

or

$$|F(H)| = |F(-H)| \quad \text{and} \quad \varphi(H) = -\varphi(H) + 2\pi HS, \quad (6b)$$

*i.e.*, if the center of symmetry does not coincide with the origin of the structure, the structure factors are affected by a phase shift of  $\exp(2\pi iHS)$ . Since the basis is fixed,  $H = (h, k, l)$  does not change. The structure factors, however, differ with respect to the enantiomorphic pairs.

The space groups of enantiomorphic structures are merohedral space groups that give rise to ambiguities with respect to handedness (Hahn & Klapper, 1992). To resolve these ambiguities, a suitable property, derivable from X-ray diffraction data, is needed (Burzlaff & Hümmner, 1988). This property can be expressed by a set of structure-factor moduli affected by anomalous dispersion or by a set of suitable triplet phases, as is shown below.

Before discussion of the triplets, it is convenient to discuss the implications connected with space groups of enantiomorphic structures and their normalizers. For enantiomorphic structures, two cases may be distinguished:

(i) The space group of an enantiomorphic structure is mapped onto itself, *i.e.* it does not 'feel' the enantiomorphic property. All space groups of this type have a normalizer (Euclidean or affine) that has a center of symmetry. Thus, it is convenient to use a center of symmetry of the normalizer for the mapping of the enantiomorphs onto each other (see above).

(ii) The space group of an enantiomorphic structure is mapped onto another so-called *enantiomorphic space group*. In this case, the normalizers are noncentrosymmetric groups. Inspection of the eleven pairs of enantiomorphic space groups, however, shows that they can be mapped onto each other by a center of symmetry placed in the origin, if the standard setting of *International Tables for Crystallography* (1992) is used.

Restrictions and special relations for structure-factor phases of enantiomorphic structures due to symmetry are treated explicitly by Koch (1986) (see also Koch & Fischer, 1992).

After this discussion, it can easily be seen that suitable triplet phases resolve the enantiomorphic ambiguity. By (6b), the following relations hold for any triplet  $H, K, -K-H$  with its triplet phase  $\Phi(H, K) = \varphi(H) + \varphi(K) + \varphi(-K-H)$ :

$$\begin{aligned} \Phi(H, K) &= \varphi(H) + \varphi(K) + \varphi(-K-H) \\ &= -\varphi(H) - \varphi(K) - \varphi(-K-H) \\ &\quad + 2\pi[H + K - (K + H)]S \\ &= -\Phi(H, K); \end{aligned} \quad (7)$$

thus, the experimental observation of  $\Phi(H, K)$  is equivalent to a determination of absolute structure. As was shown by Hümmner, Weckert & Bondza (1989) for benzil, suitable triplets can be found.

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*Acta Cryst.* (1995). **A51**, 92–94

**The use of the non-negativity criterion and histogram matching as figures of merit in direct methods of phase determination.** By CORNELIA SMYKALLA and PAUL T. BEURSKENS, *Crystallography Laboratory, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*

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#### Abstract

Two figures of merit for the selection of correct phase sets from a number of possible or trial phase sets are defined: (1) based on the criterion that significantly negative points should be sparse in electron-density maps; and (2) based on comparison of electron-density histograms with the theoretically expected histogram [Lunin (1993). *Acta Cryst.* **D49**, 90–99]. It is shown that both figures of merit are useful for judging random phase sets and useless for phase sets that originate from direct-methods procedures such as symbolic addition or tangent refinement.

#### Introduction

The first equation employed for direct phase determination, the inequality of Harker & Kasper (1948), is based on the non-negativity criterion: the electron-density function

must be zero or positive everywhere. The most important equations used in direct-methods procedures, however, are the triple-phase relationship and the tangent formula. They were derived from statistical considerations (*e.g.* Hauptman & Karle, 1953) and related to the Sayre (1952) equation, and are based on atomicity: the electron-density function consists of peaks (at discrete points) in otherwise almost empty space. We investigated the use of these two basic principles, non-negativity and atomicity, as figures of merit for trial phase sets, especially when a large number of phase sets has been generated.

