Analysis of Orientationally Disordered Structures.
IV. Correlations between Orientation and Position of a Molecule

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Abstract

The concept of a 'rotational form factor' analysis of molecular crystalline structures is generalized by allowing correlations between the orientation of a molecule and its centre-of-mass position. This coupling results in correction terms to the well known rotational form factor. The method is illustrated with the example of (i) tetrahedral molecules and (ii) dumbells at a site of cubic symmetry ($m3m$) and the rôle of the site symmetry as well as the magnitude of the mean-squared amplitude $\langle u^2 \rangle$ of the centre-of-mass motion are investigated.

I. Introduction

Various authors have outlined methods suitable for the structure analysis of molecular crystals (Kurki-Suonio, 1967; Seymour & Pryor, 1973; Press & Hüller, 1973, 1974; Kurki-Suonio, 1977), particularly for orientationally disordered molecular crystals investigated by neutron diffraction. The procedure used is essentially the following: the density distribution (weighted with the scattering length of the atoms) at a molecular site is expressed in terms of a convolution between a probability distribution function for the position of the molecular centre of mass, $p_T(\mathbf{R})$, and an orientational probability distribution function (PDF), $p_{\text{rot}}(\mathbf{r} - \mathbf{R})$.

$$\rho(\mathbf{r}) = \int p_T(\mathbf{R}) \, p_{\text{rot}}(\mathbf{r} - \mathbf{R}) \, d\mathbf{R}. \qquad (1.1)$$

$\mathbf{R}$ denotes the instantaneous centre-of-mass position of a molecule and $\mathbf{r}' = \mathbf{r} - \mathbf{R}$ connects an atom within a molecule with its centre of mass. In (1.1), it is implicitly assumed (i) that the molecules are rigid and (ii) that correlations between the rotational and translational motion of a molecule can be neglected. The structure factor then can be written

$$F(\mathbf{Q}) = \sum_j \exp(i\mathbf{Q}\mathbf{R}_{0j}) \exp[-W_j(\mathbf{Q})] F_j^{\text{rot}}(\mathbf{Q}). \qquad (1.2)$$

$\mathbf{Q}(hkl)$ is the scattering vector expressed in terms of the cell parameters and the Miller indices hkl; $\mathbf{R}_{0j}$ denotes the equilibrium centre-of-mass position of the jth molecule in the unit cell; $\exp[-W_j(\mathbf{Q})]$ is the Debye–Waller factor for the translational motion; $F_j^{\text{rot}}(\mathbf{Q})$ is the rotational form factor of a molecule. For simplicity, we take only one molecule in the unit cell and only molecules with one shell of atoms. Therefore the index j will be dropped in the following. The rotational form factor is expressed in terms of symmetry-adapted surface harmonics,

$$F^{\text{rot}}(\mathbf{Q}) = \int \rho_{\text{rot}}(\mathbf{r}) \exp(\Omega_Q) . \, d\mathbf{r}$$

$$= 4\pi \sum_{l'm'} i^{l'} j_{l'}(Q\rho) c_{l'm'} K_{l'm'}(\Omega_Q).$$

$$(1.3)$$

The $j_{l'}(Q\rho)$ are spherical Bessel functions with the argument $Q\rho$; ρ is the radius of the shell of atoms (= distance from the molecular centre of mass); the $c_{l'm'}$ are the expansion coefficients of the symmetry-adapted harmonics and Ω_Q denotes the polar angle of the scattering vector $\mathbf{Q}$. Finally, the $K_{l'm'}(\Omega_Q)$ are surface harmonics which are invariant under *all* operations of the point symmetry at a molecular site (Lage & Bethe, 1947; Bradley & Cracknell, 1972). Formulations have been given for various examples, particularly for cubic (Price, Rowe, Rush, Prince, Hinks & Susman, 1972; Rowe, Hinks, Price, Susman & Rush, 1973; Press, 1973; Levy, Sanger, Taylor & Wilson, 1974; Ahtee & Kurki-Suonio, 1978; More, Lefèbvre & Fouret, 1977; Bleif, 1978; Bleif & Dachs, 1979; Dolling, Powell & Sears, 1979) and hexagonal site symmetry (Press & Hüller, 1978).

