some years ago in a study of scattering from thin amorphous films (Gjønnes, 1959). For a crystal such a multiple scattering calculation would have to include Kikuchi-line effects. Efforts in this direction have recently been made by Høier (1973). The exclusion of the inelastic part of the background through a velocity filter might reduce this problem considerably.

The question as to whether the comparison between observed and calculated distributions should be made in intensity space or in vector space is an old one in diffraction studies. With the quite complex structure studied in the present work, a least-squares method as employed has many advantages; it relates the intensity directly to a structure, and it does automatically take relations between different vectors in the projection into account. On the other hand, the use of the vector map may, to a certain extent, be seen as a more visual representation of the experimental results, and it does directly display some of the limitations inherent in the experiment, *e.g.* due to lack of observations close to the origin of the Brillouin zone.

The present investigation produces strong diffraction evidence for the existence of tetrahedral defect clusters in disordered $VO_{1.23}$. This was expected, since the ordered state can be considered as an ordered arrangement of such tetrahedra, and also because recent measurement of the 200 structure factor (Andersson & Høier, 1973) show that there must be nearly the same fraction of interstitial vanadium atoms above the ordering temperature.

The local arrangement of clusters in the disordered structure cannot as yet be described very precisely. The comparison between observed and calculated intensity distributions shows that the local arrangement deviates from the ordered structure, $V_{52}O_{64}$. The partial Patterson projection synthesis as well as the least-squares calculation of order parameters shows that $\langle 1\frac{1}{2}\frac{1}{2}\rangle$ is the nearest-neighbour intercluster vector. This is shorter than the nearest-neighbour vector $\langle 11\frac{1}{2}\rangle$ in the superstructure.

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Characterization of Twinning

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(*Received* 6 *August* 1973; *accepted* 26 *October* 1973)

A new twinning condition is derived. It is more general than Friedel's ratios [Friedel, G. (1964). *Leçons de Cristallographie*, p. 249, Paris: Blanchard], and it allows one to predict not only the twin laws of a crystalline species, but also the regular associations of crystals mutually oriented according to non-crystallographic rotations. The deviation suffered by the twin lattice at the composition surface is better described in terms of the new twinning condition than in terms of the twin obliquity.

Introduction

Assemblages of two or more crystals, of the same or of different species, are called *random aggregates* if the mutual orientation of the constituent crystals is haphazard, and *regular aggregates* or *oriented crystal growths* if the crystals are related in well-defined ways dictated by their lattice dimensions. The crystals of a regular aggregate are mutually oriented so that they have a row, a net or a lattice exactly or approximately in common. The lattice control dictating these three types of mutual orientations is called *monodimensional*, *didimensional* and *tridimensional* respectively. *Twins* are regular aggregates consisting of individual crystals of the same species. They are called *monoperiodic*, *diperiodic* or *triperiodic* if the lattice control is mono-, di-, or tridimensional respectively (Friedel, 1933*a*, *b*). In this paper, we restrict our analysis to triperiodic twins, which are the more common.

Triperiodic twinning is usually characterized in terms of the geometrical rules developed by Bravais and Mallard and generalized by Friedel (Friedel, 1926; Cahn, 1954; Donnay, 1959). These rules, whose validity is substantiated by a large number of observations, have been extensively used because they offer the only available method for predicting twin laws from lattice geometry alone and for interpreting the complex diffraction patterns produced by twins.

The rules of the French school, however, are not always easy to apply to practical problems and, more importantly, they are not general in some significant respects. Thus it seems desirable to develop more convenient procedures for characterizing twinning. One such procedure has been derived as a particular case of the general treatment of crystal orientation in regular aggregates with tridimensional lattice control and is presented in this paper together with some generalizations of Friedel's theory. The procedure permits one to predict the formation of twins from lattice dimensions and to evaluate the mutual orientation of the individual crystals in a convenient mathematical way.

The geometrical approach to the study of twinning is empirical and its validity rests on the observation that, in the cases studied, the orientation of the constituent crystals is controlled by lattice geometry. Its main limitation is that it provides only the necessary conditions for the formation of twins. Conditions which are also sufficient cannot be obtained without considering the crystal structure (Buerger, 1945; Holser, 1958; Dornberger-Schiff, 1959, 1961).

As the method derived in this paper is adaptable to automatic computations, it can be used systematically to check whether the known twins abide by the rules of the French school without exceptions and to clarify, where the structure is known, the relationship between the geometrical and the structural theories of twinning. A critical evaluation of published twin data is under way, and its results will form the subject of a subsequent paper.

General

Let us consider a regular aggregate of two crystals, not necessarily of the same species, and let their lattices Λ' and Λ'' be described by the triplets of primitive non-coplanar translations $\mathbf{a}'_i$ and $\mathbf{a}''_i$ respectively, which define the reduced cells, or any other uniquely defined primitive cells (Niggli, 1928; Santoro & Mighell, 1970).