#### The non-negativity criterion

The non-negativity criterion is not as powerful as atomicity (for a discussion regarding this topic, see Navaza & Navaza, 1992) but as it is not explicitly used in most

direct-methods procedures it can play a role in providing a figure of merit for the quality of a phase set. Define

$$G = \iiint_{xyz=0}^1 \min[\rho(x,y,z), 0] dx dy dz,$$

where  $\rho(x,y,z)$  is the electron-density calculated for a given phase set using a limited set of reflections  $hkl$ . A correct set of phases should lead to an electron-density map with no significantly negative peaks or regions.  $G$  is negative for any truncated data set (with limitations on  $\sin \theta$  and  $|E|$ ). For an incorrect set of phases, however,  $G$  will be more negative than expected for a correct set. Thus, the best phase sets are expected to be among the phase sets that have the least-negative  $G$  values.

### The atomicity criterion

The concept of atomicity is represented by the shape of the function  $\nu(t)$ , which is usually called the electron-density histogram (Zhang & Main, 1990; Lunin, 1993).  $\nu(t)$  is the relative frequency of finding a given value of  $t$  as a function of  $t$ , where  $t$  represents a small interval in the electron-density function  $\rho(x,y,z)$ . The histogram calculated for a given phase set, denoted  $\nu_c(t)$ , is compared with the theoretical functions  $\nu_{th}(t)$ , which is the histogram predicted for the structure at hand, using the same reflection set. The predicted histogram for a small structure is obtained using the calculated phases of a generated model structure with the same composition as the true structure and with realistic geometrical features (such as interatomic distances). As a simple figure of merit, we define

$$H = \int_{t=-\infty}^{\infty} [\nu_c(t) - \nu_{th}(t)]^2 dt$$

[Lunin (1993), equation (14) with weights  $w = 1$ ]. The best phase sets are expected to be among the phase sets that have the smallest  $H$  values.

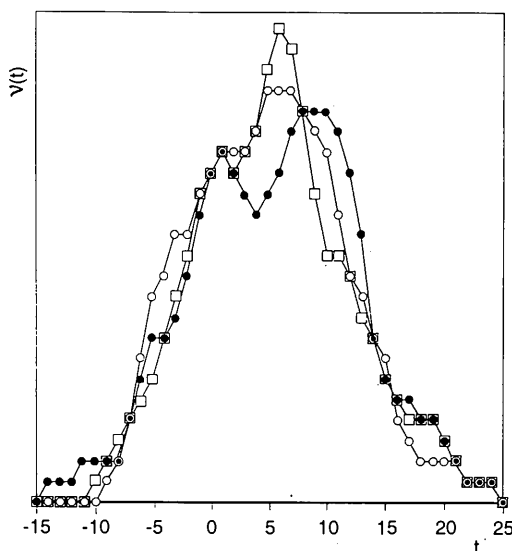


Fig. 1. Histograms for three phase sets.  $\square$   $\nu_{th}(t)$  for the correct set ( $\varphi_{true}$ );  $\circ$   $\nu_c(t)$  for an incorrect *MULTAN* phase set,  $\Delta\varphi = 86^\circ$ ;  $\bullet$   $\nu_c(t)$  for a phase set with large random errors,  $\Delta\varphi = 90^\circ$ .

Table 1. *Figures of merit for different phase sets (arbitrary scale)*

Phase set	$\Delta\varphi$ ( $^\circ$ )	$G$	$H$
Correct phases ( $\varphi_{true}$ )	0	-48	—
'Good' <i>MULTAN</i> results	21	-56	42
'Bad' <i>MULTAN</i> results	86	-54	43
Correct phases + random errors	20	-54	19
Correct phases + random errors	45	-58	62
Correct phases + random errors	90	-63	112

### Sampling the electron-density function

The two figures of merit,  $G$  and  $H$ , require an evaluation of electron densities at a limited number of points  $(x,y,z)$ . Test runs have shown that about 500 points usually are enough to obtain reliable approximations of  $G$  and  $H$ .

An efficient sampling strategy is to overlay the unit cell with a grid that is incommensurate with respect to the unit-cell dimensions. These grid points are defined by

$$x = a_1 + n_x b_1, \quad n_x = 1, 2, \dots, m_x$$

$$y = a_2 + n_y b_2, \quad n_y = 1, 2, \dots, m_y$$

$$z = a_3 + n_z b_3, \quad n_z = 1, 2, \dots, m_z,$$

where  $a_i$  and  $b_i$  ( $i = 1, 2, 3$ ) are chosen such that grid points neither coincide with special positions nor are mutually related by the space-group symmetry. The first condition prevents atoms at special positions disturbing the statistics, and the second condition ensures that the symmetry of the Fourier synthesis does not lead to redundant sampling points. The Fourier summations are evaluated for these grid points, using all reflections for which phases  $\varphi(hkl)$  are given or known.