As is found by first expanding in a coordinate system fixed within the molecule and then transforming to the crystalline frame, both the site and the molecular symmetry determine which expansion coefficients $c_{l'm'}$ may be non-zero (Press & Hüller, 1973). High symmetry means that only a few functions $K_{l'm'}(\Omega_Q)$ contribute. Furthermore, restrictions on the magnitude of the expansion coefficient $c_{l'm'}$ have recently been discussed (Hüller & Press, 1979). A necessary but not

sufficient condition on the orientational PDF is that it is positive definite. An even more stringent condition results from the requirement that the distribution function over angles $f(\omega)$ which mediates the transformation from the molecular frame to the crystalline frame also is positive definite.

In some cases it seems doubtful whether a basic assumption in the above treatment is valid: it has been assumed that the orientational PDF is independent of the instantaneous position of the molecular centre of mass $\mathbf{R}$ or, differently, that there is no orientation-translation coupling. If we take the example of larger molecules like CBr_4 (More, Lefèbvre & Fouret, 1977) or adamantane, we indeed may suspect that steric hindrance introduces such a coupling.

II. Inclusion of correlations between orientation and centre-of-mass position of a molecule

In (1.1), the density distribution $\rho(\mathbf{r})$ has been expressed in terms of a convolution between a translational PDF and an orientational PDF. Correlations which so far have been ignored can be included by the more general expression given by Press & Hüller (1973),

$$\rho(\mathbf{r}) = \int \rho_T(\mathbf{R}) \, \rho_{rot}(\mathbf{r}' \mid \mathbf{R}) \, d\mathbf{R}. \qquad (2.1)$$

The $\mathbf{R}$ dependence of the orientational PDF now enters explicitly in the conditional probability $\rho_{rot}(\mathbf{r}' \mid \mathbf{R})$. It is the conditional probability of finding a scatterer at $\mathbf{r}' = \mathbf{r} - \mathbf{R}$ if the molecular centre of mass is at $\mathbf{R}$. For small translational displacements $\mathbf{R}' = \mathbf{R} - \mathbf{R}_0$, a Taylor expansion of $\rho_{rot}(\mathbf{r}' \mid \mathbf{R})$ is performed:

$$\rho_{rot}(\mathbf{r}' \mid \mathbf{R}) = \rho_{rot}^{(0)}(\mathbf{r}') + \rho_{rot}^{(1)}(\mathbf{r}')\mathbf{R}' + \tfrac{1}{2}\mathbf{R}'\,\rho_{rot}^{(2)}(\mathbf{r}')\mathbf{R}' \dots, \qquad (2.2)$$

with

$$\rho_{rot}^{(0)}(\mathbf{r}') = \rho_{rot}(\mathbf{r}' \mid \mathbf{R})|_{\mathbf{R}=\mathbf{R}_0}, \qquad (2.2a)$$

$$[\rho_{rot}^{(1)}(\mathbf{r}')]_\alpha = \frac{\partial}{\partial R_\alpha} \rho_{rot}(\mathbf{r}' \mid \mathbf{R})|_{\mathbf{R}=\mathbf{R}_0}, \qquad (2.2b)$$

$$[\rho_{rot}^{(2)}(\mathbf{r}')]_{\alpha\beta} = \frac{\partial}{\partial R_\alpha}\frac{\partial}{\partial R_\beta} \rho_{rot}(\mathbf{r}' \mid \mathbf{R})|_{\mathbf{R}=\mathbf{R}_0}. \qquad (2.2c)$$

$\rho_{rot}(\mathbf{r}' \mid \mathbf{R})$ has the full site symmetry, hence all terms in expansion (2.2) have this symmetry too.

$\rho_{rot}^{(0)}(\mathbf{r}')$ represents the well known orientational PDF introduced in (1.1) which does not depend on the instantaneous centre-of-mass position $\mathbf{R}$. It transforms according to the completely symmetric representation of a given point symmetry (e.g. A_{1g} in $m3m$). Previous publications only take account of this term.