Let us express the relationship between the lattices Λ' and Λ'' by means of the transformation

$$\mathbf{a}''_i=\textstyle\sum_j B_{ij}\mathbf{a}'_j\,. \qquad (1)$$

As we are interested in the mutual orientation of the two crystals, we assume that matrix B represents a linear transformation, *i.e.* a transformation that leaves the origin invariant. Let us define the scalar products

$$A'_{ij}=\mathbf{a}'_i\,.\,\mathbf{a}'_j\,,\quad A''_{ij}=\mathbf{a}''_i\,.\,\mathbf{a}''_j\,. \qquad (2)$$

From equation (1) we obtain

$$\mathsf{A}''=\mathsf{B}\mathsf{A}'\tilde{\mathsf{B}} \qquad (3)$$

where $\tilde{\mathsf{B}}$ is the transpose of matrix B. Equation (3) can be rewritten as

$$\textstyle\sum_k\sum_l B_{ik}B_{jl}A'_{lk}-A''_{ij}=0\quad(i,j,k,l=1,2,3)\,. \qquad (4)$$

The aggregate will be characterized by three-dimensional lattice control if a lattice Γ', which can be either Λ' itself or a superlattice* of Λ', and a lattice Γ'', either Λ'' or a superlattice of Λ'', have equal or nearly equal lattice parameters† and if the lattices Γ' and Γ'' are, exactly or approximately, superposed. Under these conditions, it is customary to say that the two crystals have a lattice Γ in common. Obviously Γ is defined only if the superposition of Γ' and Γ'' is exact. If the superposition is approximate, Γ is taken coincident with Γ' in Λ' and coincident with Γ'' in Λ''. This geometrical situation is also described by saying that the common lattice does not extend exactly from one crystal to the other but suffers a deviation at their boundary.

Let us call $\mathbf{r}'_i$ and $\mathbf{r}''_i$ the translations describing Γ' and Γ'' respectively. We have

$$\mathbf{r}'_i=\textstyle\sum_j Q_{ij}\mathbf{a}'_j \qquad (5)$$

and

$$\mathbf{r}''_i=\textstyle\sum_j P_{ij}\mathbf{a}''_j\,. \qquad (6)$$

The matrices Q and P can be unimodular or else generate superlattices and, therefore, have integral elements Q_{ij} and P_{ij} and determinants $|\mathsf{Q}|\ge 1$ and $|\mathsf{P}|\ge 1$ (Santoro & Mighell, 1972). The relationship between $\mathbf{r}'_i$ and $\mathbf{r}''_i$ can be expressed by means of the transformation

$$\mathbf{r}''_i=\textstyle\sum_j C_{ij}\mathbf{r}'_j\,. \qquad (7)$$

From equations (1), (5), (6) and (7) we obtain

$$\mathsf{B}=\mathsf{P}^{-1}\mathsf{C}\mathsf{Q}\,. \qquad (8)$$

If the superposition of Γ' and Γ'' is exact, we must have

$$\mathbf{r}''_i\,.\,\mathbf{r}''_j=\mathbf{r}'_i\,.\,\mathbf{r}'_j\,, \qquad (9)$$

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* The term *superlattice* used in this paper indicates a lattice obtained from the original lattice by means of a transformation matrix having integral elements and determinant larger than unity (Santoro & Mighell, 1972). In some publications (Bucksch, 1971, 1972; Cassels, 1959) the superlattice, as defined in this paper, is called, *sublattice*, because it is generated by a subgroup of the translations on which the original lattice is based.

† An equally valid description of this type of regular aggregates is obtained by considering sublattices instead of superlattices. Such descriptions have been used in the past, see, *e.g.*, cryolite twinning (Wrinch, 1952; Donnay & Donnay, 1952).

and, in addition, the translations $\mathbf{r}''_i$, which define Γ'', must be lattice vectors of Γ', and *vice-versa*. Consequently, matrix C has integral elements and the elements B_{ij} of matrix B of equation (8) are rational numbers. In this case equation (4) is exactly satisfied with rational coefficients B_{ij}.

If the superposition of Γ' and Γ'' is not exact, the translations $\mathbf{r}''_i$ will only approximately be lattice vectors of Γ', and the elements C_{ij} will only approximate integral numbers. Consequently, equation (4) will be exactly satisfied with coefficients that are almost rational or, which amounts to the same thing, approximately satisfied with rational elements B_{ij}.

By combining the two cases, we may say that two crystals of metric forms A′ and A″ having, exactly of approximately, a lattice in common, satisfy the equation

$$\sum_k \sum_l B_{ik}B_{jl}A'_{lk} - A''_{ij} \simeq 0 \,, \tag{10}$$

with rational coefficients B_{ij}. On the other hand, if two crystals satisfy equation (10) with rational coefficients, they have a lattice in common. This proposition can be proven in the following way. If the elements B_{ij} are rational we may write

$$N_{ij} = n_i B_{ij} \,, \tag{11}$$

where N_{ij} and n_i are integral numbers. From equation (1) we have*

$$\mathbf{a}''_i = \sum_j (N_{ij}/n_i)\mathbf{a}'_j \,, \tag{12}$$

i.e.

