Table 3. *Test-structure results*

For each structure we give: the value of the final residual Res; the number of wrong estimates (error) for the one-phase seminvariants of first rank [SS1(1)] included in the NRIF reflections; the number of errors (Error$_{tot}$) for one-phase seminvariants of first rank [SS1(1)$_{tot}$ is their number: if SS1(1)$_{tot}$ > 1000, the calculations are limited to the first 1000] included in the NRIF$_{tot}$ measured reflections.

	Res	SS1(1)	Error	NRIF$_{tot}$	SS1(1)$_{tot}$	Error$_{tot}$
RH5	0.25	92	0	1420	441	13
FREIES	0.26	48	0	972	148	44
CUPP	0.27	86	0	7455	1000	47
AGI	0.27	60	0	11463	1000	45
TRICL	0.46	22	4	2425	196	51
BAVO	0.07	28	0	620	57	1

Table 4. *Results for BAVO*

For each one-phase seminvariant of the second rank for BAVO the |E| values, the true and the estimated phases and the G values are given.

h k l	|E|	φ_{true}	φ_{calc}	G
2 6 2	1.8	192	171	2.95
2 2 4	1.41	6	9	1.92
8 2 2	1.30	179	181	1.84
2 4 4	1.29	6	-19	1.71
8 4 4	1.25	333	18	1.45
4 6 2	1.23	357	8	1.38

scaling procedure ($s = \sin \theta / \lambda$). Thus, any reflection **h** satisfying $\mathbf{h}(\mathbf{I} - \mathbf{R}_n) = \mathbf{H}$ and the Harker vectors $\mathbf{U}_j$ can be used directly for calculating $F'_{p\mathbf{H}}$ and then for estimating $F_{\mathbf{H}}$.

If $\mathbf{C}_n$ commutes with all $\mathbf{C}_s$ operators then $(\mathbf{R}_n - \mathbf{I})\mathbf{C}_s\mathbf{r}_j \equiv \mathbf{C}_s(\mathbf{R}_n - \mathbf{I})\mathbf{r}_j = \mathbf{C}_s\mathbf{U}_j(n, 1)$ and the usual algebra of the structure factors can be used. Thus (A.1) reduces to

$$F'_{p\mathbf{H}} \simeq \langle f(\mathbf{H})/f(\mathbf{h}) \rangle F'_{p\mathbf{h}}, \qquad (A.2)$$

where $F'_{p\mathbf{h}}$ is a structure factor of index **h** in which the atomic positions are replaced by the interatomic vectors $\mathbf{U}_j$.

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The Enumeration and Symmetry-Significant Properties of Derivative Lattices

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Abstract

For a lattice in two dimensions, the number of distinct derivative lattices of index n is given by the arithmetic function $\sigma_1(n)$ which is the sum of the divisors of n, including 1 and n. The function $\sigma_1(n)$ has as its generating function the Dirichlet series $\zeta(s)\zeta(s-1)$ where $\zeta(s) = \sum_{n=1}^{\infty} n^{-s}$ is the Riemann zeta function. That is, $\zeta(s)\zeta(s-1) = \sum_{n=1}^{\infty} \sigma_1(n)n^{-s}$. The probability that s points chosen at random on the two-dimensional lattice do not lie on any of the derivative lattices so enumerated is therefore $[\zeta(s)\zeta(s-1)]^{-1}$. The equivalent results in three dimensions are: the arithmetic function $\sum_{d|n} [n/d]^2 \sigma_1(d)$, where the sum

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is over the divisors d of n, the generating function $\zeta(s)\zeta(s-1)\zeta(s-2)$ and the probability $[\zeta(s)\zeta(s-1)\zeta(s-2)]^{-1}$. Applied to the reciprocal lattice, this provides a method of estimating whether such a particular non-primitive arrangement of strong reflections could occur by chance. This number-theory approach may be adopted to the enumeration of derivative lattices in the general case. However, when considering potential sublattices in practice, only those belonging to the same Laue class are of any interest, in which case the general formula only holds for the Laue class $\bar{1}$. For all other space groups, the effect must be considered of choosing s points at random together with all the other points related to them through the diffraction symmetry. This leads to a generating function that is identical for space groups belonging to the same Patterson symmetry, that is Laue class and lattice type. In all 24 cases, the form is $A(s)/F(s)$ where F depends only on the Laue class and is a product of infinite series, chiefly zeta functions, but also Dirichlet L functions. $A(s)$ in turn derives from the lattice type, but varies depending on what other lattice types are available as potential sublattices in that Laue class. It represents an adjustment to one prime-number term in the infinite-product form of F, it being the $p=2$ term in the monoclinic, orthorhombic, tetragonal and cubic crystal classes and the $p=3$ term in the trigonal and hexagonal classes. The numerous results concerning generating functions, arithmetic functions and probabilities are given in the tables.

Introduction

It has long been recognized that rational dependence of atomic fractional coordinates can give rise to problems with crystallographic direct methods, as a result of differences in the average intensities of different reflection classes. Hauptmann & Karle (1959) suggested renormalization of the intensities of the various parity classes within the reciprocal-lattice points as the solution in these cases and the standard direct-methods programs evaluate the relevant averages. However, various alternative approaches to the phase problem in cases of rational dependence have since been advanced, an excellent survey of the relevant literature having been given by Cascarano, Giacovazzo & Luić (1985). In that paper they present perhaps the only attempt so far to provide an objective method, suitable for implementation on computer, for recognizing the existence of the phenomenon in more general cases. The original intention of the work described here was to derive a rational-dependence screening test, operating in an alternative and complementary way to this existing procedure.

