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Symmetry Operations for Displacively Modulated Structures

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Displacive modulation is defined as periodic distortion with an incommensurable **k** vector. If the phase of the distortion is t, a symmetry operation can be expressed as a normal space-group operation combined with a sign reversal and/or a shift in the variable t. Earlier results obtained by de Wolff [*Acta Cryst.* (1974), A **30**, 777–785] are reformulated in terms of these operations. The periodic functions defining the displacements of two symmetry-related atoms are shown to be related by a simple equation. Applications to published structures are given. The validity of this equation depends on a symmetry-adapted choice of the vector **k**. It is shown by a two-dimensional example that there are cases for which that choice of **k** requires the introduction of 'improper symmetry translations' with an extra t shift of $\frac{1}{2}$ or $\frac{1}{3}$. The ensuing Bravais lattice types are similar to those used for the description of magnetic symmetry.

1. Introduction

A crystal structure is said to be displacively modulated if it can be derived from a normal structure, the 'basic structure' with N atoms per unit cell, by displacing all atoms as follows: (*a*) if $N=1$, an atom of the basic structure situated at the position **r** with respect to some fixed origin in the crystal, is given a displacement $\mathbf{u}_1(\mathbf{k}.\mathbf{r})$. Here **k** is the 'modulation vector', and $\mathbf{u}_1(\alpha)$ is a periodic vector function: $\mathbf{u}_1(\alpha)=\mathbf{u}_1(\alpha+1)$. It follows that displacements are the same for atoms in equidistant planes perpendicular to **k** and spaced $\lambda=1/|k|$ apart; (*b*) if $N>1$, each of the N atoms in the unit cell can have its own modulation function $\mathbf{u}_i(\alpha)$, again obeying $\mathbf{u}_i(\alpha)=\mathbf{u}_i(\alpha+1)$. The displacement for atoms of the ith kind is now given by $\mathbf{u}_i(\mathbf{k}.\mathbf{r})$; **k** is the same for all i.

The diffraction pattern of such a structure is known to contain extra reflexions ('satellites') at positions $\mathbf{H}+m\mathbf{k}$ in reciprocal space, where **H** is a basic-structure reciprocal-lattice vector and m a small integer, the 'order' of the satellite.

Many patterns of this type have been encountered in X-ray, electron and neutron diffraction. Within the last decade, several of these patterns have been reliably analysed in terms of displacive modulation, *cf.* examples in §3. The displacements usually amount to 0·1–1 Å so that modulation functions can be determined with a good relative precision; in some cases they show significant deviations from harmonicity.

All these structures could be regarded as mere superstructures if the components of **k** were simple fractions. This is not the case, however; some such components have even been shown to depend smoothly upon the temperature. Therefore we have to define modulated structures as a separate class, for which **k** is incommensurable with the basic structure. Accordingly, the symmetry of modulated structures is low when judged by conventional criteria. In particular, the incommensurability of **k** means that true translational symmetry can be present in at most two dimensions (*e.g.* in the *ab* plane if $\mathbf{k}\|\mathbf{c}^*$).

However, a new kind of symmetry can be defined which restores the lost elements [de Wolff (1974), to be referred to as (I)]. In §2 we shall recapitulate the results of (I). It is difficult to apply this new symmetry concept without knowledge of the relation between the displacements of symmetry-related atoms. This relation will be derived in §3, whereas §4 discusses a new type of Bravais lattice pertaining to a certain class of modulated structures.

The symmetry description presented here is easily adapted to the case where a scalar quantity is modulated, as in substitutional modulation. Magnetic modulations (*e.g.* helical magnetic structures) are not so simple, the magnetic moment being an axial vector, though a similar treatment seems possible. Finally it should be stressed that we deal here with structures having a single modulation vector **k** (*cf.* the more general treatment by Janner & Janssen, 1976).