$$\mathbf{s}_i = n_i\mathbf{a}''_i = \sum_j N_{ij}\mathbf{a}'_j \,. \tag{13}$$

As the elements n_i of the diagonal matrix n and the elements N_{ij} of matrix N are integral, the translations $\mathbf{s}_i$ define a superlattice common to Λ' and Λ''. There are infinitely many such superlattices. In fact, if S is a matrix with integral elements and determinant $|\mathsf{S}| > 1$, the matrices Sn and SN generate a new superlattice also common to Λ' and Λ''. The smallest of the superlattices common to Λ' and Λ'' can be obtained as follows. Let J be a unimodular matrix with integral elements. An equivalent way of generating the superlattice defined by the translations $\mathbf{s}_i$ is provided by the transformations

$$\mathbf{s}'_i = \sum_j (J_{ij}n_j)\mathbf{a}''_j = \sum_j \sum_k (J_{ij}N_{jk})\mathbf{a}'_k \,, \tag{14}$$

where

$$\mathbf{s}'_i = \sum_j J_{ij}\mathbf{s}_j \,. \tag{15}$$

If p_i is the common divisor of the coefficients $(J_{ij}n_j)$ and $(\sum_j J_{ij}N_{jk})$ also the vectors $\mathbf{s}''_i = \mathbf{s}'_i/p_i$ define a superlattice common to Λ' and Λ''. If $p_i > 1$, this superlattice has a smaller multiplicity than the superlattice defined by the translations $\mathbf{s}'_i$. The superlattice with the smallest multiplicity is obtained when there exists no common divisor larger than unity.

The necessary and sufficient conditions for the existence of a supercell common to two given lattices have been stated by Bucksch (1972) who has also described an algorithm for the calculation of the smallest supercell. A second method, applied to the study of coincidence-site lattices, has been given by Santoro & Mighell (1973). In the study of regular aggregates in general, and twinning in particular, the use of equation (10) is more convenient than the previously proposed procedures. This equation, in fact, expresses in a compact way the geometrical conditions necessary for the formation of the aggregate, and it gives as solution the elements B_{ij} required for defining the mutual orientation of two individuals in the aggregate.†

The solutions of equation (10) correspond to all the possible mutual orientations of Λ' and Λ'' for which a common lattice exists. In many cases more than one mutual orientation of the two crystals is consistent with the same superlattice. For example, if Γ possesses symmetry or pseudo-symmetry in addition to the center, equation (7) has more than one set of solutions with elements C_{ij} integral or approximately integral and therefore the same common lattice results by orienting Λ' and Λ'' in more than one way. This observation forms the basis of the method used by Friedel (1926) for determining twin laws.

The differences

$$\Delta_{ij} = \sum_k \sum_l B_{ik}B_{jl}A'_{lk} - A''_{ij}$$

are a measure of the misfit of the lattices Γ' and Γ'' in the aggregate or, in different words, of the deviation suffered by the common lattice as it crosses the boundary between the two crystals. The extent of the permissible deviation can only be established empirically, but it is reasonable to expect that the smaller the values of the individual Δ_{ij} are, the more the formation of the aggregate is favored.

Twinning conditions

The individuals of a triperiodic twin are of the same crystalline species, *i.e.*

$$\mathsf{A}' = \mathsf{A}'' \equiv \mathsf{A} \,, \tag{17}$$

and they are mutually oriented so that they have, exactly or approximately, a common lattice, called the *twin lattice*, which is either the crystal lattice or one of its superlattices (see Friedel, 1926; Donnay, 1959). The twinning condition, therefore, is a particular case of equation (10) and can be expressed in the following way: 'A crystal of metric form A may twin if the condition

$$\sum_k \sum_l B_{ik}B_{jl}A_{lk} - A_{ij} \simeq 0 \tag{18}$$

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* We suppose here that Γ' and Γ'' are exactly superposed. The extension to the case of approximate superposition is obvious.

† The rational elements B_{ij} define the mutual orientation of Λ' and Λ'' only if the superposition of Γ' and Γ'' is exact. If the superposition is approximate, the elements B_{ij} will specify this orientation only approximately.

is satisfied, for all the elements A_{ij}, with rational coefficient B_{ij}, provided that these coefficients do not represent a symmetry operation of the crystal'.*

Equation (18) is more general than the twinning conditions given by Friedel. According to Friedel (1926, pp. 454, 455), twinning is the result of the accidental presence in a lattice of a net and a row, sufficiently dense, that are exactly or approximately perpendicular. The twinning condition is therefore equivalent to the condition of perpendicularity of a net and a row. In the general case, a row $[w_1w_2w_3]$ is perpendicular to a net $(h_1h_2h_3)$ if (see Donnay & Donnay, 1959)

$$p\mathbf{h}=\mathsf{A}\mathbf{w}\,, \tag{19}$$

where p is any number, rational or irrational, $\mathbf{w}$ is the column vector of the symbols w_1, w_2, w_3 and $\mathbf{h}$ is the column vector of the indices h_1, h_2, h_3. As the elements of $\mathbf{w}$ and $\mathbf{h}$ are integral, Friedel concludes (p. 249) that equation (19) is satisfied if the ratios

$$A_{11}:A_{22}:A_{33}:A_{12}:A_{13}:A_{23} \tag{20}$$

are, or approach, rational numbers.

It can be shown that conditions (18) and (20) are equivalent in all cases except in the monoclinic and triclinic systems. Let us consider, for example, a monoclinic lattice of reduced form

$$\begin{pmatrix} A_{11} & A_{22} & A_{33} \\ 0 & A_{13} & 0 \end{pmatrix}. \tag{21}$$

If $A_{13}=2A_{11}-A_{33}$, equation (18) is satisfied by the matrices

$$\mathsf{B}_1=(\tfrac{1}{3}0\tfrac{2}{3}/0\bar{1}0/\tfrac{4}{3}0\tfrac{\bar{1}}{3}) \quad \text{and} \quad \mathsf{B}_2=(\tfrac{\bar{1}}{3}0\tfrac{\bar{2}}{3}/0\bar{1}0/\tfrac{\bar{4}}{3}0\tfrac{1}{3})\,.$$

Twinning is clearly possible. This result is independent of the rationality of the ratios $A_{11}:A_{22}:A_{33}:A_{13}$. Actually the parameters of the monoclinic cell could be chosen so that these ratios are irrational (for example: $A_{11}=\sqrt{2}$; $A_{22}=$any; $A_{33}=\sqrt{2}+2$; $A_{13}=\sqrt{2}-2$).

