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$$\frac{|F^+|^2 - |F^-|^2}{r''}$$

the same for all wavelengths (Karle, J, 1984, *Acta Cryst* A40, 1-4). In a process called REVISE observed anomalous intensities are modified, taking into account their standard deviations, so that the relationship is obeyed. Pre-processing the data with REVISE improves the results obtained with AGREE and ROTATE.

Using three-wavelength Photon Factory data with the structure of core streptavidin (Hendrickson, W A, Pähler, A, Smith, J L, Satow, Y, Merritt, E A and Phizackerley, R P, 1989, *Proc Nat Acad Sci* 86, 2190-2194) the best results gave a mean phase error of 54.3° for 4,018 reflections with a map correlation coefficient of 0.549.

Finally, criteria are suggested for the selection of suitable wavelengths for multi-wavelength anomalous scattering to give the best conditions for defining phases.

02.03 – Strategies for *ab initio* Structure Determination
from Powder Data

MS-02.03.01 DIRECT DETERMINATION OF POWDER STRUCTURES BY ENTROPY MAXIMISATION AND LIKELIHOOD RANKING. By G. Bricogne, Department of Molecular Biology, Biomedical Centre, Box 590, 751 24 Uppsala, Sweden; and LURE, Bâtiment 209D, 91405 Orsay, France.

Classical direct methods for structure determination from single-crystal data are based on the derivation of intensity statistics and of probabilistic relations between structure factors. The three-dimensional indexing of the observed data is deeply embedded both in the formal structure of these relations and in their computer implementations.

The hallmark of the powder diffraction field, on the other hand, is the phenomenon of intensity overlap which spoils this indexing scheme to a considerable and irreparable extent. The direct determination of powder structures therefore requires a new formal framework in which the internal book-keeping of the statistical relations between structure factors would be decoupled from the mode of presentation of the data. The method of phase determination based on entropy maximisation and likelihood ranking [Bricogne (1984), *Acta Cryst.* A40, 410-445; Bricogne & Gilmore (1990), *Acta Cryst.* A46, 284-297] does fulfill this criterion, in that phase relations result from maximising entropy while the data are consulted by likelihood evaluation. Extending this method to powder data – and to data from other disordered specimens such as fibres – is then simply a matter of deriving the likelihood criterion adapted to the pattern of intensity overlap corresponding to each type of specimen disorder.

This lecture will describe the mathematical techniques by which this goal was achieved [Bricogne (1991), *Acta Cryst.* A47, 803-829]. It will be shown that the loss of information caused by intensity overlap in powder diagrams may be put on the same footing as the usual loss of phase for single-crystal data by a judicious use of a multiplicity-weighted metric and of the *n*-dimensional spherical geometry associated with that metric. Structure determination from powder diffraction data is thus cast in the form of a *Hyper-Phase Problem* in which the dimensionality varies from one data item to another. This geometric picture enables probability distributions for overlapped intensities to be derived not only under the standard assumption of a uniform distribution of random atoms – thus extending Wilson's statistics to powder data – but also for non-uniform distributions such as those occurring in maximum-entropy phase determination. The corresponding conditional probability distributions and likelihood functions are then derived. The possible presence of known fragments is also considered.

Besides yielding the desired extension of the aforementioned direct method, and thus enabling the *ab initio* determination of crystal structures from powder data, these new distributions and likelihood functions will be shown to lead to new methods of data normalisation; to new statistical tests for space-group assignment; to a generalisation of the partial-structure recycling method; and to a new criterion for conducting crystal structure refinement against powder data.

This analysis was implemented as part of a long-standing collaboration with Chris Gilmore and coworkers [Gilmore, K. Henderson & Bricogne (1991), *Acta Cryst.* A47, 830-841] and has been the basis of a rapidly growing number of *ab initio* determinations of inorganic and organic crystal structures from X-ray powder diffraction data [Tremayne, Lightfoot, Mehta, Bruce, Harris, Shankland, Gilmore & Bricogne (1992), *J. Solid State Chem.* 100, 191-196; Tremayne, Lightfoot, Glidewell, Harris, Shankland, Gilmore, Bricogne & Bruce (1992), *J. Mater. Chem.* 2, 1301-1302; Shankland, Gilmore, Bricogne & Hashizume (1993), *Acta Cryst.* A49, in the press; Lightfoot, Tremayne, Harris, Glidewell, Shankland, Gilmore & Bruce (1993), *Material Science Forum*, in the press].

Current developments are directed towards the application of the multichannel maximum-entropy formalism [Bricogne (1988), *Acta Cryst.* A44, 517-545] which will enable the method to deal more

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exactly with heterogeneous structures, and also with neutron powder diffraction data.

The geometric treatment and the analytical results derived in this work [Bricogne (1991), *loc. cit.*] can also be applied to the harmonic overlap problem which affects single-crystal data collected by the Laue method

MS-02.03.02 DETERMINATION OF MOLECULAR CRYSTAL STRUCTURES ON A LABORATORY POWDER DIFFRACTOMETER. P. Lightfoot*, M. Tremayne, K. D. M. Harris and P. G. Bruce, Department of Chemistry, University of St Andrews, St Andrews, Fife, Scotland.

