

## 02-Methods for Structure Determination and Analysis, Computing and Graphics

**PS-02.08.16** HOW TO IMPROVE QUARTET ESTIMATES: A SIMPLE STRATEGY. By C. Giacovazzo, Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche, CNR, c/o Dipartimento Geomineralogico, Università di Bari, 70124 Bari, Italy; M.C. Burla\*, Dipartimento di Scienze della Terra, Università, 06100 Perugia, Italy.

In some recent papers new attention has been devoted to the role of the quartet invariants in the phasing procedures. The main drawbacks of their use are: the strong correlation with triplet invariants and the relative weakness of the formulas estimating quartets. If triplets are estimated with high accuracy [e.g., from P10 formula (G. Cascarano, C. Giacovazzo, M. Camalli, R. Spagna, M.C. Burla, A. Nunzi and G. Polidori, *Acta Cryst.*, 1984, A34,278-283) or from physical measurements or from isomorphous data] then this information can be transferred into quartet estimates, which can be so evaluated with larger accuracy without any penalty in computing time. The first applications will be shown.

**PS-02.08.17** NEW STRATEGIES FOR DIRECT METHODS: THE ACTIVE USE OF NEGATIVE TRIPLETS, NEGATIVE QUARTETS AND PSI-ZERO TRIPLETS. By G. Cascarano and C. Giacovazzo\*, Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche, CNR, c/o Dipartimento Geomineralogico, Università di Bari, 70124 Bari, Italy.

The joint probability distribution method described in two recent papers (C. Giacovazzo, M.C. Burla and G. Cascarano, *Acta Cryst.*, 1992a,b, A48,901-906, 906-912) has been considered in order to obtain a function which is maximized by the true crystal structure. The phasing process is carried out by maximizing such a function via a modified tangent refinement: this implies the active use of negative triplet and quartet relationships. More recently a method has been derived (C. Giacovazzo, *Z. f. Krist.*, 1993, 000-000) which suggests an active use of *psi-zero* triplets. These, combined with positive and negative triplets and with negative quartets, give rise

to a function which is maximized by the true structure. The theory and the applications of such a new strategy are described.

**PS-02.08.18** INTEGRATION OF PATTERSON AND DIRECT METHODS: ABOUT THE USE OF INTERATOMIC TRIANGLES. By A. Altomare, C. Giacovazzo, A.G.G. Moliterni\*, Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche, CNR, c/o Dipartimento Geomineralogico, Università di Bari, 70124 Bari, Italy.

In some recent papers (C. Giacovazzo, *Acta Cryst.*, 1991, A47-256-263; A. Altomare, G. Cascarano & C. Giacovazzo, *Acta Cryst.*, 1992a,b, A48,30-36,495-500) probabilistic formulas were obtained which estimate triplet invariants given prior information on non-Harker or on Harker peaks. The formulas require prior information on the value of the interatomic vectors and on their peak intensity. It is now possible to integrate Direct Methods with a further information: the existence of interatomic triangles. The final formula estimating a triplet invariant will depend on the location of the Patterson peaks and on their intensities. Triplet phase estimates lying everywhere between 0 and  $2\pi$  are allowed.

**PS-02.08.19** XTAL3.2: A CRYSTALLOGRAPHIC SOFTWARE SYSTEM James M. Stewart University of Maryland, College Park MD; Sydney R. Hall University of Western Australia, Nedlands Australia; Keith D. Watenpaugh The Upjohn Co. Kalamazoo MI; Howard D. Flack University of Geneva, Geneva, Switzerland; Douglas M. Collins The Naval Research Laboratory, Washington DC; David A. Grosse Wright State University, Dayton, OH;

Xtal3.2 package is an international development project involving about 40 researchers over a full spectrum of crystallographic interests. This development has been supported by many national and international agencies and commercial institutions since the first version in 1983. The 1992 release, Xtal3.2, contains software for 90 different calculations. These range from the processing of raw diffraction data to interactive molecular graphics, atomic charge estimation, electronic publication preparation, and the structure solution and refinement of small and macromolecules.

Xtal3.2 may be installed on any computer or OS. The standard distribution is a single 1/2 inch magnetic tape with implementation and application documentation. A customized version is also available for PCs on disks. The versatility and portability of the Xtal package is particularly important in the increasingly common networked computing and workstation environments.