However, as the work progressed, it became clear that the approach taken relied on the existence of a powerful number-theory technique for the enumer-

ation of all derivative lattices of a given lattice, subject to the appropriate symmetry restrictions. This is the theory of multiplicative arithmetic functions (see, for example, Hardy & Wright, 1979). In particular, the number of derivative lattices generated by the rules of Billiet & Rolley-Le Coz (1980) for the triclinic case and of Bertaut & Billiet (1979) for the more symmetric cases can be found for any index by the use of the appropriate Dirichlet series as generating functions.

One-dimensional case

It is appropriate to begin with the one-dimensional analogue, which is the probability that s random integers have no common factor other than one. This is

$$P(s, 1) = 1 - \sum_i^\infty p_i^{-s} + \sum_i^\infty \sum_{j>i}^\infty (p_i p_j)^{-s}$$

$$- \sum_i^\infty \sum_{j>i}^\infty \sum_{k>j}^\infty (p_i p_j p_k)^{-s} \ldots,$$

where the ps are the prime numbers. If we rearrange the terms in order of increasing denominator, we get

$$P(s, 1) = 1 - 2^{-s} - 3^{-s} - 5^{-s} + 6^{-s} - 7^{-s} + 10^{-s} \ldots,$$

which shows that there is a term in the series for each 'square-free' number. In fact the series is based on the Moebius function, that is

$$P(s, 1) = \sum \mu(a)a^{-s}$$

where

$$\mu(a) = (-1)^{\Omega(a)} \quad \text{if } a \text{ is square free}$$

$$= 0 \quad \quad \text{otherwise}$$

and $\Omega(a)$ is the number of prime factors of a, i.e. r if $a = p_1 p_2 p_3 \ldots p_r$.

Fortunately, this series can be related to one which is more easily evaluated and more frequently tabulated, because the Moebius function is the inverse under Dirichlet multiplication of the Riemann zeta function, where the term in a^{-s} is 1 for all a. As a result of this, the two corresponding series are also inverses, i.e.

$$P(s, 1) = [\zeta(s)]^{-1}.$$

This series converges for $s > 1$ and is analytic for s even.

A further formulation which will be useful is the so-called infinite product form, in which the function is expressed as a product over the primes

$$\zeta(s) = \prod_p (1 - p^{-s})^{-1};$$

$$P(1, s) = \prod_p (1 - p^{-s}).$$

Yet another approach is to note that, in the theory of arithmetic functions, the function

$$F(s) = \sum_n \alpha_n n^{-s}$$

is called the generating function of the arithmetic function α_n, where n is a natural number. In this case $\alpha_n = 1$ for all n and simply represents the number of occurrences of the number n. In the case of lattices in more than one dimension, α_n will represent the number of distinct lattices of index n and the inverse of the generating function will be the associated probability. In fact, the generating function can be considered to play the same role as the partition function in statistical mechanics, for the probability that n is the highest common divisor (HCD) of s numbers taken at random is

$$\alpha_n n^{-s} \Big/ \sum_{n=1}^{\infty} \alpha_n n^{-s} = \zeta^{-1}(s) n^{-s}$$

and the probability that 1 is the HCD is $\zeta^{-1}(s)$.

It should be noted at this point that the variable s has no significance as far as the enumeration properties of the function are concerned, but has an important physical interpretation in its statistical aspect, in which case the convergence of the series for given s must be considered.

Two-dimensional case

The two-dimensional case is considerably more complicated, but for a very simple reason. The numbers that contain repeated prime factors are ignored in the one-dimensional case, because the probabilities associated with each are correctly dealt with in the series of square-free numbers. This is true because each number that contains repeated factors can be referred uniquely to one of its factors that is square free, that number being the product of all its prime factors taken once. That is, a general number $p_1^a p_2^b \ldots p_R^r$ is included with $p_1 p_2 \ldots p_R$.

However, in two (and higher) dimensions, we must consider the structures associated with particular lattices of index (unit-cell area ratio) n. These Abelian groups were recognized by Harker (1978), in his studies of colour symmetry, and were hence called by him the 'colour lattice groups'. However, it was subsequently shown by Rolley-Le Coz, Senechal & Billiet (1983) that the same groups describe the arrangements giving rise to derivative lattices for a wide range of phenomena. A future paper will consider the use of Dirichlet series to classify lattices according to these underlying Abelian groups (Rutherford, 1992).

Returning to the factorization of two-dimensional lattices, one has that their factorization into lattices whose indices are the powers of distinct primes is unique and a problem is only encountered when

further factorization is attempted and a particular prime factor is repeated. As was recognized by Kucab (1981), the lattice group corresponding to a repeated prime factor $p^{(a)}$, in a space of d dimensions, can have that factor distributed over the lesser of a and d dimensions. For example, in two dimensions, the group structure of the factor group that represents vector addition of reciprocal-lattice points with respect to a sublattice can have the forms:

$$G_{p^2} = C_{p^2}; \quad G'_{p^2} = C_p \otimes C_p;$$

$$G_{p^3} = C_{p^3}; \quad G'_{p^3} = C_{p^2} \otimes C_p;$$

$$G_{p^4} = C_{p^4}; \quad G'_{p^4} = C_{p^3} \otimes C_p; \quad G''_{p^4} = C_{p^2} \otimes C_{p^2};$$

C_n is the cyclic group of order n.

