular he dealt with the development of Fourier analysis techniques as applied to diffractometer output and with the work carried on at the Cement and Concrete Associa-

tion utilizing data from mixtures of synthetic cement minerals in conjunction with the internal-standard method. Because data were collected using a diffractometer, the problem of generator stability was stressed and the effect on the final analysis of background subtraction, sample positioning and misalignment between the standard and measured data was examined. Autoclaved cement-quartz materials are of great use in the building industry and in thermal insulation. Professor H. F. W. Taylor (University of Aberdeen) detailed the way in which X-ray diffractometry using an internal-standard technique has been used in conjunction with a least-squares fitting procedure to determine quantitatively tobermorite and other phases in the autoclaved material. Although difficulties were experienced because the phases involved vary in crystallinity it has definitely been shown that the highest compressive strengths are not associated with those samples containing the highest percentage of tobermorite.

Mrs J. E. Forsyth (Pilkington Brothers) determined the percentage crystallinity and hence the reaction rates occurring in the manufacture of glasses such as float glass and fibreglass by analysis of intensity information gained using a Guinier focusing camera. The X-ray method compared favourably with DTA measurements. However the former was preferred since the information obtained was more detailed, allowing a rapid qualitative and semi-quantitative analysis of minor phases. X-ray analysis showed that whilst the major phase present during the melting reaction is quartz the next most common phase is α -cristobalite, a result at variance with previous thin-section and optical microscopy which had suggested that tridymite was more important. In another study of the crystallization of glasses Dr F. P. Glasser (University of Aberdeen) gave evidence for the existence of a new ternary phase in the Na₂O–BaO–SiO₂ system; its formula, Na₂Ba₄Si₁₀O₂₅, obtained as a result of single-crystal studies, density measurements and phase-equilibrium determinations disagrees with existing data on the system. From quantitative X-ray powder diffractometry studies Dr Glasser was able to follow and suggest a mechanism for the kinetics of the crystallization process.

In view of the health hazard involved in the airborne transfer of asbestos materials it was timely to hear Mr A. L. Rickards (Turner Brothers Asbestos

Co.) describe two X-ray diffraction techniques using internal and external standards with detection limits of 50 and 10 μg respectively of chrysotile asbestos deposited on membrane filters. The method, although developed for chrysotile estimation, can be applied to other substances where a sample can be obtained on a membrane filter, being particularly suitable for the investigation of airborne materials. Since permissible atmospheric dust levels vary for different types of asbestos, it is important from the health point of view to be able to characterize asbestos minerals quickly and accurately. Mr G. Plowman described work undertaken to this end by the Central Electricity Generating Board using X-ray diffraction techniques which have proved superior to infrared and thermal analysis. Data have been collected on standard reference asbestos samples from the International Union Against Cancer; the effect of heat on these standards, the resulting changes in composition and structure and the influence of these on the powder patterns were investigated since in industrial applications asbestos might be maintained at high temperatures for thousands of hours.

The detection and characterization of amounts of material in the microgram range have obvious applications not only in the environmental health situation, as shown by Mr Rickards, but also in other fields. In the section of the conference dealing with equipment Drs E. Dykes and J. C. Elliot (London Hospital Medical College) described a unique modification of the toroidal camera enabling it to be used as a powder diffraction camera. The resolution is comparable with that of the Guinier camera but less sample is required, the minimum amount being much less than 100 μg . The camera was used to study the process involved in the formation and destruction of the mineral components of bone and dental enamels where the ability to detect less than 2% by weight of impurities is particularly important. Dr J. B. Nelson described an X-ray diffractometer, produced by McCrone Research Associates, capable of producing powder patterns from less than 10 μg of material. This extremely flexible instrument with specimen holders capable of handling a very wide range of sample types has provision for both photographic and counter recording. Up to 40 patterns encompassing a variable 2θ range of 22.5° can be recorded on one strip of standard 35 by 280mm film curved to conform to the Brentano focusing circle.

Dr Nelson, showing numerous applications, stressed the importance of the two-dimensional nature of photographic recording as opposed to the one dimensional diffractometer record, a point made by several other speakers.

Professor Rooksby in his opening paper had stated that the X-ray diffractometer, by virtue of its construction, is not always suited to the rather harsh extremes of an industrial environment. However, Mr J. C. Nutter (Applied Analysis Ltd.) described a novel form of diffractometer containing no moving parts, designed for industrial use with continuously presented sample strands. A white radiation X-ray source is used and X-rays diffracted at a chosen angle are measured by a lithium-drifted silicon detector with sufficiently high energy resolution to separate the various diffraction peaks. The spacings present in the material are thus measured rapidly and simultaneously. As a bonus the detector also records the characteristic fluorescent spectra of the elements present in the sample.

Considerable discussion was provoked by a low-cost hard-wire system for the automatic control of a powder diffractometer built by Mr M. T. Frost (Royal School of Mines) and Mr D. G. Whitehead (University of Hull). As described, the paper-tape-controlled configuration does not have the flexibility of a computer-based system but can be built for about £1000 and should be of interest to laboratories with limited funds.

The first paper specifically related to computer programming was presented by Dr I. F. Ferguson (UKAEA). He described a comprehensive suite of some 30 programs for correcting and extracting information from powder diffraction data. Since this system required 4 years to develop, Dr. Ferguson suggested that a national approach to the problem of crystallographic computer programming should be adopted.