In order to obtain invariants of the type $\rho_{rot}^{(1)}(\mathbf{r}')\mathbf{R}'$, it is required that $\rho_{rot}^{(1)}(\mathbf{r}')$ and $\mathbf{R}'$ belong to the same representation. In the present case this is the vector representation. For cubic symmetry $(m3m)$, $\mathbf{R}'$ transforms like T_{1u} and therefore in an expansion of $\rho_{rot}^{(1)}(\mathbf{r}')$,

$$\rho_{rot}^{(1)}(\mathbf{r}') = \frac{1}{\rho^2}\,\delta(r' - \rho) \sum_{l'm'} \mathbf{c}_{l'm'}^{(1)}\, K_{l'm'}(\Omega), \qquad (2.3)$$

only functions $K_{l'm'}$ enter which transform like T_{1u} (Lage & Bethe, 1947; Bradley & Cracknell, 1972). The vector denotes that there are always triples of such functions with $m' = (m_1, m_2, m_3)$.

Similarly one may decompose $R_\alpha R_\beta$ into its irreducible representations and combine them with $[\rho_{rot}^{(2)}(\mathbf{r}')]_{\alpha\beta}$ of the same symmetry. This will be done explicitly for a dumbell type of molecule. So far we have only discussed consequences of the site symmetry. By a generalization of the 'formal development' given by Press & Hüller (1973), we also can introduce the symmetry of a molecule. On the lines of the above treatment the probability $f(\omega)$ of finding a molecule with the orientation ω (ω = Eulerian angles) is replaced by the conditional probability $f(\omega \mid \mathbf{R})$ and then is expanded into a Taylor series. The result is the same as in the case of no correlation between translational and rotational motion; expansion coefficients $c_{l'm'}^{(k)}$ are zero, if there is no non-zero surface harmonic of order l' in an expansion in the molecular frame. For a tetrahedral molecule there are no functions $K_{l'm'}(\Omega)$ with $l = 1, 2, 5$ for this reason. The same result is found by calculation of $F^{rot}(\mathbf{Q})$ for a molecule with its origin displaced from $\mathbf{R}_0$ and then summing over all molecular centre-of-mass positions and molecular orientations generated by the site symmetry.

When Fourier transforming (1.1) to obtain the structure factor $F(\mathbf{Q})$, use is made of the convolution theorem. Then the orientational PDF and the translational PDF can be treated separately. The same procedure can be applied to (2.1)–(2.3), if $\int \exp(i\mathbf{Q}\mathbf{R})\rho_T(\mathbf{R})\,d\mathbf{R}$ is replaced by

$$\int \exp(i\mathbf{Q}\mathbf{R})\,(R_\alpha R_\beta \dots R_k)\,\rho_T(\mathbf{R})\,d\mathbf{R}, \qquad (2.4)$$

for the various orders k of the expansion in (2.2). In the following we specialise for a Gaussian PDF $\rho_T^G(\mathbf{R})$ with isotropic mean-squared amplitudes $\langle u^2 \rangle = \langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle.$*

$$\rho_T^G(\mathbf{R}') = G \exp\left[-\left(\sum_{\alpha=1}^{3} R_\alpha'^2\right)\bigg/2\langle u^2\rangle\right], \qquad (2.5)$$

G is a normalization constant. With

$$-\frac{\partial}{\partial Q_\alpha} \int \exp(i\mathbf{QR}) \, \rho_T^G(\mathbf{R}) \, d\mathbf{R} = \langle u^2 \rangle \, Q_\alpha f(\mathbf{Q}), \quad (2.6)$$

the Fourier transformation can readily be performed. $f(\mathbf{Q}) = \exp[-W(\mathbf{Q})]$ is the Fourier transform of $\rho_T^G(\mathbf{R}')$. The result is

$$F(\mathbf{Q}) = \int\int \rho_T(\mathbf{R}') \, \rho_{rot}(\mathbf{r}'|\mathbf{R}') \, d\mathbf{R}' \exp(i\mathbf{Qr}) \, d\mathbf{r}$$

$$= \exp[-W(\mathbf{Q})] \exp(i\mathbf{QR}_0) \sum_k F_{(k)}(\mathbf{Q}). \quad (2.7)$$

Here, $F_{(0)}(\mathbf{Q}) = F^{rot}(\mathbf{Q})$ is given in (1.3),

$$F_{(1)}(\mathbf{Q}) = 4\pi \sum_{l'm'} -i^{(l'+1)} \langle u^2 \rangle \, c_{l'm'}^{(1)} \, Q j_{l'}(Q\rho) \, K_{l'm'}(\Omega_Q),$$

$$(2.8)$$

and so on. Only functions $K_{l'm'}(\Omega_Q)$ which transform like $\mathbf{Q}$ contribute, which guarantees that (2.8) is invariant under the operations of the site symmetry. For a molecule which has no centre of inversion, (2.8) represents the lowest-order correction term to $F^{rot}(\mathbf{Q})$. For molecules with an inversion centre, $F_{(2)}(\mathbf{Q})$, which is not written down explicitly, is the first correction term.