The important point for the present argument is that not all of these structures may be directly referred to a unique lattice of index p and, in fact, the best that can be done is to refer each cycle group to its own prime-factor group, for example

$$C_p \text{ includes } C_{p^2}, \ C_{p^3}, \ C_{p^4}, \ldots;$$

$$G'_{p^2} \text{ includes } G'_{p^3}, \ G'_{p^4}, \ G''_{p^4}, \ldots \text{ etc.}$$

This means that we do not simply consider one occurrence of p in calculating probabilities, but must identify, at least in principle, all occurrences of lattices with underlying structures up to d such independent factor groups. Fortunately, we have the work of Billiet & Rolley-Le Coz (1980) to draw on here, since they have shown how the number of lattices of each index may be derived from a consideration of the triangular form of the associated matrix. The extension of this to distinguish between the alternative possible structures is relatively straightforward. An example is for index p^2 in two dimensions, the Billiet & Rolley-Le Coz procedure predicts $(p^2 + p + 1)$ lattices and, in particular, for $p^2 = 2^2$ the following seven matrices:

$$\begin{bmatrix} 4 & \bar{1} \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 4 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 4 & 1 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 4 & 2 \\ 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} 2 & 1 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 4 \end{bmatrix}.$$

Examination of the corresponding lattices shows that only one of these has the structure $C_2 \otimes C_2$ and, for two dimensions in general, there will be only one lattice with structure $C_p \otimes C_p$, but $(p^2 + p)$ lattices with structure C_{p^2}. Only when the matrix elements all have a common factor will the group structure consist of the product of two cycles.

The above analysis is essential, in that the normal assumption of independent probabilities does not apply in some of the cases to be considered and it is necessary to have rules to identify the exceptions, as follows.

(1) Probabilities are independent for all lattices of index p^n for distinct p.

(2) All lattices involving cycle indices p^{n_1}, $p^{n_2}, \ldots$ with at least one $n > 1$, but for only one value of p, are sublattices of one unique lattice where the cycle indices are all p and can therefore be included in that lattice for probability purposes.

(3) The unique lattice of d independent index-p cycles is a sublattice of all other lattices involving index-p cycles only, such as in rule (2). This implies that only the structures C_p, $C_p \otimes C_p, \ldots$ up to d factor groups need be considered.

(4) Probabilities are also independent if any lattice of index p^n, consisting of n independent cycles, is a maximal sublattice of only two independent lattices of lower index.

(5) Otherwise, the probabilities associated with the lattices in rule (3) are not independent and must be calculated for the explicit tree of sublattices involved.

The relevant tree for $p = 2$ in two dimensions is shown in Fig. 1. The matrix $[2\,0/0\,2]$ represents a lattice of index 4 which is a sublattice of all three lattices of index 2. This means that the lattice is not counted once at the higher level, as it would if it could be subsumed in a lattice of lower index, or twice, as it would if the probabilities were independent, but three times. This becomes $(p + 1)$ times for a general prime p, and therefore p occurrences must be subtracted to correct the count. This gives as the probability in two dimensions:

$$P(2, s) = \prod_p [1 - (p + 1)p^{-s} + p \times p^{-2s}]$$

$$= \prod_p (1 - p^{-s} - p^{-s+1} + p^{-2s+1})$$

$$= \prod_p (1 - p^{-s})(1 - p^{-s+1})$$

$$= [\zeta(s)\zeta(s - 1)]^{-1}.$$

This is convergent for $s > 2$.

This formula can be justified in another way. The probability that the lattice defined by the chosen points is primitive in the direction of the first point chosen is simply the one-dimensional case. Now, this first point cannot help define the second basis vector, so it is the $(s - 1)$ remaining points that influence the primitivity of the lattice in this second direction, giving a second one-dimensional probability of $\zeta^{-1}(s 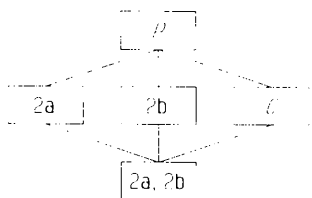- 1)$. The overall probability is the product of the two, as above. This shows that $\zeta(s)\zeta(s - 1)$ is the generating function of an α_n, which is the number of distinct lattices of index n. However, this arithmetic function is known in number theory as σ_1 and is the sum of the divisors of n (see Hardy & Wright, 1979). This correspondence may be readily explained by reference to the triangular matrix form, since each divisor d of n will occur exactly d times in the upper left corner of the matrix.

Three-dimensional case

The three-dimensional case follows in the same way as above. The number of lattices of the relevant structures are $(p^2 + p + 1)$ for C_p, $(p^2 + p + 1)$ for $C_p \otimes C_p$ and only 1 for $C_p \otimes C_p \otimes C_p$. This leads to

$$P(3, s) = \prod_p \{1 - (p^2 + p + 1)p^{-s}$$

$$+ (p^2 + p + 1)[(p + 1) - 1]p^{-2s}$$

$$- 1[(p^3 + p^2 + p) - (p^2 + p + 1) + 1]p^{-3s}\}$$

$$= \prod_p [1 - (p^{-s} + p^{-s+1} + p^{-s+2})$$

$$+ (p^{-2s+1} + p^{-2s+2} + p^{-2s+3}) - p^{-3s+3}]$$

$$= \prod_p (1 - p^{-s})(1 - p^{-s+1})(1 - p^{-s+2})$$

$$= [\zeta(s)\zeta(s - 1)\zeta(s - 2)]^{-1}.$$

This is clearer when referred to Fig. 2, the $p = 2$ tree in three dimensions. The various terms enclosed in square brackets in the first line of the derivation above represent the number of times each lattice has been counted at the various higher levels. A lattice of $C_p \otimes C_p$ type is a maximal sublattice of $(p + 1)$ of the C_p type, while the sole $C_p \otimes C_p \otimes C_p$-type lattice is a maximal sublattice of all $(p^2 + p + 1)$ of the $C_p \otimes C_p$ type, as well as being a sublattice of all $(p^2 + p + 1)$ of the C_p type.