2. The main principles

First, the results of (I) will be illustrated by looking at the one-dimensional case in which **k**, **r** and **u** are scalars: k, x, and $u=u_i(kx)$. The latter equation will now be written more explicitly for the ith kind of atom, in the pth unit cell. If its fractional coordinate in the basic structure is x_i^0 we have for this atom $x=p+x_i^0$, and we write

$$u(i,p,t)=u_i[k(p+x_i^0)+t]. \qquad (1)$$

The addition of the phase parameter t to the argument of each u_i is the essential feature upon which the new symmetry concept is based. It is permissible since for an incommensurable k, a change of t does not effectively change the structure: after the change, the same sequence of displacements occurs elsewhere in the chain, with a precision limited only by the distance one is prepared to go in looking for it. (Changing t also leaves the diffraction intensities the same.)

The initial symmetry translations $x' = x + n$ ($n =$ integer) of the basic structure are lost in the modulated structure. However, if we add the operation $t' = t - kn$, they are restored without any approximation. This is seen by substitution in (1), which yields

$$u(i, p+n, t') = u(i, p+n, t-kn) = u(i, p, t) .$$

Thus, replacing t by $t' = t - kn$ alone has the effect of attaching the displacement of each atom to the corresponding atom n unit cells away in the $+x$ direction. As a result, one finds exactly the same situation at $x' = x + n$ as (before changing t) at x. Fig. 1 illustrates the case $n = 1$. (The replacement of x by x' could be regarded as a movement of the crystal; however, it is easier to understand these and all further operations if one leaves the crystal where it is.) Moreover addition of any integer s to t is also an identity operation, because of the periodicity of $u_i(\alpha)$. Hence the group of symmetry translations consists of operations (n, $-kn+s$), or in full:

$$x' = x + n \quad t' = t - kn + s \; (n, s \text{ integer}) . \qquad (2)$$

We now turn our attention to general symmetry operations. Just as for translations, such operations can be expected to affect t as well as x. The fact that t is a constant for the whole crystal forbids interdependence of x and t, and this leads to the form

$$x' = \gamma x + \varrho \quad t' = \varepsilon t - k\varrho + \eta \quad |\gamma| = |\varepsilon| = 1 . \qquad (3)$$

The term $-k\varrho$ in (3) merely serves to accomodate symmetry translations (2) with an integer value (s) of η. Conservation of lengths prescribes $\gamma = \pm 1$, whereas $\varepsilon = \pm 1$ follows from the condition that the trivial symmetry translations $(0, s)$ must be conserved.

We shall now prove that $\gamma = \varepsilon$. Starting from the symmetry translation $(1, -k)$ the following sequence of symmetry translations is produced: transformation with (3): $(\gamma, -\varepsilon k)$; multiplication by γ: $(1, -\gamma\varepsilon k)$, since $\gamma^2 = 1$; subtracting $(1, -k)$: $[0, (1-\gamma\varepsilon)k]$. This last symmetry translation is of the type $(0, s)$ which has to have integer s. We conclude that $\gamma\varepsilon = -1$ can occur only if $k = \frac{1}{2}$, a value clearly unacceptable for modulated structures. Hence $\gamma\varepsilon = +1$, which is equivalent to $\varepsilon = \gamma$. This proof is illustrated in Fig. 2 showing the impossibility of $\varepsilon = -1$ when $\gamma = +1$.

If we call the homogeneous part of (3) ($x' = \gamma x$ and $t' = \varepsilon t$) a point-group operation, it follows from $\gamma = \varepsilon$ that these operations act on x just as they act on t.

The corresponding property for three-dimensional crystals is: point-group operations act on certain vectors just as they act on t. The proof consists in applying a projection operator. This was done in (I) with respect to a reciprocal-lattice vector. It can equally well be done with respect to an arbitrary symmetry translation. The latter procedure was actually carried out above. We shall not repeat it for the three-dimensional case but merely state the result in terms of appropriately generalized equations (1)–(3).