From equation (19) it is clear that the rationality of the ratios (20) is a sufficent, but certainly not a necessary, condition for the perpendicularity of a row and a net. Equation (19), in fact, requires that the ratios

$$\sum_i w_iA_{1i}:\sum_i w_iA_{2i}:\sum_i w_iA_{3i}\,, \tag{22}$$

and not ratios (20) must approach rational numbers. As irrational numbers are not closed under addition, subtraction, multiplication and division (Niven, 1961), it may well happen that conditions (22) are satisfied even if conditions (20) are not. For example, it can be shown that the monoclinic lattice of reduced form (21) is consistent with an orthorhombic superlattice that is obtained from the monoclinic reduced cell by means of the transformation $(010/\bar{1}01/201)$. In fact, ratios (22), applied to our example become

$$[(w_1+2w_3)A_{11}-w_3A_{33}]:[w_2A_{22}]:[2w_1A_{11}+(w_3-w_1)A_{33}]\,.$$

These ratios show that the rows $[10\bar{1}]$ and $[201]$ are perpendicular to the nets $(\bar{1}02)$ and (101) respectively. Conditions (18) and (22) are equivalent. However, conditions (22) are only indirectly related to the geometrical situation involved in twinning, while equation (18) not only is more suitable for automatic computations, but also yields matrix B which describes the mutual orientation of the twinned crystals.

Determination of twin laws

A twin operation or 'twin law' specifies the mutual orientation of two twinned crystals. It is usually expressed by the rotation necessary to bring one of the lattices into coincidence with the other. The information needed to compute a twin law is contained in matrix B. To determine if twinning is possible and, if so, the possible orientations of the twinned lattices, equation (18) must be solved for the unknown elements B_{ij}. By taking into consideration equation (11). equation (18) can be rewritten

$$\sum_k \sum_l N_{ik}N_{jl}A_{lk}\simeq n_in_jA_{ij}\,, \tag{23}$$

where N_{ij} and n_i are integers. The solutions of equation (23) can be found by systematically substituting for N_{ij}, n_i and n_j all the integral values lying between preselected upper and lower limits. The values of these limits depend on the multiplicity of the superlattices that may act as twin lattices.† From the elements N_{ij} one calculates the elements B_{ij} by means of equation (11). Of the matrices B determined in this way, only those with determinant $|\mathsf{B}|=1$ that do not express a symmetry operation of the crystal need to be retained.

The rotation relating the twinned lattices can be obtained from matrix B in the following way. Let us consider the transformations

$$\mathbf{e}'_i=\sum_j W_{ij}\mathbf{a}'_j\,, \quad \mathbf{e}''_i=\sum_j W_{ij}\mathbf{a}''_j \tag{24}$$

$$\mathbf{f}'_i=\sum_j M'_{ij}\mathbf{e}'_j\,, \quad \mathbf{f}''_i=\sum_j M''_{ij}\mathbf{e}''_j \tag{25}$$

and

$$\mathbf{y}'_i\doteq\sum_j L_{ij}\mathbf{f}'_j\,, \quad \mathbf{y}''_i=\sum_j L_{ij}\mathbf{f}''_j\,. \tag{26}$$

In the above transformations, (i) $\mathbf{e}'_i$ and $\mathbf{e}''_i$ define the conventional cells of Λ' and Λ'' (the matrices W transforming reduced cells into conventional cells are given in *International Tables for X-ray Crystallography*, 1969), (ii) $\mathbf{f}'_i$ and $\mathbf{f}''_i$ are sets of translations symmetrically equivalent to $\mathbf{e}'_i$ and $\mathbf{e}''_i$ respectively (*i.e.* matrices M′ and M″ represent symmetry operations of the crystal), (iii) $\mathbf{y}'_i$ and $\mathbf{y}''_i$ define Cartesian reference systems attached to the lattices Λ' and Λ'' (for a convenient

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* This statement becomes necessary in twinning as we are dealing with one and the same lattice in two or more different orientations. Symmetry operations of the crystal give trivial solutions of equation (18).

† The multiplicity of a twin lattice is usually small. A choice of all integral values between −5 and 5 for the N_{ij}'s and the n_i's seems to be adequate for most cases.

expression for matrix L see, *e.g.*, Santoro, 1970). From the above equations and from equation (1) we obtain

$$\mathbf{y}_i'' = \textstyle\sum_j R_{ji}^{-1}\mathbf{y}_j' , \qquad (27)$$

where

$$\mathsf{R} = (\tilde{\mathsf{L}})^{-1}(\tilde{\mathsf{M}}'')^{-1}\mathsf{D}(\tilde{\mathsf{M}}')\,(\tilde{\mathsf{L}}) , \qquad (28)$$

and

$$\mathsf{D} = (\tilde{\mathsf{W}})^{-1}(\tilde{\mathsf{B}})^{-1}(\tilde{\mathsf{W}}) . \qquad (29)$$