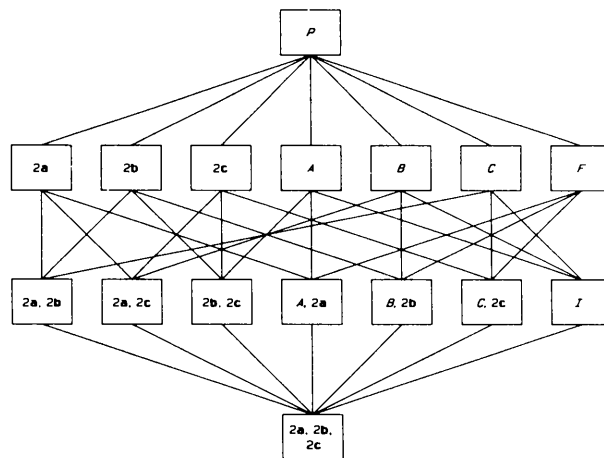Fig. 1. The index-4 square lattice and its superlattices.

Fig. 2. The index-8 cubic lattice and its superlattices.

It is convenient to know the arithmetic function generated by $\zeta(s)\zeta(s-1)\zeta(s-2)$, as this gives the required number of occurrences for any value of n. We begin with a more general result that can be derived by methods outlined by Hardy & Wright (1979), who define the arithmetic functions $\sigma_k(n)$ 'the sum of the kth powers of the divisors of n' and $d_k(n)$, 'the number of ways of expressing n as a product of k positive factors (of which any number may be unity), expressions in which only the order of the factors is different being regarded as distinct'. These definitions include as special cases the number of divisors of n, expressible either as $d_2(n)$ or as $\sigma_0(n)$, as well as $\sigma_1(n)$, which was introduced earlier.

It is then possible to show that, subject to certain restrictions,

$$\prod_{i=1}^{k} \zeta(s-a_i) = \sum_{n=1}^{\infty} \left[\sum_{j=1}^{d_k(n)} \prod_{i=1}^{k} c_{ij}^{a_i} \right] n^{-s},$$

where $\prod_{i=1}^{k} c_{ij}$ is the jth representation of n as k factors, in the sense of the definition of $d_k(n)$. The restrictions that apply are that $0 \le a_i \le (s-1)$ for all i, where the upper limit ensures convergence.

Special cases of the above are two formulae in Hardy & Wright (1979):

$$\zeta^2(s) = \sum_{n=1}^{\infty} d_k(n)n^{-s}$$

and

$$\zeta(s)\zeta(s-a) = \sum_{n=1}^{\infty} \sigma_a(n)n^{-s},$$

which of course includes the two-dimensional case. Our present expression is of the form

$$\zeta(s)\zeta(s-a)\zeta(s-b) = \sum_{n=1}^{\infty} \alpha_n n^{-s},$$

for which

$$\alpha_n = \sum_{d|n} [n/d]^a \sigma_b(d) = \sum_{d|n} [n/d]^b \sigma_a(d).$$

Here the symbol $d|n$ implies a sum over the divisors, denoted d, of n, and the two forms of the expression for α_n arise depending on the grouping of the triple-product terms in the expression

$$\alpha_n = \sum_{j=1}^{d_3(n)} c_{1j}^0 c_{2j}^a c_{3j}^b.$$

In particular, $\zeta(s)\zeta(s-1)\zeta(s-2)$ generates

$$\sum_{d|n} [n/d]^2 \sigma_1(d) = \sum_{d|n} [n/d]\sigma_2(d),$$

which is the desired result. The left-hand expression corresponds to the triangular matrix form of Billiet & Rolley-Le Coz (1980), if n/d is taken as the first diagonal element.

The effects of symmetry

The required probabilities each constitute a Dirichlet series, that is, an infinite series in n^{-s}, where the ns are the natural numbers and s is the number of sets of symmetry-related points considered. To evaluate these probabilities, it is best to express the series as a product of simpler known series, such as the zeta functions used above. Two general approaches to this type of problem were implied there; it is now profitable to present them explicitly.

The first approach is to recognize that such a Dirichlet series is multiplicative in the number-theory sense, that is, multiplicative in the primes, and can therefore be expressed as an infinite product

$$G^{-1}(s) = \prod_p h(p, s),$$

where the function h may be further factored into a product of terms $[1 \pm f_i(p, s)]^{\pm 1}$, where the f are fairly simple functions of s and the prime numbers p. (Above, they were p^{-s}, p^{-s+1} and p^{-s+2} only, and rules were given to achieve the appropriate factorization in the triclinic case.) The next step in this approach is to reorder the terms of $G^{-1}(s)$ as a product of infinite products of suitable form, perhaps along with additional terms in specific primes, so that the factors that are standard Dirichlet series (ζ and L functions) become apparent.