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Xtal3.2 includes 30 programs especially for macromolecular calculations. Additional applications are under development. Current macromolecular programs include merging and scaling of multiple data sets from heavy-atom derivatives; MIR phasing; geometrically constrained refinement (PROLSQ); energy minimization restrained refinement (CEDAR); density modification; maximum entropy phasing; and forward and reverse fast-Fourier transform calculations. All programs are symmetry general. Soft interfaces to other packages such as PRODO, XENGEN, SCHAKAL, MOGLI, SHELX and Mathematica are also incorporated. §

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**PS-02.08.20 SOFTWARE SYSTEM FOR MICROCRYSTALLOGRAPHY WITH WHITE SR LAUE METHOD.** By K.Hagiya (1), T.Takase (2), Y.Shimizugawa (3), K.Ohsumi (4), M.Miyamoto (2) and M.Ohmasa (1)

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For structural studies of very small crystals with the sizes of submicrometer range, the Laue method combined with synchrotron radiation (SR) has been proved to be a powerful tool (K.Ohsumi et al., 1991, J. Appl. Cryst., 24, 340-348). A software system to deal with the Laue pattern recorded on an imaging plate (JP: Fuji Co. Ltd; J. Miyahara et al., Nucl. Instrum. Methods, 1986, A246, 572-578) has been developed and successfully applied to some inorganic materials (K.Ohsumi et al., 1992, Rev. Sci. Instrum., 63(1), 1181-1184).

The software systems for the Laue method have been developed and applied to many cases of protein crystals (for example; J.R.Helliwell et al., 1989, J. Appl. Cryst., 22, 483-497), but it is unsuitable to inorganic materials in the sense of precise determination of crystal structures.

The features of the present software is that the intensities of Laue spots which are superposition of several Bragg reflections are used as observed values in the course of least-squares refinement of the structure, and an evaluation of the result obtained by this refinement is made.

The procedure of data processing and structure refinement are shown below.

### Data processing

1. determination of indices of Laue reflections based on interplane angles.
2. simulation of the Laue pattern to confirm indices assigned.
3. refinement of crystal orientation based on coordinates (x, y) of Laue spots on IP, with parameters of camera length, origin of IP, inclination of IP and axial ratio of the sample.
4. integration of intensities with determination of background level.

### Refinement of a structure

1. data correction for absorption and extinction if necessary.
2. refinement of the structure based on intensities of Laue spots by minimizing R

$$R = \frac{\sum_h |I_0(h) - k \cdot I_C(h)|^2}{\sum_h |I_0(h)|^2}, \quad \sigma^2(p_i) = M_i^{-1} \left( \frac{\sum_{j=1}^n W_j \Delta_j^2}{m-n} \right)$$

considering such factors as, structural parameters, polarization of incident white SR, spectrum of incident white SR, and quantum efficiency of IP with respect to the wavelength.

3. evaluation of the whole process of the refinement based on the comparison of observed and calculated structure factors,

$$r = \frac{\sum_h |I_0(nh) - I_{FC}(nh)|}{\sum_h |I_0(nh)|}, \quad |F_0(nh)| = \left( |I_0(nh)| \times \frac{I_C(h)}{I_0(h)} \right)^{1/2}$$

and symmetry related reflections

$$R_{eq} = \frac{\sum_{i,j} |I_0(h_i) - I_0(h_j)|^2}{\sum_i |I_0(h_i)|^2}$$

**PS-02.08.21 SYMMETRY TESTING DURING LEAST-SQUARES REFINEMENT.** By H.D. Flack, Laboratoire de Cristallographie, University of Geneva, 24 quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland.

One is aware from the work of R.E. Marsh and others of the fairly frequent occurrence of the publication of structures in a space group of lower symmetry than that really necessary for the diffraction data used in the structure refinement. Symmetry testing programs such as Le Page's *MISSYM* enable potential cases of incorrect symmetry to be detected from the assumed space group, the cell dimensions and the refined atomic coordinates. However a robust methodology for quantifying the deviations (and their statistical significance) of a structure in one space group from that in another are clearly lacking. The poster will present the first steps in the development of such a suitable technique and some practical tests of its application. The basis of the technique is to split the electron density of the model into a fully symmetric part and an 'anti-symmetric' component premultiplied by a global population parameter. The 'anti-symmetric' component expresses the deviations of the low space-group symmetry structure from the best expression of the diffraction data that can be obtained in the high-symmetry space group. Such a decomposition respects Marsh's criterion that the atomic electron density representation in the low- and high-symmetry space groups should be identical in order to avoid an implicit 'anharmonicity' being interpreted as an explicit 'non-centrosymmetry'. The correct treatment of any potential twinning is another essential element of the method. Test examples are drawn from the literature e.g. 1,8 octanediamine dihydrobromide,  $C_8H_{20}N_2 \cdot 2HBr$  [Brisson, J. and Brisse, F. (1984) *Acta Cryst.* C40, 1405-1407]. It will be shown that the use of a realistic atomic model is essential to the treatment of such cases. The question of the quantification for non-centrosymmetric space groups of their polarity and/or enantiomorphism is also being considered.

**PS-02.08.22 A SYSTEMATIC STUDY OF COORDINATE PRECISION IN X-RAY STRUCTURE ANALYSIS: INDICATORS OF STRUCTURAL PRECISION FOR USE WITH THE CAMBRIDGE STRUCTURAL DATABASE.** Jason C. Cole\* and Judith A.K. Howard, Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK and Frank H. Allen, Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Experimental and structural features affecting the precision of the atomic coordinates of any atom A, as determined by X-ray analysis, were studied by Cruickshank [Acta Cryst. (1960), 13, 774-777]. He showed that  $\bar{\sigma}(A)$