The rotation necessary to bring $\mathbf{y}_i'$ into coincidence with $\mathbf{y}_i''$ is obtained from matrix R derived from B by means of equations (28) and (29).* The angle of this rotation is given by the expression

$$\cos\alpha = (\textstyle\sum_i R_{ii} - 1)/2 . \qquad (30)$$

The ratios of the Cartesian direction cosines of the rotation axis are given by

$$u_1 : u_2 : u_3 = (R_{23} - R_{32}) : (R_{31} - R_{13}) : (R_{12} - R_{21}) , \qquad (31)$$

if $\alpha \neq 180°$. For $\alpha = 180°$, the ratios (31) are not defined and the direction cosines u_i are obtained from the expression

$$u_1 : u_2 : u_3 = (R_{11} + 1)^{1/2} : (R_{22} + 1)^{1/2} : (R_{33} + 1)^{1/2} . \qquad (32)$$

The relative signs of the u_i's are given in this case by the equation

$$(\text{sign})\ u_i u_j = (\text{sign})\ R_{ij} . \qquad (33)$$

The direction cosines obtained from (31) or (32) are expressed in the reference system defined by the translations $\mathbf{y}_i'$. Often it is more convenient to express them in one of the symmetrically equivalent systems defined by the conventional translations $\mathbf{f}_i'$. This is done by means of the transformation

$$\mathsf{v} = \mathsf{T}\mathsf{u} , \qquad (34)$$

where

$$\mathsf{T} = (\tilde{\mathsf{M}}')\,(\tilde{\mathsf{L}}) . \qquad (35)$$

In what follows, we indicate the rotation relating the lattices Λ' and Λ'' with the symbols $[u_1u_2u_3]_\alpha$ or $[v_1v_2v_3]_\alpha$, where α is the rotation angle and $[u_1u_2u_3]$ or $[v_1v_2v_3]$ specify the direction of the rotation axis in the systems $\mathbf{y}_i'$ or $\mathbf{f}_i'$.

In twinning by merohedry and reticular merohedry, the mutual orientation of the twinned crystals is precisely defined. The elements B_{ij} give an exact solution of equation (18) and matrix R yields the exact twin law corresponding to the expression of B.

In twinning by pseudo-merohedry and reticular pseudo-merohedry, however, any of the neighboring orientations of the twinned lattices having a lattice approximately in common are possible twinning orientations (the ambiguity in defining exactly the mutual orientation of the twinned crystals in this case is equivalent to the ambiguity in defining exactly the direction of an element of pseudo-symmetry: see, *e.g.*, Donnay, 1959). The rational elements B_{ij}, in other words, give only an approximate solution of equation (18), *i.e.* the differences.

$$\Delta_{ij} = \textstyle\sum_k \sum_l B_{ik}B_{jl}A_{lk} - A_{ij} , \qquad (36)$$

are only approximately equal to zero. Therefore, one calculates from B approximate expressions for matrices D and R and from these matrices, which we indicate as D_a and R_a, one obtains a rotation $[v_1v_2v_3]_\alpha$ that only approximates the twin law $[w_1w_2w_3]_\alpha$. This law can easily be recognized, however, because we know from experience that a twin operation is a crystallographic rotation about a row line or reflection in a net plane (Law of Mallard).

As an example of the computation of a twin law, let us consider the mineral djurleite (Takeda, Donnay, Roseboom & Appleman, 1967; Takeda, Donnay & Appleman, 1967). This mineral is orthorhombic *P* with lattice parameters that obey

$$c \simeq 2a , \quad c \simeq b\sqrt{3} . \qquad (37)$$

(In this paper, the *a* and *c* parameters given by Takeda *et al.* have been interchanged to conform to the convention $a \le b \le c$ used by Niggli (1928) in reduction theory.) Among the numerous matrices B that satisfy equation (18) let us consider $(\frac{1}{2}\frac{3}{4}0/1\bar{\frac{1}{2}}\,0/00\bar{1})$. As the lattice is primitive orthorhombic $\mathsf{W} = \mathsf{I}$ and $(\tilde{\mathsf{L}})^{-1} = (a00/0b0/00c)$. Therefore we have $\mathsf{D}_a = (\tilde{\mathsf{B}}(^{-1} = (\frac{1}{2}10/\frac{3}{4}\bar{\frac{1}{2}}0/00\bar{1})$; $\mathsf{R}_a = (\tilde{\mathsf{L}})^{-1}\mathsf{D}_a(\tilde{\mathsf{L}}) = \left(\frac{1}{2}\,\frac{a}{b}\,0/\,\frac{3b}{4a}\,\bar{\frac{1}{2}}\,0/00\bar{1}\right)$. From R_a we obtain

$$\cos\alpha = -1 ;\ (R_{11} + 1)^{1/2} : (R_{22} + 1)^{1/2} : (R_{33} + 1)^{1/2} = \sqrt{3}/\sqrt{2} : 1/\sqrt{2} : 0 .$$

Therefore

$$\mathsf{v} = (\tilde{\mathsf{L}}) \begin{pmatrix} \sqrt{3}/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{pmatrix} = \begin{pmatrix} \sqrt{3}/a\sqrt{2} \\ 1/b\sqrt{2} \\ 0 \end{pmatrix} ,$$

i.e.

$$v_1 : v_2 : v_3 = \sqrt{3}/a : 1/b : 0 \simeq 2 : 1 : 0$$

and the twin law is $[210]_{180°}$.