A paper by Dr G. S. Johnson (Pennsylvania State University) described a computer search/match program for the identification of unknown phases using the JCPDS powder diffraction file of over 21000 standard reference patterns stored on magnetic tape. The program input parameters consisting of the measured spectra from the unknown phase together with a large range of other data including any chemical information such as elemental or functional groups were listed. The reference file is searched using mathematical criteria selected either by the user or the program. Under

ideal conditions the program is capable of identifying seven components of a complex mixture in less than one minute on an IBM 360/65; quantitative analysis is only possible in the few instances where the JCPDS file contains the *corundum* data. A computer system in which the powder patterns are represented by a 2900-dimensional vector was described by Mr J. Fiala (Central Research Institute, Plzen). Various criteria similar to those of Johnson are used to provide the possible solutions. Dr I. F. Ferguson and Mr T. E. Hughes (British Nuclear Fuels Ltd.) giving a user's experience of a search program reported that in speed of operation a human operator is superior if only one phase is present. Mr Hughes concluded that whilst the computer system is a useful assistant, provision should be made for considerable operator intervention and the resulting computer output analysed carefully and critically. During the identification, the chemical information should be used with caution unless X-ray fluorescent or spectrographic analyses are available to support the findings. To limit the number of possible solutions it was suggested that a sufficiently large range of interplanar d spacings should be measured, for example all the data on a Guinier film, and the error window in the d value should be as small as possible. To this end good experimental technique to reduce errors is very important, a point made repeatedly by other speakers. Additional difficulties were experienced because of inaccuracies in the powder file and the fact that the method cannot cope with solid solutions or materials which are not included in the JCPDS file.

The fourth session on indexing opened with the presentation by Professor H. Lipson (University of Manchester Institute of Science & Technology) of an interesting invited paper on the art of the derivation of unit-cell dimensions from powder photographs. After a brief review of the graphical methods he showed the beauty of Bradley's technique using numerical methods to solve the structure of Ni_3Al . This led to many numerical methods including that of Ito. Professor Lipson, stressing that the worker in this field must adopt a critical approach, gave a series of guide lines: the experimental data obtained from a large radius camera should be accurate to about 3 in the fourth decimal place in $\sin^2 \theta$; the determined unit cell must be sensible; there should be a reasonable number of lines present with any absences making sense; and the density

must be measured to an accuracy of about 0.2%. He also advised the adoption of some criterion of correctness such as the M_{20} function of Professor de Wolff. Professor Lipson expressed surprise at the small influence the computer had had to date in the development of methods of indexing. However, a use of the computer was described by Dr R. Shirley (University of Surrey) who systematically examined the first 23 solutions in order of probability obtained using a powder indexing program on data from a single compound. Disturbingly, at first sight all 23 solutions appeared almost equally plausible and in fact any of these would almost certainly have been accepted for publication. After a plea for the strengthening of the criteria of correctness he repeated that it is well worth spending as much time measuring the density accurately as in measuring the powder pattern as this provides a powerful means of locating the correct unit cell.

A different aspect of the problem was presented by Dr J. I. Langford, Miss G. F. Marriner and Professor A. J. C. Wilson (University of Birmingham) who described the various methods for systematically ascribing indices to reflexions on powder patterns. Dr Langford made a plea for some measure of the accuracy of powder data, suggesting that the error in θ should be included in published work as a matter of routine, stressing that with the increasing use of computer search techniques to identify powder patterns a knowledge of the error in line positions is of extreme importance. He also emphasized that there is no substitute for good experimental technique and that time spent on sample preparation, camera alignment and film processing is time well spent. An inter-

esting geometrical approach to the problem of indexing powder patterns was outlined by Mr D. J. Dyson (British Steel Corporation). The method, in an early state of development, involves use of a computer together with operator intervention to reconstruct the reciprocal lattice from the measured d values. Again, accuracy of the experimental data was one of the main limitations.

The concluding paper was by Dr R. Bucksch (AEG Telefunken, Frankfurt) who presented an algebraic method for the determination of compatible reciprocal nets from selected-area electron-diffraction patterns. By this method it is also possible to gain information on the number of phases present in the sample under investigation.

The points emerging as important from this conference are not new; in the main they concern problems which have bedevilled crystallography since its inception. Dr Claringbull in the opening address mentioned the problem of specimen characterization in connexion with the pre-ASTM ore mineral lists of Harcourt. The X-ray powder method, he said, could very easily identify the presence of a particular phase or compound but other methods of analysis must be used to ensure the correct characterization of the material, a point further stressed by Professor Rooksby and others during the conference. One aspect of this problem was detailed by Mr Zwell of JCPDS, who emphasized that to strive for accuracy in lattice parameter measurements in excess of the accuracy of specimen characterization was a wasted effort.

Accuracy in general was a theme running through a great many papers. The increasing use of computer search programs for the identification of powder

patterns is dependent upon accurate measurement of line positions as well as accuracy in the JCPDS file. The importance of good experimental technique to minimize errors was constantly stressed and the suggestion was made that published powder data should include some estimate of accuracy. Authors were further urged to adopt the $///_{\text{corundum}}$ system proposed by the JCPDS in order to place line intensities on the same relative basis which would facilitate quantitative analysis.

The most disturbing item of the conference was contained in the paper by Dr Shirley in which he revealed the multiplicity of plausible unit cells obtained as a result of computerized analysis of the powder pattern of a single phase. The fact that an accurate measurement of the density helped in the elimination of the incorrect solutions only served to underline the point made by several other speakers that the benefits accruing from a knowledge of the density make its accurate determination of overwhelming importance.

Instruments and techniques extending the detection limit of the powder method into the 10 μg range have many potential applications and together with such devices as the energy dispersive diffractometer and the automated diffractometer will serve to extend further the already manifold variety of fields in which X-ray analysis has gained an indispensable position.

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