Displacements similar to (1):

$$\mathbf{u}(i, \mathbf{p}, t) = \mathbf{u}_i[\mathbf{k} . (\mathbf{p} + \mathbf{r}_i^0) + t] \qquad (4)$$

where $\mathbf{p}$ now is a basic-structure lattice vector, and $\mathbf{r}_i^0$ defines the position of the ith atom within the unit cell, are shifted to atoms a lattice vector $\mathbf{n}$ away if t is replaced by $t' = t - \mathbf{k} . \mathbf{n}$. The group of symmetry translations consists of operations

$$\mathbf{r}' = \mathbf{r} + \mathbf{n} \quad t' = t - \mathbf{k} . \mathbf{n} + s \qquad (5)$$

which we denote by $(\mathbf{n}, -\mathbf{k} . \mathbf{n} + s)$. The general symmetry operation takes the form

$$\mathbf{r}' = S\mathbf{r} + \boldsymbol{\varrho} \quad t' = \varepsilon t - \mathbf{k} . \boldsymbol{\varrho} + \eta \quad \varepsilon = \pm 1 \qquad (6)$$

where the first equation is an operation which, as we will show in §3, belongs to the basic structure's space group; S is a point-group operation.

Consider the group of symmetry operations (6) valid for a given modulated structure. The different pairs $\{S, \varepsilon\}$ occurring in these operations again define a point group, just as $\{\gamma, \varepsilon\}$ in the one-dimensional case. The above-mentioned property is: there exist vectors $\mathbf{v}$ which satisfy $S\mathbf{v} = \varepsilon\mathbf{v}$ for all point-group elements (compare $\gamma x = \varepsilon x$ in one dimension).

The set of all such vectors constitutes either a line, a plane or the whole space; this set will be called L_t. The three cases correspond to $\mathbf{k}$ having one, two or three independent irrational components. Stated in the language of group theory: the representation ε of the point group occurs at least once in the representation S. The number of times it actually occurs is the dimension of L_t. In terms of the systems introduced in (I)'s Table 1, L_t is the plane perpendicular to the unique axis in the monoclinic system II[*] and L_t is that axis itself in the remaining systems, except the triclinic where it is the whole space.

In order to describe a given modulated structure, various choices of $\mathbf{k}$ are possible. For instance, if there is a description with $\mathbf{k} = \mathbf{k}_1$, then there is another with $\mathbf{k} = \mathbf{k}_1 + \mathbf{H}$ ($\mathbf{H}$ being a reciprocal vector of the basic structure) differing from the first merely by phase changes in the functions $\mathbf{u}_i(\alpha)$. We shall show in §4 that $\mathbf{k}$ may always be chosen to lie within L_t. This

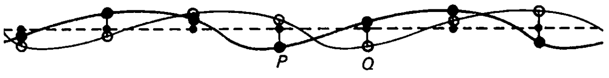

Fig. 1. Modulated chain. Small dots: basic structure. Large dots, thick line: modulated structure and u curves plotted as a function of x. Circles, thin line: same for $t' = t - k$, which moves each displacement u to the next atom, *e.g.* from P to Q. If $x' = x + 1$, the situation for any (x, t) equals that for (x', t').

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[*] Here we use the three-dimensional 'system of the average structure' and distinguish the two monoclinic systems by the numbers of their four-dimensional counterparts, II and III.

means that for each symmetry operation (6) of the structure

$$S\mathbf{k}=\varepsilon\mathbf{k} \qquad (7)$$

a result which we shall use in the next section.

3. Symmetry relations

Suppose an atom of the ith kind is imaged by the symmetry operation (6) into one of the jth kind. Abbreviating the basic structure position vector $\mathbf{p}+\mathbf{r}^0_i$ by the symbol $\mathbf{r}^0_{ip}$, we then obtain

$$\mathbf{r}^0_{jq}+\mathbf{u}(j,\mathbf{q},t')=S[\mathbf{r}^0_{ip}+\mathbf{u}(i,\mathbf{p},t)]+\boldsymbol{\varrho}\,. \qquad (8)$$