Many problems in materials chemistry require detailed structural information about the materials under study. Traditionally such information has been obtained by single crystal X-ray diffraction, however, many materials cannot be obtained in single crystal form. In recent years it has been shown that simple crystal structures can be determined *ab initio* by powder diffraction techniques, often at a synchrotron source (A. K. Cheetham and A. P. Wilkinson, *J. Phys. Chem. Solids*, 1991, 52, 1199). However, in order for the technique to become viable as a more routine tool for day-to-day use, a strategy for structure determination on laboratory-based powder diffractometers is required. We are currently testing existing methods for structure determination by X-ray powder diffraction on a state-of-the-art laboratory-based diffractometer (P. Lightfoot et al., *J. Mater. Chem.*, 1992, 2, 361; P. Lightfoot et al., *J. Chem. Soc. Chem. Commun.*, 1992, 1012; M. Tremayne et al., *J. Solid State Chem.*, 1992, 100, 191; M. Tremayne et al., *J. Mater. Chem.*, 1992, 2, 1301). We shall present examples covering a range of moderately complex structures, including both organics and organometallics, such as $C_2H_4N_2O_2$, $[(C_5H_5)Fe(C_5H_4)CH_2NMe_3]^+I^-$ and $PhSO_2NH_2$, chosen to illustrate the strategies of structure solution and refinement involved. Our experience suggests that laboratory-based powder diffractometer data will be invaluable in obtaining useful structural information for materials where sufficiently large single crystals cannot be grown.

MS-02.03.03 TEXTURE CORRECTION OF POWDER DATA FOR AB INITIO STRUCTURE DETERMINATION. By R. Peschar* and H. Schenk. Laboratory for Crystallography. University of Amsterdam. The Netherlands and P. Capkova. Faculty of Mathematics and Physics. Charles University. Prague. Czechoslovakia.

The crystal structure determination from powder data by means of Direct Methods relies on the crystallite distribution being random. Deviations caused by the non-uniformity of the distribution can obstruct the solution of the structure by *ab initio* methods. In general texture correction requires the knowledge of the complete structure and the orientation distribution function, for example via pole-figure measurements. Therefore, an alternative texture correction procedure will be presented, based on a statistical analysis of the deconvoluted intensities, which needs neither a structural model nor pole-figure measurements. The texture correction procedure is valid for disc- or rod-shaped crystallites and requires the use of a specimen spinner to ensure axial symmetry. The only information being necessary, besides the indexed powder pattern, is the contents of the unit cell. Under the above assumptions the texture function P_H can be modelled as a simple exponential form involving a single adjustable parameter G ,

$$P_H(\varphi_h) = \exp[-G \sin^2(\varphi_h)]$$

in which the texture direction $\underline{h} = (hkl)$ makes an angle φ_h with a reflection $\underline{h} (hkl)$. Both the texture direction H and the parameter G can be established by means of a least-squares analysis of the integrated intensities. The influence of symmetry-equivalent reflections will be discussed and test results will be presented which demonstrate the potential use of the new method for *ab initio* structure determination from powder data.

MS-02.03.04 SIRPOW.92: A USEFUL TOOL FOR SOLVING CRYSTAL STRUCTURES FROM POWDER DATA. By A. Altomare, G. Cascarano, C. Giacovazzo*, A. Guagliardi, Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche, CNR, c/o Dipartimento Geomineralogico, Universita' di Bari, 70124 Bari, Italy.

A Direct Methods package optimized for powder data is described. It is able in most cases to overcome the difficulties generated by reflections overlapping and, in some degree, by preferred orientation. Among the main characteristics: a) both neutron and X-ray data can be treated; b) care is taken over reflection overlapping, and strategies are designed in order to reduce its effect on the phasing process; c) weak reflections are suitably exploited; d) a procedure for automatic partial refinement of the structure is designed; e) care is taken over the preferred orientation. Several experimental tests have been performed which prove the usefulness of SIRPOW.92.

MS-02.03.05 STRUCTURE SOLUTION FROM POWDER DIFFRACTION DATA - INCORPORATING PRIOR CHEMICAL KNOWLEDGE By W I F David and M A Estermann, ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, OXON., OX11 0QX, U.K.

Prior chemical knowledge can play a crucial role in structure determination from powder diffraction data. Structure factor data can rarely be extracted from even a high resolution powder diffraction pattern without severe overlap, particularly in the important d-spacing range of 1.0Å to 1.5Å. This usually leads to the failure of conventional crystallographic techniques since atomic resolution has not been obtained. In contrast most powder diffraction patterns are still relatively free of overlap at d-spacings above 2.5Å. This paper focusses on exploiting the combined use of these longer d-spacing reflections with available prior chemical knowledge. A number of algorithms for structure solution are presented that are based upon locating larger structural elements. Examples will be principally drawn from the analysis of silicate framework structures and small organic molecules.