The various terms $F_{(k)}(\mathbf{Q})$ are of order $(\langle u^2 \rangle Q)^k$ and obviously the significance of terms with $k \geq 1$ depends crucially on the magnitude of the mean-squared amplitude $\langle u^2 \rangle$.

Examples for the practical calculation of $F_{(1)}(\mathbf{Q})$ and $F_{(2)}(\mathbf{Q})$ will be given in the next section.

III. Examples

(a) Tetrahedral molecule at cubic site (m3m)

An expansion of the orientational PDF into symmetry-adapted surface harmonics within the molecular frame shows that there are no such functions of order $l' = 1, 2$ and 5. This somewhat reduces the number of functions $K_{l'm'}(\Omega)$ which have to be considered and thus the number of parameters which enter a specific problem. We follow the formulation of Press & Hüller (1973),

$$F_{rot}(\mathbf{Q}) = 4\pi \sum_{l'm'} i^{l'} j_l(Q\rho) \, c_{l'm'}^{(0)} \, K_{l'm'}(\Omega_Q), \quad (3.1)$$

with functions $K_{l'm'}$ transforming according to A_{1g}. In the lowest-order term which takes account of correlations between orientation and translation, $F_{(1)}(\mathbf{Q})$, we only have to include harmonics within T_{1u}. There is one set of functions of order $l' = 1$ and 3, two sets of functions of order $l' = 5$ and 7 and so on. We need not consider terms of order $l' = 1$ and $l' = 5$, because of

the tetrahedral symmetry. Hence the leading term in $F_{(1)}(\mathbf{Q})$ is of the order $l' = 3$ and

$$F_{(1)}(\mathbf{Q}) = c_{31}^{(1)} \, i^3 j_3(Q\rho) \, (-i\langle u^2 \rangle \mathbf{Q})$$

$$\times [K_{32}(q_x), K_{33}(q_y), K_{34}(q_z)] + ..., \quad (3.2)$$

with $\mathbf{q} = \mathbf{Q}/Q$ and

$$K_{32}(q_x) = \sqrt{7/4} \, (5q_x^3 - 3q_x). \quad (3.2a)$$

The other functions are obtained by replacing q_x by q_y and q_z, respectively. Factors 4π are omitted in (3.2).

$$F_{(1)}(\mathbf{Q}) = -\langle u^2 \rangle Q j_3(Q\rho) c_{31}^{(1)} \, [q_x K_{32}(q_x)$$

$$+ q_y K_{33}(q_y) + q_z K_{34}(q_z)] + ...$$

$$= \langle u^2 \rangle Q j_3(Q\rho) \, \tilde{c}_{31}^{(1)} \, K_{41}(\Omega_Q) + ... \quad (3.3)$$

Several constants have been absorbed into a new expansion coefficient $\tilde{c}_{31}^{(1)}$. We see that $F_{(1)}(\mathbf{Q})$ indeed has cubic symmetry. If the expansion is carried further to terms of order $l' = 7$ one obtains

$$F_{(1)}(\mathbf{Q}) = \langle u^2 \rangle Q j_3(Q\rho) \, \tilde{c}_{31}^{(1)} \, K_{41}(\Omega_Q)$$

$$+ \langle u^2 \rangle Q j_7(Q\rho) [\tilde{c}_{71}^{(1)} \, \tilde{K}_1(\Omega_Q)$$

$$+ \tilde{c}_{72}^{(1)} \, \tilde{K}_2(\Omega_Q)] + ... \quad (3.4)$$

with

$$\tilde{K}_1(\Omega_Q) = -\frac{3\sqrt{11}}{\sqrt{85}} K_{81}(\Omega_Q) + \frac{9\sqrt{15}}{2\sqrt{26}} K_{61}(\Omega_Q),$$