We assume that the average displacements vanish, *e.g.*

$$\int_0^1 \mathbf{u}(i,\mathbf{p},t)\mathrm{d}t=\mathbf{0}\,. \qquad (9)$$

Integrating both sides of (8) over a period of t and using (9) we find

$$\mathbf{r}^0_{jq}=S\mathbf{r}^0_{ip}+\boldsymbol{\varrho}\,. \qquad (10)$$

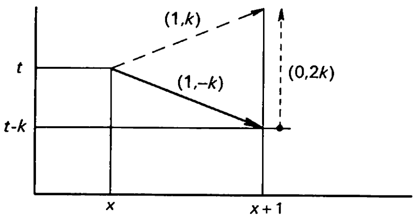

Fig. 2. In this t–x plot the translation from Fig. 1 is the vector $(1,-k)$. If a symmetry operation $x'=x$, $t'=-t$ existed, this would act like a mirror producing $(1,k)$ and, thereby, $(0,2k)$, which yields $k=\frac{1}{2}$.

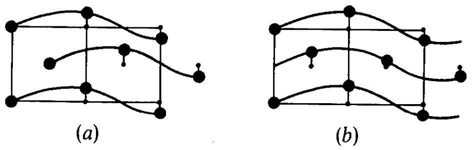

Fig. 3. When the diffraction pattern has $h+k=$ even for all main and satellite reflexions (C centring), the functions $\mathbf{u}(\alpha)$ are the same for atoms x,y,z and $\frac{1}{2}+x,\frac{1}{2}+y,z$. This is expressed correctly by (b), not by (a).

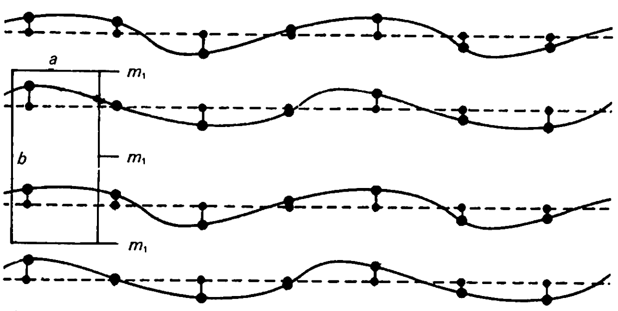

Fig. 4. Mirrors 'm_1', for which the mirror operation includes a shift $\eta=\frac{1}{2}$ in t. Small and large dots as in Fig. 1.

Thus the $\mathbf{r}$ operation of (6) belongs to the space group of the basic structure, and S to its point group. Subtracting (10) from (8) yields

$$\mathbf{u}(j,\mathbf{q},t')=S\mathbf{u}(i,\mathbf{p},t)\,,$$

or, from (4)

$$\mathbf{u}_j(\mathbf{k}\,.\,\mathbf{r}^0_{jq}+t')=S\mathbf{u}_i(\mathbf{k}\,.\,\mathbf{r}^0_{ip}+t)\,. \qquad (11)$$

We substitute (10) and (6) in the argument of $\mathbf{u}_j$:

$$\begin{aligned}\mathbf{k}\,.\,\mathbf{r}^0_{jq}+t'&=\mathbf{k}\,.\,(S\mathbf{r}^0_{ip}+\boldsymbol{\varrho})+\varepsilon t-\mathbf{k}\,.\,\boldsymbol{\varrho}+\eta\\ &=\mathbf{k}\,.\,(S\mathbf{r}^0_{ip})+\varepsilon t+\eta\,. \qquad (12)\end{aligned}$$

Now, because of (7) and since $\varepsilon^{-1}=\varepsilon$

$$\mathbf{k}(S\mathbf{r}^0_{ip})=(S^{-1}\mathbf{k})\,.\,\mathbf{r}^0_{ip}=\varepsilon\mathbf{k}\,.\,\mathbf{r}^0_{ip}\,.$$

Substitution in (12) and in (11) yields

$$\mathbf{u}_j[\varepsilon(\mathbf{k}\,.\,\mathbf{r}^0_{ip}+t)+\eta]=S\mathbf{u}_i(\mathbf{k}\,.\,\mathbf{r}^0_{ip}+t)\,. \qquad (13)$$

This must be true for any value of t, or of

$$\alpha=\varepsilon(\mathbf{k}\,.\,\mathbf{r}^0_{ip}+t)+\eta\,,$$

so the required relation is

$$\mathbf{u}_j(\alpha)=S\mathbf{u}_i[\varepsilon(\alpha-\eta)]\,. \qquad (14)$$

With the aid of (14), extinction conditions can be established, enabling us to derive symmetry elements from systematic extinctions. Knowing these elements, one can use (14) again to find the structure factors given in principle in (I), equation (13).