### Test results

Test results are presented for one compound [ $C_{15}H_{16}N_2O_2S$ ,  $P2_12_12_1$ ,  $Z = 4$  (Noordik, Beurskens, Ottenhilm, Herscheid & Tjihuis, 1978)]. The 1684 structure factors were input to *MULTAN* (Main, 1985) and output reflection data sets consisting of 230 reflections with the largest  $|E|$  values were used for the test runs presented in Table 1 and Fig. 1. As Fourier coefficients, we used the observed structure factors with phases as indicated in the table. The quality of a phase set is expressed by the average phase error:

$$\Delta\varphi = \langle |\varphi_{true} - \varphi| \rangle,$$

where  $\varphi_{true}$  are the phases calculated from the known structural parameters and  $\varphi$  is the nearest (mod  $360^\circ$ ) to  $\varphi_{true}$ . Other phase sets for this structure and tests with other structures led to similar results.

### Concluding remarks

As expected, the tangent refinement leads to good and bad phase sets all showing 'atomicity' and the figures of merit  $G$  and  $H$  cannot distinguish between good and bad. On the other hand,  $G$  and  $H$  can be used as early figures of merit in 'random-phase' procedures, prior to the more time-consuming tangent refinements. More experience is needed for optimization of the procedures.

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### Space groups rare for organic structures. III. Symmorphisms and inherent molecular symmetry.

**Errata.** By A. J. C. WILSON, *Cambridge Crystallographic Data Centre, Cambridge CB2 1EZ, England*

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#### Abstract

A check of the tables in the paper by Wilson [*Acta Cryst.* (1993), **A49**, 795–806] has revealed errors in three of them and the use of outdated symbols in a fourth.

*Table 4.* In the column 'Tending to antimorphism', the entry  $P4_2cm^0$  occurs twice. The second entry should be  $P4_2nm^0$ .  $P4mc^0$  should be  $P4_2mc^0$  and two more entries,  $P4/mnc^0$  and  $P4_2/nm^0$ , should be added to this column.

*Table 6.* The entry for the nonexistent space group  $P6_3cc^0$  should be deleted.

*Table 7.*  $Id\bar{3}\dagger$  should be  $Ia\bar{3}\dagger$ . The row for the arithmetic crystal class  $432P$  should read:

$432P$	$\dots$	$*P432$	$P4_232$	$P4_{1,3}32\dagger$	$\dots$
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*Table 15.* Space groups in the geometric classes  $m\bar{3}$  and  $m\bar{3}m$  now retain the overbar in their standard symbols. The seven space groups in these classes in *Table 15* should thus be printed as  $Im\bar{3}$ ,  $Pa\bar{3}$ ,  $Ia\bar{3}$ ,  $Pn\bar{3}n$ ,  $Pn\bar{3}m$ ,  $Fd\bar{3}m$  and  $Ia\bar{3}d$ .

All information is given in the *Abstract*.

#### Books Received

The following books have 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.

*Acta Cryst.* (1995). **A51**, 94

**Time-of-flight diffraction at pulsed neutron sources.** Edited by JAMES D. JORGENSEN and ARTHUR J. SCHULTZ. Pp. v+117. Buffalo: American Crystallographic Association, 1994. Price US \$25.00. ISBN 0-937140-38-4. Volume 29 of the *Transactions of the American Crystallographic Association*, the book contains the proceedings of a symposium, held at the annual meeting of the ACA at Albuquerque, New Mexico, in May 1993, dealing with time-of-flight experiments and instrumenta-

tion at pulsed spallation neutron sources in the United States, Japan and the United Kingdom. An editors' preface is followed by transcripts of 11 symposium presentations. The opening review, by Jorgensen, points out that 'the effective fluxes of (pulsed and reactor) sources are now nominally equivalent for most diffraction experiments' and looks forward to increasing fluxes from the new planned generation of pulsed sources, which would make possible 'qualitatively new capabilities in neutron scattering'. The book is available from the Polycrystal Book Service, PO Box 3439, Dayton, OH 45401, USA.