The second approach is to ignore explicit factorization of n, and seek to express the number of occurrences of appropriate derivative lattices of index n as an arithmetic function. The generating function of g is then the inverse under Dirichlet multiplication of the required probability function, and the problem reduces to identifying g and, from it, G.

In deriving the results presented here, the first method was used to find a general form of the generating function for each Laue group, in which the h function obeys the same formula for all primes and which represents the number of P lattices of index n that are sublattices of the basic P lattice according to some symmetry rule. The second approach was then applied to deduce the proper modification in one prime-number term to allow for all the sublattices, of various centrings, that occur for the particular lattice considered.

Once the general form for the Laue group was established, an arithmetic function was set up for the P lattice to allow for centred lattices. For example, for $p2/m$, there is a second term for the C-lattice type:

$$g(n) = \sum_{\substack{d|n \\ P \text{ lattices}}} \sigma_1(d) + 3 \sum_{\substack{2c|n \\ C \text{ lattices}}} \sigma_1(c),$$

where the factor 3 enumerates the three lattices A, I and C, all of them belonging to the C-lattice type in monoclinic symmetry. The modifications for P lattices are straightforward. In the monoclinic case, the

$p = 2$ term is altered by a factor $(1 + 3 \times 2^{-s})$. A basic lattice that is centred is generally more difficult to handle, for, although it is useful to relate the sublattices to an intermediate P sublattice for which the function is already known, it is not always possible to do this for all sublattices; the following example of $C2/m$ shows this.

The index-2 sublattices of a $C2/m$ lattice are three in number, namely the primitive lattice of the same dimension and two centred cells, C and I, with $c' = 2c$. The corresponding function $h^{-1}(2, s)$ can therefore be constructed from the sum of three terms:

$$\underset{\text{(index 1)}}{1} + \underset{\text{(index-2 } P \text{ lattice and its sublattices)}}{2^{-s}(1 + 3 \times 2^{-s})[(1 - 2^{-s})^2(1 - 2 \times 2^{-s})]^{-1}}$$

$$+ \underset{\text{(additional } C \text{ lattices)}}{2 \times 2^{-s}[1 + 2 \times 2^{-s} + 4 \times 2^{-2s} \ldots]}.$$

The third term sums to $2 \times 2^{-s}[1 - 2 \times 2^{-s}]^{-1}$ and the sum of all three simplifies to

$$(1 - 2^{-s} + 4 \times 2^{-2s})/[(1 - 2^{-s})^2(1 - 2 \times 2^{-s})],$$

where the denominator derives from the expression for general p. It is possible, therefore, to write for $C2/m$

$$g(n) = \sum_{d|n} \sigma_1(d) - 2 \sum_{2c|n} \sigma_1(c) + 4 \sum_{4b|n} \sigma_1(b).$$

However, the individual terms no longer represent specific types of sublattice.

Results

These are quoted as the probability expression; the generating function will be the inverse of this.

Two-dimensional nets

(1) *P2*. This case was considered above. The appropriate expression is

$$[\zeta(s)\zeta(s-1)]^{-1} \quad \text{or} \quad \prod_p (1 - p^{-s})(1 - p^{-s+1}).$$

(2) *P2mm*. If we were to consider only sublattices having the symmetry $P2mm$, we would then have two independent coordinates, and the probability would be $[\zeta^2(s)]^{-1}$. However, sublattices of the type $C2mm$ must also be considered. This means that all three index-2 sublattices are possible, rather than the two possible for a general prime index. This means in turn that the term $(1 - 2^{-s})^2$ in the infinite-product form must be replaced by $(1 + 2^{-s})^{-1}(1 - 2^{-s})^2$. In other words, the final expression is

$$(1 + 2^{-s})/\zeta^2(s).$$

(3) *C2mm*. Again, this is based on the $[\zeta^2(s)]^{-1}$ form, but this time there is only one appropriate sublattice of index 2. The expression therefore is $[(1 - 2^{-s})\zeta^2(s)]^{-1}$.

(4) *P4*. Valid sublattices are here restricted to squares in any orientation. Their number is therefore related to the number of representations of the index as a sum of two integer squares, *i.e.* $n = A^2 + B^2$, in fact it is $r(n)/4$ where $r(n)$ is the number of such representations. Four such representational points fall on each lattice, namely $(A, B), (B, -A), (-A, -B)$ and $(-B, A)$. This expression is then $[\zeta(s)L\{s, \chi(2)\}]^{-1}$, where $L\{s, \chi(2)\}$ is the Dirichlet L function given by

$$1 - 2^{-s} + 3^{-s} - 4^{-s} + 5^{-s} - 6^{-s} \ldots.$$

It should be noted that not all values of n are possible in this case, the restriction being that, among the factors of n, primes of the type $(+1 \bmod 4)$ may only appear to even powers. Thus n may take on only the values

$$1, 2, 4, 5, 8, 9, 10, 13, 16, \ldots.$$

(5) *P4mm*. The square sublattices here can have only two orientations: the same as the original, or rotated by 45°. All valid sublattices of index p^n are sublattices of either the rotated sublattice of index 2, or of a sublattice of index p^2, $p \neq 2$. This means the basic expression is $\zeta(2s)$, but modified in the $p = 2$ term. In fact, it is