After the structure parameters have been found, (14) is once more needed to obtain a picture of the structure. The whole procedure is of course essentially the same as in the analysis of normal structures. In published work, however, elaborate *ad hoc* calculations have often been made where (14) could have been applied instead. This will now be illustrated by some examples.

(i) The parameters of a symmetry translation (5) are $S=1$, $\varepsilon=+1$, $\eta=0$; hence (14) yields $\mathbf{u}_j(\alpha)=\mathbf{u}_i(\alpha)$. This result is less trivial when there are centring conditions, *e.g.* $h+k=$ even for a C-centred lattice. As long as such conditions hold for all main reflexions as well as satellites, the result is the same. This case occurs in $K_2Mn(C_2O_4)_2.2H_2O$ (Schulz, 1974); hence the slight phase shift assumed by Schulz to exist between atoms connected by $\frac{1}{2}\mathbf{a}+\frac{1}{2}\mathbf{b}$ is not in accordance with the pattern (Fig. 3). (Actually the choice by Schulz of a short modulation vector '$\mathbf{b}^*_{\rm sub}$' masked the centring, which is obvious only for $\mathbf{k}=\mathbf{b}^*-\mathbf{b}^*_{\rm sub}$.)

(ii) A reflexion condition $k=0$, $m=$ even occurs in two monoclinic II-structures: $(TTF)_7I_5$ (Johnson & Watson, 1976) and Na_2CO_3 (van Aalst, den Hollander, Peterse & de Wolff, 1976). (In the first case the condition applies to a description based on the 'TTF-subcell'.) It can be interpreted as a mirror plane perpendicular to $\mathbf{b}$ accompanied with a 't-glide', that is, $\eta=\frac{1}{2}$. Such a mirror element 'm_1' is illustrated in Fig. 4, for a two-dimensional structure. Since the mirror plane coincides with L_t and thus leaves **k** unchanged, $\varepsilon=+1$, *cf.* (7). For the components u^n ($n=1,2,3$) of **u**, (14) gives

$$u_j^1(\alpha)=u_i^1(\alpha+\tfrac{1}{2}),\ u_j^2(\alpha)=-u_i^2(\alpha+\tfrac{1}{2}),\ u_j^3(\alpha)=u_i^3(\alpha+\tfrac{1}{2}). \qquad (15)$$

In a projection of the structure along **b**, atoms j and i together are invariant for $t'=t+\frac{1}{2}$ so that **k** is apparently doubled, which is the above reflexion condition. Relations equivalent to (15) were obtained by Johnson & Watson (1976) in a very indirect manner. For Na_2CO_3 (15) was stated without adequate proof.

(iii) In thiourea (Shiozaki, 1971) the reflexion condition in the ($h0l$) zone is $h+l+m=$even. Here the explanation is a mirror plane with an n glide as well as a t glide. Since the vector $\boldsymbol{\varrho}=\frac{1}{2}\mathbf{a}+\frac{1}{2}\mathbf{c}$ for the n glide does not figure in (14), the relations (15) are valid here as well. Apart from a deliberately made approximation, (15) agrees with Shiozaki's results, though again the symmetry operation was not explicitly stated.

Symmetry operations with $\varepsilon=-1$ do not give rise to satellite extinctions. A two-dimensional example (m') is easily drawn with the help of (14). For instance, an atom imaged by m' in itself (which in the basic structure lies on the mirror line) yields $u_i(\alpha)=u_i(-\alpha)$ for displacements parallel to m', as in Fig. 5.