As mentioned earlier, the matrices B used for finding twin laws must give $|\mathsf{B}| = 1$. The corresponding matrices R, therefore, express proper rotations only. Clearly, if a set of elements B_{ij} satisfies condition (18), then the set $-B_{ij}$ too satisfies this equation. From the elements $-B_{ij}$ one obtains a matrix R_i related to R by the equation

$$\mathsf{R}_i = (-\mathsf{I})\mathsf{R} . \qquad (38)$$

The operation represented by matrix R_i is a combination of the operation R and the inversion $-\mathsf{I}$. It follows that for any twin operation $[w_1w_2w_3]_\alpha$ there exists a twin operation $[w_1w_2w_3]_\alpha \,.\, i$, where i indicates the in-

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* The matrices B obtained as solution of equation (18) are all the possible ones within the chosen limits of the elements N_{ij} and n_i. To avoid duplication of results, the expression for matrix R is therefore derived from equation (28) by putting $\mathsf{M}' = \mathsf{M}'' = \mathsf{I}$, where I is the identity matrix.

version of the lattice vectors. Remembering that a rotation through an angle $\alpha = 180°$ followed by an inversion is equivalent to a reflection in the plane normal to the rotation axis, we have

$$[w_1w_2w_3]_{180°} \, . \, i \equiv (h'_1h'_2h'_3) \simeq (h_1h_2h_3) \, .$$

The indices $(h'_1h'_2h'_3)$ define a plane exactly perpendicular to $[w_1w_2w_3]$ and are such that the ratios $h'_1 : h'_2 : h'_3$ are not necessarily rational, while the indices $[h_1h_2h_3]$ define a plane approximately perpendicular to $[w_1w_2w_3]$ and are such that the ratios $h_1 : h_2 : h_3$ are rational. The plane $(h_1h_2h_3)$ is therefore a net and a reflection in it represents a possible twin operation. For example by adding an inversion to the twin rotation $[210]_{180°}$ previously obtained for djurleite we have

$$[210]_{180°} \, . \, i \equiv (2a^2, b^2, 0) \simeq (320) \, .$$

The problem of predicting twin laws with the previous method becomes indeterminate unless restrictions are imposed on the values of the integers N_{ij} and n_i. Also with these restrictions, the theory predicts more twin laws than are observed. The same situation is encountered if the twin laws are obtained according to Friedel's method, from the symmetry or pseudosymmetry of the twin lattice. This is because, if Λ' and Λ'' have a lattice in common, then they have infinitely many lattices in common. For example the monoclinic lattice of cryolite (Donnay, 1952) of parameters $a \simeq b$, $a \simeq c\sqrt{2}$, $\beta \simeq 90°$ is consistent with a pseudo-cubic superlattice of multiplicity $\Delta = 2$ (transformation from monoclinic to pseudocubic: $1\bar{1}0/110/001$), and the 13 twin laws of this mineral have been predicted on the basis of this superlattice. For $\Delta = 3$, however, cryolite is consistent with a pseudo-orthorhombic lattice (transformation from monoclinic to pseudo-orthorhombic: $100/011/0\bar{2}1$) whose operations of pseudo-symmetry, referred to the conventional cell of cryolite, are the rotations $[100]_{180°}$, $[011]_{180°}$, $[0\bar{2}1]_{180°}$, and the reflections in (100), (012) and $(0\bar{1}1)$. The pseudo-symmetry elements [011], (012) and $(0\bar{1}1)$ do not belong to the pseudo-cubic symmetry and the axis $[0\bar{2}1]$ is twofold in the pseudo-orthorhombic superlattice and threefold in the pseudo-cubic superlattice. These additional elements are characterized by a twin index 3 and a twin obliquity comparable to that of twins predicted from the pseudo-cubic cell and, theoretically, could well be twin elements. The fact that they have not been observed may be due to accident or, more likely, to structural reasons not yet explained.

Twin obliquity

As previously stated, the differences Δ_{ij} of equation (36) are a measure of the deviation suffered by the twin lattice in crossing the boundary from one individual to the other and they are therefore related to the twin obliquity (Friedel, 1926, p. 436). The differences Δ_{ij}, however, are more satisfactory than the obliquity in describing the deviation of the twin lattice. They also apply to cases in which the twin axis is other than twofold. This can best be seen with an example.

Chromium-doped VO_2 (Marezio, Dernier & Santoro, 1973) is monoclinic, pseudo-orthorhombic ($\beta \simeq 90°$) with $a \simeq 2c$. One possible twin law is a 90° rotation about the unique b axis; the corresponding matrix is $\mathsf{B} = (00\bar{2}/010/\tfrac{1}{2}00)$. The obliquity in this case is not defined. The definition given by Friedel applies only to twofold axes; if one tries to extend it to the fourfold axis of the example, one obtains a value zero although the twin lattice suffers a rather severe deviation. On the other hand, from equation (36) we have

$$\Delta_{11} = a^2 - 4c^2, \; \Delta_{33} = c^2 - a^2/4,$$
$$\Delta_{13} = 2ac \cos \beta, \; \Delta_{22} = \Delta_{12} = \Delta_{23} = 0 \, .$$

These results show that the deviation of the twin lattice takes place in the net ac and that it is due to the facts that $2c$ is only approximately equal to a and β is only approximately equal to 90°.