$$(1 - 2^{-s})/[(1 - 2^{-2s})\zeta(2s)].$$

(6) *P6*. The arguments are similar to *P4*, but with the number of representations of the form

$$n = A^2 + B^2 + AB \quad \text{or} \quad n = A^2 + B^2 - AB$$

being involved. [The two are equivalent quadratic forms, see for example Davenport (1952).] Each lattice contains six points corresponding to such representations, rather than four, and the appropriate function involves

$$L\{s, \chi(3)\} = 1 - 2^{-s} + 4^{-s} - 5^{-s} + 7^{-s} - 8^{-s} \ldots$$

rather than $L\{s, \chi(2)\}$. Again, there are restrictions on the permissible values of n; here primes of the form $(-1 \bmod 3)$ must appear to even powers in the factorization of n. This yields as the permitted values

$$1, 3, 4, 7, 9, 12, 13, 16, 19, \ldots.$$

(7) *P6mm*. The arguments are similar to case (5), but the alternative orientation is rotated by 30° and the rotated maximal sublattice has index 3, therefore the $p = 3$ term is the one affected. The expression is

$$(1 - 3^{-s})/[(1 - 3^{-2s})\zeta(2s)].$$

Three-dimensional lattices

These are treated as reciprocal lattices, but are referred to according to the Patterson symmetry of the space group. In particular, the symbols I and F describe the centring of the corresponding real basic

Table 1. *Summary of results for three-dimensional Laue groups*

The arithmetic functions used, other than σ_1 and d_3, which are explained in the text, are intended to indicate the number of representations of the relevant number in the integer forms: χ_2, f_2, χ_3, f_3: $A^2 + B^2$, A^2, $A^2 + B^2 + AB$, A^3 respectively. s_{min} is the minimum value of s for which the series converges and s_{99} its value corresponding to the 99% confidence level.

Symmetry	Generating function	Arithmetic function	s_{min}	s_{99}
$P\bar{1}$	$\zeta(s)\zeta(s-1)\zeta(s-2)$	$\sum_{d\mid n}(n/d)^2\sigma_1(d)$	4	10
$P2/m$	$(1+3\times 2^{-s})\zeta^2(s)\zeta(s-1)$	$\sum_{d\,n}\sigma_1(d)+3\sum_{2c\mid n}\sigma_1(c)$	3	10
$C2/m$	$(1-2^{-s}+4\times 2^{-2s})\zeta^2(s)\zeta(s-1)$	$\sum_{d\mid n}\sigma_1(d)-\sum_{2c\mid n}\sigma_1(c)+4\sum_{4b\mid n}\sigma_1(b)$	3	9
$Pmmm$	$(1+4\times 2^{-s}+2^{-2s})\zeta^3(s)$	$d_3(n)+d_3(n/2)+d_3(n/4)$	2	10
$Cmmm$	$(1+3\times 2^{-2s}+2\times 2^{-3s})\zeta^3(s)$	$d_3(n)+3d_3(n/4)+d_3(n/8)$	2	9
$Immm$	$(1+2^{-2s}+4\times 2^{-4s})\zeta^3(s)$	$d_3(n)+d_3(n/4)+d_3(n/16)$	2	9
$Fmmm$	$(1-2\times 2^{-s}+7\times 2^{-2s})\zeta^3(s)$	$d_3(n)-2d_3(n/2)+7d_3(n/4)$	2	9
$P4/m$	$(1+2^{-s})\zeta^2(s)L[s,\chi(2)]$	$\sum_{d\,n}\chi_2(d)+\sum_{2c\mid n}\chi_2(c)$	2	9
$I4/m$	$(1-2^{-s}+2\times 2^{-s})\zeta^2(s)L[s,\chi(2)]$	$\sum_{d\mid n}\chi_2(d)-\sum_{2c\mid n}\chi_2(c)+2\sum_{4b\mid n}\chi_2(b)$	2	7
$P4/mmm$	$(1+2^{-s})^2\zeta(s)\zeta(2s)$	$\sum_{d\mid n}f_2(d)+2\sum_{2c\mid n}f_2(c)+\sum_{4b\mid n}f_2(b)$	2	9
$I4/mmm$	$(1+2^{-2s}+2\times 2^{-3s})\zeta(s)\zeta(2s)$	$\sum_{d\mid n}f_2(d)+\sum f_2(c)+2\sum f_2(b)$	2	7
$P\bar{3}$	$(1+2\times 3^{-s})\zeta^2(s)L[s,\chi(3)]$	$\sum_{d\,n}\chi_3(d)+2\sum_{3c\,n}\chi_3(c)$	2	7
$P6/m$	$\zeta^2(s)L[s,\chi(3)]$	$\sum_{d\mid n}\chi_3(d)$	2	7
$R\bar{3}$	$(1-3^{-s}+3\times 3^{-2s})\zeta^2(s)L[s,\chi(3)]$	$\sum_{d\mid n}\chi_3(d)-\sum_{3c\mid n}\chi(c)+3\sum_{9b\mid n}\chi_3(b)$	2	7
$P\bar{3}1m$	$(1+3\times 3^{-s}+2\times 3^{-2s})\zeta(s)\zeta(2s)$	$\sum_{d\,n}f_2(d)+3\sum_{3c\,n}f_2(c)+2\sum_{9b\mid n}f_2(b)$	2	7
$R\bar{3}m$	$(1+2\times 3^{-2s}+3\times 3^{-3s})\zeta(s)\zeta(2s)$	$\sum_{d,n}f_2(d)+2\sum_{9c\mid n}f_2(c)+3\sum_{27b\mid n}f_2(b)$	2	7
$P\bar{3}m1, P6/mmm$	$(1+3^{-s})\zeta(s)\zeta(2s)$	$\sum_{d\,n}f_2(d)+\sum_{3c\mid n}f_2(c)$	2	7
$Pm\bar{3}, Pm\bar{3}m$ $Fm\bar{3}, Fm\bar{3}m$	$(1+2^{-s}+2^{-2s})\zeta(3s)$	$f_3(n)+f_3(n/2)+f_3(n/4)$	1	7
$Im\bar{3}, Im\bar{3}m$	$(1+2^{-2s}+2^{-4s})\zeta(3s)$	$f_3(n)+f_3(n/4)+f_3(n/16)$	1	4