$$(3.4a)$$

$$\tilde{K}_2(\Omega_Q) = \frac{16}{5\sqrt{561}} K_{81}(\Omega_Q) + \frac{96\sqrt{2}}{55\sqrt{13}} K_{61}(\Omega_Q)$$

$$- \frac{4\sqrt{7}}{11\sqrt{3}} K_{41}(\Omega_Q). \quad (3.4b)$$

Because $x = K_{11}(\Omega)$, orthogonality of the symmetry-adapted functions requires $\int x K_{l'm'}^{T_{1u}}(\Omega) \, d\Omega = 0$ if $(l', m') \neq (1,1)$. Therefore $K_{01}(\Omega) = 1$ does not appear in (3.4).

By comparison with (3.1) it becomes obvious that differences only concern factors which depend on $Q = |\mathbf{Q}|$. As for example the functional behaviour of $j_4(Q\rho)$ is very similar to the one of $Q j_3(Q\rho)$ for $Q\rho \lesssim 12$ except around $Q\rho \simeq 7\cdot5$, the coefficients $c_{41}^{(0)}$ and $c_{31}^{(1)}$ should be highly correlated in a least-squares fit of structural data. This indeed is found when fitting the structural data of CBr_4I (More, Lefèbvre & Fouret, 1977; More et al., 1979) with inclusion of a rotation–translation coupling.

Inclusion of the parameters entering in (3.4) in addition to the ones used by More, Lefèbvre & Fouret (3.1 with $l' \leq 8$) poses somewhat of a problem both with 14 observed reflections (More, Lefèbvre & Fouret,

1977) and 23 observed reflections (More *et al.*, 1979). The results for the latter data set are given in Table 1.* The refinement of the less complete data set yields very similar results. Successive inclusion of $\tilde{c}_{31}^{(1)}$ and $\tilde{c}_{71}^{(1)}$, $\tilde{c}_{72}^{(1)}$ improves the weighted R factor from $R_w = 7.7\%$ *via* $R_w = 5.1\%$ to a final $R_w = 3.4\%$. The anomalously large coefficient $c_{61}^{(0)}$ in phase I of CBr_4 thereby is reduced from -0.83 ± 0.07 to -0.57 ± 0.07 with three additional parameters. This leads us to suppose that the correlations between orientation and translation expressed in (3.4) are effectively absorbed into the parameters of (3.1), if only the latter equation is used for analysing the structural data. Inclusion of the leading term in $F_{(2)}^{A_{1g}}(\mathbf{Q})$ (see next paragraph) does not significantly improve the fit. One also could think of generalizing the Debye–Waller factor beyond the harmonic approximation.

Another possible explanation of the anomalously large value of $c_{61}^{(0)}$ has recently been given by Hüller & Press (1979).

(b) Dumbell at cubic site (m3m)

An expansion into surface harmonics within the molecular frame shows that there are only harmonics of even order for a dumbell (due to its inversion symmetry). At a site with symmetry $m3m$, the rotational form factor is given by the same expression as for tetrahedral molecules (equation 3.1). As only functions with l' even may appear, there are no invariants which transform like T_{1u} and, therefore, $F_{(1)}(\mathbf{Q}) \equiv 0$. The first correction term to $F^{rot}(\mathbf{Q})$ is given by $F_{(2)}(\mathbf{Q})$.

Now $R_\alpha R_\beta$ may be decomposed into a part which transforms like A_{1g} ($x^2 + y^2 + z^2$) and a part which transforms like T_{2g} (xy, yz, zx). The first part combines with functions transforming like A_{1g} and the second part with functions of type T_{2g}.† We only quote the result of a straightforward calculation.

$$F_{(2)}^{A_{1g}}(\mathbf{Q}) = (3\langle u^2 \rangle - \langle u^2 \rangle^2 Q^2)[c_{01}^{(2)} j_0(Q\rho) \\ + c_{41}^{(2)} j_4(Q\rho) K_{41}(\Omega_Q) + \dots] \quad (3.5)$$

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* See previous footnote.