Equivalence of twin laws

Let us consider the equations

$$\mathsf{R} = (\tilde{\mathsf{L}})^{-1}\mathsf{D}(\tilde{\mathsf{L}}) \quad \text{and} \quad \mathsf{R}' = (\tilde{\mathsf{L}})^{-1}\mathsf{D}'(\tilde{\mathsf{L}}) \, . \qquad (39)$$

The matrices R and R′ are said to be 'equivalent' if

$$\mathsf{D}' = (\tilde{\mathsf{M}}'')^{-1}\mathsf{D}(\tilde{\mathsf{M}}') \, . \qquad (40)$$

In the above expression, M″ and M′ are symmetry operations of the crystal. The R matrices related by equations (39) and (40) describe the same mutual orientation of two individuals in a twin and represent different, but equivalent, ways of bringing the twinned lattices into coincidence.*

Let us consider as an example a cubic primitive lattice. In this case B = D = R. From the matrix

$$\mathsf{B} = (\tfrac{2}{3}\tfrac{2}{3}\tfrac{1}{3}/\tfrac{1}{3}\tfrac{\bar{2}}{3}\tfrac{2}{3}/\tfrac{2}{3}\tfrac{\bar{1}}{3}\tfrac{\bar{2}}{3}) \, ,$$

we obtain the rotation $[311]_{146\cdot4°}$. The rotation angle 146·4° is not crystallographic. The operation $[311]_{146\cdot9°}$, however, is equivalent to the rotation $[111]_{60°}$ which is obtained from the matrix

$$\mathsf{D}' = (001/0\bar{1}0/100)\mathsf{D}(100/001/0\bar{1}0) \, .$$

In these cases, according to the law of Mallard (Friedel, 1926), the twin law is always specified by the crystallographic rotation about a row. If two or more matrices related by expressions (39) and (40) define crystallographic rotations about rows, the twin law they represent can be expressed indifferently by any one of them. For the cubic lattice of our example, matrix

$$\mathsf{D}'' = (001/010/\bar{1}00)\mathsf{D}(001/\bar{1}00/0\bar{1}0)$$

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* This definition of equivalence of twin laws is based on the classical point-group theory of twinning. It may well happen that twin laws that are equivalent according to equations (39) and (40) become distinct if the space-group symmetry of the crystal structure is taken into account. See, *e.g.*, Donnay, Sundarsanan & Young (1972).

gives $[211]_{180^\circ}$. By expressing the axes symbols in the same reference system, for example that in which [211] is expressed, we obtain

$$[11\bar{3}]_{146 \cdot 9^\circ} \equiv [211]_{180^\circ} \equiv [\bar{1}11]_{60^\circ}$$

and the twin law can be expressed indifferently as $[211]_{180^\circ}$ or $[\bar{1}11]_{60^\circ}$.

There are other cases in which from condition (18) one obtains non-crystallographic rotations that are not equivalent to any of the possible twin laws of a given lattice. These cases are found when the crystal lattice is consistent with two or more twin lattices having symmetry or pseudo-symmetry operations whose combinations result in non-crystallographic operations (*i.e.* the symmetry or pseudo-symmetry operations of the possible twin lattices, considered together, do not form a crystallographic group). For example the lattice of djurleite is consistent with two superlattices, one pseudo-tetragonal and the other pseudo-hexagonal, which can be obtained from the orthorhombic primitive cell by means of the transformations $(010/200/00\bar{1})$ and $(00\bar{1}/020/2\bar{1}0)$, respectively [the transformation $(001/200/\bar{1}10)$ from the pseudo-tetragonal cell to the pseudo-hexagonal cell, shows that the pseudo-hexagonal lattice is a superlattice of the pseudo-tetragonal lattice]. Let us consider the matrix

$$\mathsf{B} = (0\tfrac{3}{4}\tfrac{1}{4}/0\tfrac{1}{2}\tfrac{\bar{1}}{2}/\bar{2}00)\ ,$$

which satisfies the twinning condition (18) for djurleite. From it we obtain

$$\mathsf{R}_a = \left(0\,\frac{a}{b}\,\frac{a}{c}\Big/\,0\,\frac{1}{2}\,\frac{3b}{2c}\Big/\,\frac{\bar{c}}{2a}\,00\right),$$

which gives the rotation

$$\left[-\frac{3b}{2a}\,;\quad -\frac{2a^2+c^2}{2ab}\,;\quad \frac{a}{b}\right]_{104 \cdot 5^\circ}. \qquad (41)$$

The direction of the axis and the rotation angle found from R_a have to be considered as approximate, because they have been derived by using a matrix B that satisfies condition (18) only approximately. The analysis of all possible matrices B for djurleite shows that this rotation is not equivalent to any of the possible twin laws. However, if we consider the combination of the twin laws $[010]_{90^\circ}$ and $[100]_{60^\circ}$, we have

$$\mathsf{R}_{90^\circ} = (00\bar{1}/010/100)\ ,$$

$$\mathsf{R}_{60^\circ} = \left(100/0\,\frac{1}{2}\,\frac{\sqrt{3}}{2}\Big/\,0\,\frac{-\sqrt{3}}{2}\,\frac{1}{2}\right),$$

and

$$\mathsf{R}_{tot} = \mathsf{R}_{60^\circ}\mathsf{R}_{90^\circ} = \left(00\bar{1}\Big/\,\frac{\sqrt{3}}{2}\,\frac{1}{2}\,0\Big/\,\frac{1}{2}\,\frac{-\sqrt{3}}{2}\,0\right).$$