Table 2. *Probabilities* ($\times 10^4$ *corresponding to up to the* 99% *confidence level) that s reflections define a primitive cell for each Patterson symmetry*

Symmetry \ s =	1	2	3	4	5	6	7	8	9	10
$P\bar{1}$				4673	7413	8758	9401	9709	9857	9930
$P2/m$			3060	5980	7856	8901	9446	9723	9862	9931
$C2/m$			4488	7451	8835	9456	9741	9875	9939	
$Pmmm$		1057	3760	6271	7959	8934	9457	9726	9863	9931
$Cmmm$		1843	5479	7792	8942	9490	9752	9878	9940	
$Immm$		2084	5663	7856	8960	9495	9753	9879	9940	
$Fmmm$		2397	6699	8741	9498	9786	9904			
$P4/m$		3228	6349	8124	9053	9526	9763	9882	9941	
$I4/m$		4611	7881	9131	9618	9823	9916			
$P4/mmm$		3595	6461	8151	9059	9527	9763	9882	9941	
$I4/mmm$		5135	8021	9162	9624	9825	9916			
$P\bar{3}$		3870	7289	8862	9515	9787	9903			
$P6/m$		4730	7829	9081	9594	9813	9912			
$R\bar{3}$		5109	8095	9191	9633	9827	9917			
$P\bar{3}1m$		4136	7341	8871	9516	9787	9903			
$R\bar{3}m$		5460	8154	9199	9634	9827	9917			
$P\bar{3}m1$ / $P6/mmm$		5055	7885	9090	9595	9814	9912			
$Pm\bar{3}, Pm\bar{3}m$ / $Fm\bar{3}, Fm\bar{3}m$	4754	7489	8750	9375	9688	9844	9922			
$Im\bar{3}, Im\bar{3}m$	6338	9217	9824	9958						

or derivative lattice and have their normal meanings interchanged in reciprocal-lattice terms. The results are collected in Tables 1 and 2.

(1) *Triclinic*. This was dealt with above.

(2) *Monoclinic*. Monoclinic symmetries combine an oblique net with a line and therefore have the basic form

$$[\zeta(s)\zeta(s-1)]^{-1}[\zeta(s)]^{-1}$$

or $[\zeta^2(s)\zeta(s-1)]^{-1}$. The $p=2$ term in the infinite-product form would be $(1-2^{-s})^2(1-2^{-s+1})$, but this is modified because in $P2/m$ all seven index-2 sublattices are possible, rather than the four registered by the general term above. This case and $C2/m$ were discussed previously.

(3) *Orthorhombic*. Orthorhombic symmetries have three independent axes and therefore have the basic

Table 3. *The triclinic probability function and the index of the reciprocal lattice defined by the s largest* |E| *values for pyridoxal 5-phosphate oxime dihydrate* (*PPOD*) *and potassium hydroxylaminedisulfonate hydrate* (*KNSS*), *for s values up to* 10

		PPOD			KNSS		
s	P(s, 3)	h, k, l	|E|	Index	h, k, l	|E|	Index
1	–	5, 3, 2̄	3.5	–	1, 13, 1̄1̄	6.07	–
2	–	1, 4, 1̄	3.4	–	8, 10, 6̄	6.06	–
3	–	5, 5, 1	3.4	57	6, 11, 2̄	6.02	522
4	0.4673	5, 1, 5̄	3.2	57	7, 13, 5̄	5.94	6
5	0.7413	4, 1̄, 1̄	3.1	57	4̄, 2, 10	5.46	6
6	0.8758	0, 2, 3	3.1	57	8, 15, 2̄	5.42	6
7	0.9401	3, 1, 1	3.1	1	11, 12, 10	5.33	3
8	0.9709	3, 3̄, 2	3.0	1	12, 10, 4	5.30	3
9	0.9857	2, 6, 4̄	2.9	1	3, 15, 3̄	5.06	3
10	0.9930	5, 3̄, 4	2.7	1	2̄, 9, 4̄	5.05	3

form $\zeta^{-3}(s)$. The $p = 2$ term, which is $(1 - 2^{-s})^3$, assumes three independent sublattices of index 2. In fact, all seven are allowed for *Pmmm* and the argument for *P2/m* can be modified for this case, as that for *C2/m* can be for *Cmmm*, *Immm* and *Fmmm*.

(4) *Laue group* 4/m. The *p*4 net is combined with a line to give $[\zeta^2(s) L\{s, \chi(2)\}]^{-1}$. However, this does not take into account the possible *F* reciprocal sublattice of index 2 for *P*4/*m*, while for *I*4/*m* there is only one valid sublattice of this index.