† E_g does not contribute because terms like $R_\alpha^2 \partial^2/\partial R_\beta^2$ with $\alpha \neq \beta$ do not appear in (2.2).

and

$$F_{(2)}^{T_{2g}}(\mathbf{Q}) = \langle u^2 \rangle^2 Q^2 \left(c_{22}^{(2)} j_2(Q\rho)\{[K_{41}(\Omega_Q)] - 2/5\} \right.$$

$$+ \tilde{c}_{42}^{(2)} j_4(Q\rho)\left\{ 3[K_{61}(\Omega_Q)] \right.$$

$$\left. - \frac{16}{77}[K_{41}(\Omega_Q) + \frac{2}{35}\right\} + \dots \right). \quad (3.6)$$

$[K_{l'm'}(\Omega_Q)]$ denotes harmonics $K_{l'm'}$ with the normalization omitted.

IV. Conclusions

In general, the quality of structural data will not allow the inclusion of correlations into the rotational form factor approach. In most cases the available single crystals are not of the best quality. Also, the number of independent reflections from orientationally disordered crystals is mostly rather low, because there are only a few (small) molecules in the unit cell. If correlations are ignored, they will be absorbed into effective expansion coefficients in (1.3) which may mask the connection to orientation-dependent potentials. On the other hand, an expansion of $F_{(1)}(\mathbf{Q})$ or $F_{(2)}(\mathbf{Q})$ in general needs not to be extended to the same order as in $F^{rot}(\mathbf{Q})$. The $F_{(k)}(\mathbf{Q})$ with $k \geq 1$ are only corrections to this description which may be important if $\langle u^2 \rangle^k$ is large. With this in mind we find a surprisingly low number of additional parameters required for a proper treatment of correlations between translation and orientation in a structural refinement. It may be hoped that an increasing number of precise diffraction experiments of molecular crystals with orientational disorder – which allow the inclusion of correlations into the analysis – will be available in the future.

An extension of the present work which appears to be desirable concerns the connection to physically meaningful potentials. Such a connection has been given for rotational potentials $V(\omega)$ (*e.g.* Hüller & Press, 1979). A generalization to potentials $V(\omega, \mathbf{R})$ by combining the approaches of Hüller & Press and Michel & Naudts (1977) seems useful and possible.

Table 1. *Final parameters in a least-squares fit of the structural data of* CBr_4I (*More et al.*, 1979) *with* 23 *reflections included*

The meaning of the parameters is given in the text.

Model	Scale factor	$\langle u^2 \rangle$ (Å²)	ρ_{CBr} (Å)	$c_{41}^{(0)}$	$c_{61}^{(0)}$	$c_{81}^{(0)}$	$\tilde{c}_{31}^{(1)}$	$\tilde{c}_{71}^{(1)}$	$\tilde{c}_{72}^{(1)}$	R_w (%)
(a)	17·9 (2·4)	0·170 (20)	1·937 (23)	0·06 (2)	−0·83 (7)	0·14 (14)	—	—	—	7·7
(b)	19·0 (1·7)	0·177 (12)	1·924 (14)	−0·12 (4)	−0·75 (5)	0·33 (11)	0·04 (1)	—	—	5·1
(c)	20·6 (1·3)	0·192 (10)	1·926 (12)	−0·37 (9)	−0·57 (8)	0·85 (17)	0·10 (2)	0·05 (1)	−0·13 (4)	3·4

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Crystallographic Description of Coincidence-Site Lattice Interfaces in Homogeneous Crystals

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Abstract

Coincidence-site lattice interfaces (CSLI) are frequently observed in crystals where a rigid framework remains invariant on both sides of the interface. They also seem to minimize the interface energy, for example, in metals where, empirically, the greater the density of the coincidence-site lattice the more stable the grain boundary becomes. Group-theory considerations allow the determination of all the possible interface operations which leave a given sublattice invariant. A classification of these CSLI with respect to the number of equivalent sublattices they leave invariant is a guide for the prediction of the most stable type of interfaces with respect to the sublattice considered. Examples from different types of crystals illustrate the method, which also applies for translation boundaries, twins and grain boundaries.

Introduction

It has often been verified that, in homogeneous crystals which present coherent boundaries, a fraction of the structure – which may be an atomic lattice or a partial set of atoms distributed on a lattice – remains undisturbed when crossing the boundary. This idea was first proposed by Mallard and Friedel (see, for instance, Friedel, 1926) for explaining the merohedral (or penetration) twins and the twins formed by reticular