4. Proper and improper symmetry translations

A new kind of symmetry translation can occur in modulated structures as defined in §1. It can be described formally by (5), but unlike the translations considered so far it has non-integer values for the shift s of the t parameter. The following two-dimensional example shows how it may arise from a combination of known elements, as shown in Fig. 6.

The basic structure is orthogonal, plane group *pm*. We assume modulation with a vector **k** parallel to **a**, and we assign t glides $\eta=\frac{1}{2}$ to every second mirror line of the basic structures. The ensuing sequence of alternating m and m_1 lines fits into a group very similar to the normal plane group *cm* with its alternation of m and g lines. The translation **b** is of the new kind since it is the product of adjacent m and m_1 operations and therefore has a shift in t equal to the sum $0+\frac{1}{2}=\frac{1}{2}$ of their η values.

The reciprocal net of this structure shows another anomaly (Fig. 7): there are satellites which cannot be assigned to a main reflexion with integer indices. We have to allow half-integral values of the index k, and the reflexion condition is $2k+m=$even. Fig. 7 also shows that the structure is not really anomalous at all. If we describe it by the oblique modulation vector **k**′, all satellites can have integer indices triplets (hkm). Moreover, the translation **b** again falls into the ordinary kind, with integer s in (5).

However, the description with **k**′ is undesirable for practical reasons. The vector **k**′ is ambiguous, since its mirror image **k**″ is equivalent to it. It does not lie within L_t (here the a axis), so that (7) and especially (14) are not valid. Most important is the fact that a description with **k**′ as the modulation vector would

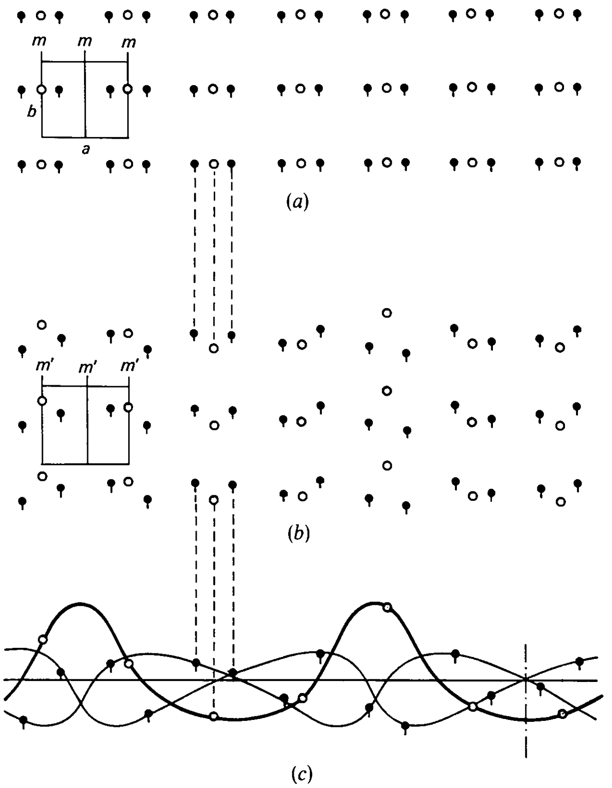

Fig. 5. Mirrors m' ($x'=-x, t'=-t$). (*a*) Basic structure; (*b*) modulated with displacements parallel to **b**, while **k** is parallel to **a**; (*c*) same, one row magnified × 3 in the **b** direction showing the modulation functions. Two mirror-related atoms have $u_i(\alpha)=u_j(-\alpha)$ resulting in mirror lines (one shown as a dot-dash line) for the curves.