(5) *Laue group* 4/*mmm*. Here it is the *P*4*mm* net that is combined with a line and the basic form is $[\zeta(2s)\zeta(s)]^{-1}$. However, the index-2 sublattices are identical to those in the 4/*m* case.

(6) *Laue groups* 3̄ *and* 6/m. The *P*6 net is combined with a line, while there are additional *R* sublattices (index 3) to be considered in the trigonal case. The basic expression $[\zeta^2(s)L\{s, \chi(3)\}]^{-1}$ applies to *P*6/*m*. [We may note that there is a recurring analogy between a trigonal case that involves *R* lattices and a tetragonal case involving an *F* reciprocal lattice (case 4 here)].

(7) *Remaining trigonal and hexagonal Laue groups.* Here the *P*6*mm* net is combined with a line and these are analogous to 4/*mmm*.

(8) *Cubic.* Probabilities in cubic lattices involve the function $\zeta(3s)$, but with the $p = 2$ terms modified according to the other available sublattice types (of *P*, *I* and *F*). In respect of the probabilities, there is no distinction between the Laue groups.

Application

Table 1 includes for each Patterson symmetry the minimum *s* value for which the appropriate function converges, as well as the *s* value corresponding to the 99% confidence level. These values were used as limits for Table 2, which lists the actual probabilities to four significant figures. The actual application is shown in Table 3, which gives the indices of the ten largest |E| values for two real examples in symmetry *P*1̄: pyridoxal 5-phosphate oxime dihydrate (Barrett

& Palmer, 1969), used as an example where direct methods apply by Ladd & Palmer (1980), and a potassium hydroxylaminedisulfonate hydrate (Rutherford, Robertson, Guttormson & Russell, 1988). In each case the three largest |E| values were used to generate a transformation matrix whose determinant is the index of the relevant derivative lattice. To classify the fourth and subsequent reciprocal-lattice points, it is necessary to find the inverse transformation matrix and apply it to each reciprocal-lattice vector in turn. If a newly chosen vector belongs to the derivative lattice already defined, it will have integral coordinates after this transformation; otherwise it will represent a lattice of lower index, the reduction factor being the lowest common denominator of the fractional components of the transformed vector. It was by repeated use of this procedure to include all the previous vectors used that the index entries of Table 3 were determined. When we examine the results, we see that in the first case there is a notably large sublattice of index 57 in evidence, but the probability that the six largest |E| values would define a non-primitive cell, if random, is not itself significantly small. However, in the second case, the ten (actually fourteen) largest |E| values all belong to a sublattice of index 3 and there is a very strong indication of non-random behaviour. This latter structure was solved as an index-6 derivative lattice.

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Analysis of Neutron Diffraction Data in the Case of High-Scattering Cells. II. Complex Cylindrical Cells

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Abstract

A new numerical program for the calculation of neutron scattering intensities in a complex cell made of n concentric cylinders has been developed with the purpose of analysing the diffraction data of fluid metals under high-temperature and high-pressure conditions. A simulation of the experiment on liquid Cs at $T = 1673$ K and $P = 86 \times 10^5$ Pa contained in such a cell has been performed in order to test the accuracy of standard data-analysis procedures employed to derive the static structure factor.

1. Introduction

In the last few years there has been a great deal of interest in the study of fluids at high pressures and/or elevated temperatures. Structural, thermodynamic and electronic properties of fluid metals up to their liquid-gas critical point have been investigated both experimentally (Hensel, Juengst, Noll & Winter, 1985; Freyland & Hensel, 1985) and theoretically (March, 1989, and references therein). Special experimental high-temperature high-pressure techniques have been developed in order to deal with the problem of containing highly corrosive metals in uncontaminated form in these extreme thermodynamic conditions. In particular, a quite complex cell has been designed for neutron diffraction studies in these systems (Freyland, Hensel & Glaser, 1979) and successfully employed for measurements of the static structure factor in liquid Cs ($T_c = 1924$ K, $P_c = 92.5 \times$

10^5 Pa) and Rb ($T_c = 2090$ K, $P_c = 140 \times 10^5$ Pa) (Franz, Freyland, Glaser, Hensel & Schneider, 1980; Freyland, Hensel & Glaser, 1984; Winter & Bodensteiner, 1988; Winter, Hensel, Bodensteiner & Glaser, 1987). The manufacture of such a cell opens the possibility of studying the microscopic properties of many fluids in critical conditions, even though the neutron scattering investigation turns out to be complex. As described in Freyland, Hensel & Glaser (1979), such a cell can be schematically depicted as a set of n concentric cylinders of different materials representing the sample container, the heater elements, the heat shields and the pressure vessel. High pressures at the sample can be established by using a relatively thin-walled sample container and, at the same time, compensating the internal sample pressure by surrounding the container with Ar gas under pressure (Freyland, Hensel & Glaser, 1979). Therefore, the compensating gas can be thought of as playing the role of an additional cylinder constituting the complex cell. The use of such a cell in a neutron diffraction measurement entails a high background contribution from the sample containment to the total scattered intensity. Therefore, accurate data treatment is necessary in order to derive the correct static structure factor $S(Q)$ from the measured intensities.

In a previous paper (Petrillo & Sacchetti, 1990), a data-reduction procedure applicable to neutron diffraction measurements in low-scattering-power fluids contained in high-scattering cells has been presented. The main purpose of that paper was to optimize the subtraction of contributions coming