From R_{tot} we obtain

$$\left[\frac{\sqrt{3}}{a}\,;\quad \frac{3}{b}\,;\quad \frac{-\sqrt{3}}{c}\right]_{104 \cdot 5^\circ}. \qquad (42)$$

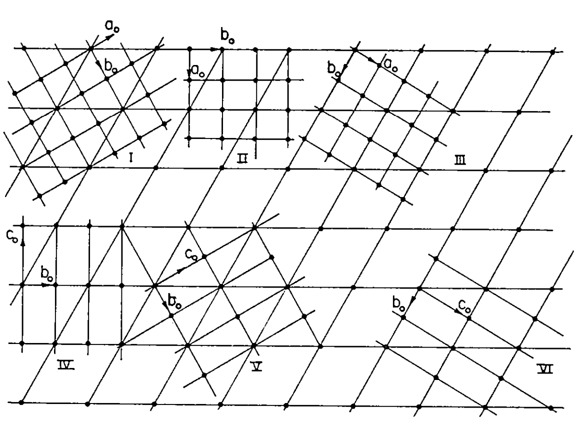

Fig. 1. Twinning in djurleite. Individuals I and II are related by the operation $[001]_{60^\circ}$ and individuals II and IV by the operation $[010]_{90^\circ}$. Individuals I and IV, therefore, are related by the operation $\left[\frac{\sqrt{3}}{a}\ \frac{3}{b}\ -\frac{\sqrt{3}}{c}\right]_{104 \cdot 5^\circ}$.

As the parameters of djurleite are related by expressions (37), operations (41) and (42) are close to each other and close to $[23\bar{1}]_{104 \cdot 5^\circ}$ (Fig. 1). If we are dealing with a genuine combination of twin operations, we have no reason to choose the rotation about the row, as the combination is correctly described only by the operation (42).

In the classical theory of twinning, thanks to the law of Mallard, a twin element can always be restricted to a lattice element (net plane or row line). Operations like the one found for djurleite have always been described as combinations of twin operations. Such descriptions have been characterized as mathematical formulations without structural significance (Hartman, 1956; Holser, 1958), but the fact remains that associations of crystals mutually oriented according to non-crystallographic rotations do occur (Drugman, 1939, 1943). Because of its generality, condition (18) allows the prediction and the characterization of such associations in each case.

The author wishes to thank Professor J. D. H. Donnay for many helpful discussions and for reading the manuscript.

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Debye Temperature of NaF and RbBr by X-ray Diffraction

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(*Received* 17 *July* 1973; *accepted* 8 *August* 1973)

Debye temperatures of NaF and RbBr have been determined by X-ray diffraction from room temperature up to about 800°K using methods due to Paskin [*Acta Cryst.* (1957). **10**, 667–669] and Chipman [*J. Appl. Phys.* (1960). **31**, 2012–2015]. The anharmonic contribution to the Debye Θ is shown to come essentially from thermal expansion. The plot of the reduced thermal expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\Theta^2$ gives a common curve. Here $\alpha_{m/2}$ is the value of α at $T=\frac{1}{2}T_m$, T_m being the melting point, A is the mean atomic weight and a the lattice constant. The energy of vacancy formation is computed using an equation established by Pathak & Trivedi [*Proc. Nucl. Phys. Solid State Phys. Symp. Roorkee, India*, (1969). pp. 50–53].

Introduction

On searching the literature it is found that no systematic investigation of the temperature variation of the Debye temperature Θ_M of NaF and RbBr has been undertaken. Still however, room-temperature values of Θ_M for NaF have been determined by several workers – notably by Brindley (1930), Shonka (1933), Wasastjerna (1946) and Meisalo & Merisalo (1966). Their values are respectively 398, 442, 440 and 400°K.

Experimental

The experimental procedure is fully described by Pathak & Vasavada (1970; hereafter called Paper I). The profiles of lines 420 and 422 were recorded on a chart recorder and planimetered. The background was determined by a method described by Mitra & Misra (1966).

The basic equation from which the X-ray Debye temperature Θ_M is calculated, (Pathak & Trivedi, 1973; hereafter called Paper II), is

$$R=\frac{mK}{12h^2}\,\frac{\lambda^2}{(1-\beta)\sin^2\theta}\left[\ln\frac{I}{I_0}-\ln\frac{B'}{B'_0}\right]=\frac{T_0\psi_0}{\Theta^2_{M0}}-\frac{T\psi}{\Theta^2_M}\,\frac{\sin^2\theta}{\sin^2\theta_0}\,, \tag{1}$$

where I and I_0 are the measured integrated intensities at temperatures T and T_0, and θ is the Bragg angle.

ψ and B' are respectively given by

$$\psi=\frac{1}{x}\int_0^x\frac{u\mathrm{d}u}{e^u-1}+\frac{x}{4}$$

$$B'=Npf^2\,\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}$$

where $x=\Theta_M/T$, N is the number of unit cells irradiated, p is the multiplicity factor and f is the atomic scattering factor.

The quantity $(1-\beta)$ takes into account the one-phonon thermal diffuse scattering (TDS) contribution to the measured intensity according to Chipman &