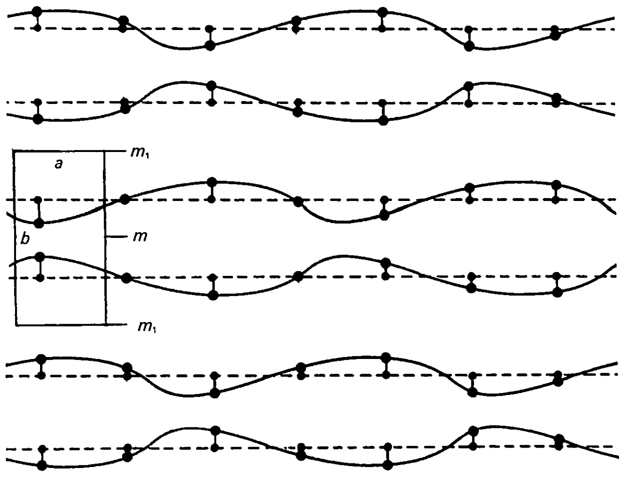

Fig. 6. A structure containing a sequence of alternating m and m_1 mirrors. Small and large dots as in Fig. 1.

make it necessary to include components of **k** in directions perpendicular to L_t (here $\frac{1}{2}\mathbf{b}^*$) in the notation for the symmetry group. Therefore we prefer (*a*) to normalize the modulation vector by always choosing it in L_t, (*b*) to express the 'improper' symmetry translation (here **b**) in the lattice symbol. This can be done by using symbols for magnetic Bravais lattices, such as p_{2b} in the case of Fig. 6, *cf.* Opechowsky & Guccione (1965). Indeed the value of s is, with one exception, restricted to $\frac{1}{2}$, so the extra shift, being a binary operation which commutes with all translations, is formally equivalent to time reversal.

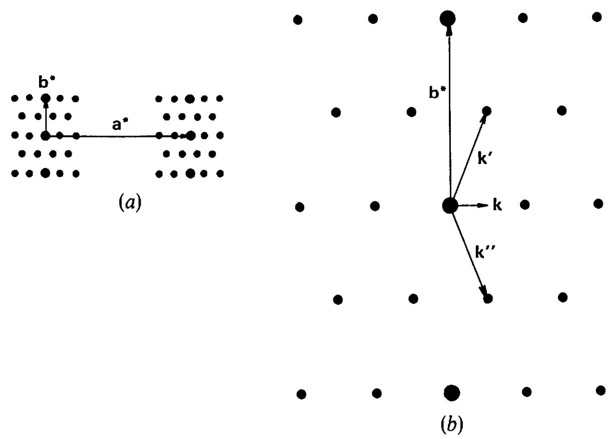

Fig. 7. The reciprocal net of Fig. 6. (*a*) Overall picture; (*b*) surroundings of the origin, magnified.

The exception is the trigonal system which allows $s=\pm\frac{1}{3}$ for improper translations. A table of Bravais-lattice types including all inequivalent lattices with and without improper symmetry translations, for each of the seven systems from (I) Table 1 is given in Table 1.*

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* Table 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32323 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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An Interactive Model-Building Program for Macromolecules

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A computer model-building program (suitable for interactive use on a small machine) is described. The program fits a polymer chain with idealized stereochemistry to a number of guide coordinates, by rotation about single bonds. It has been used to record accurate atomic coordinates from a skeletal wire model of a protein in a fraction of the time which manual measurement would have taken.

Introduction

A sufficiently large number of protein and nucleic acid structures have now been solved at atomic resolution, that the strategy of structure determination and refinement has become well-established. Much thought is currently being given to automation of the more routine aspects of such work such as X-ray data collection. One step which has not generally been automated is the measurement of atomic coordinates from a skeletal wire model which has been fitted to an electron density map. One approach to this problem is to abandon physical models, and to carry out the fitting by computer, either tracing the polymer chain automatically (Greer, 1976), or building a computer model to fit the density while both are displayed on an interactive graphics terminal (Feldmann, 1976). Nonetheless, a physical model has undeniable advantages for visualizing the structure as a whole, and it seems unlikely that the traditional methods will be totally supplanted.

The computer model-building program described here may be used in conjunction with a model to generate a stereochemically acceptable set of coordinates with a minimum of measurement.

Computer model-building

A preliminary to the refinement of a macromolecular structure is the recording of the coordinates of each