

## IV. Symmetry and its Implications

KAARLE KURKI-SUONIO

Department of Physics, University of Helsinki, SF-00170 Helsinki 17, Finland

**Abstract.** Significance of symmetry in representing real- and reciprocal-space properties of a crystal and of its constituents is discussed in terms of symmetry eigenfunctions. The formation of the site-symmetrized multipole expansion for the 32 crystal point symmetries is shown, and the mutual relations between the real- and reciprocal-space expansions are discussed. The origin of the symmetry-based phase relations, equivalences and extinction rules of structure amplitudes is pointed out. Distinction is made between the accurate and approximate ones arising from the true space-group symmetry and from the approximate free-particle symmetry of the constituents, respectively. Finally, the symmetry imposed by reality of charge density and its violation through anomalous dispersion are discussed in terms of symmetric and antisymmetric contributions of atomic charge densities.

### SYMMETRY AND CONSTITUENTS OF MATTER

*Symmetry* is the most fundamental property of any physical system. It is an *exact requirement* fulfilled by all observable properties of the system. Particularly, symmetry defines the constants of motion. The true symmetry is never violated, and any higher symmetry can be realized only approximately.

The idea of *constituents* is a general scheme for "understanding" properties of a physical system. It involves identification of structural units with some free particles. In principle, a bound particle is never identical with a free one. Identification is made possible by characteristic invariants which remain unchanged under the influence of binding forces. This stipulates that the internal interactions responsible for the characteristics of the constituents are stronger than their mutual interactions. Constituents with their free-particle properties, held together by their mutual interactions, form a zeroth-order model for the system. The accuracy of this description depends on the degree of invariance of their free-particle properties.

Nuclei and electrons form a very good zeroth-order model for matter, since nuclear forces are much stronger than the electromagnetic interactions. It is just a beautiful surprise of Nature that atoms and molecules are invariant enough to be treated as constituents of matter. Since both the internal and the mutual interactions are electromagnetic it is obvious that the corresponding zeroth-order model will not be sufficient for detailed understanding of matter. The changes of atoms and molecules due to bonding forces are important.

One of the primary aims of charge-density studies is the observation and characterization of deviations of bound atoms and molecules from free ones. Basic reduction of symmetry occurs when a free particle becomes a part of a larger system. The free-particle symmetry remains, however, as an approximate symmetry of the

bound particle. It will be violated in a way which exactly follows the true reduced symmetry and to an extent depending directly on the strength of the bonding.

Symmetry and its consequences therefore form the basis for understanding the nature of the bonding problem. This paper gives a simple approach to symmetry and its consequences in charge-density studies. Special attention is paid to violations of approximate symmetries, since any observation of them would serve as a direct measure of the deviations from free-particle properties and, thus, of the bonding effects.

### SYMMETRY OPERATORS AND EIGENFUNCTIONS

The basic symmetries correspond to unitary transformations of the Euclidean space or operators acting on spatial functions  $g(\mathbf{r})$ . Table 1 defines four basic symmetry operators using alternatively the position vector  $\mathbf{r}$  or the corresponding conventional Cartesian and spherical coordinates chosen according to the symmetry elements. All symmetry operators can be formed as products of these basic ones.

A unitary transformation corresponds to a symmetry of the system if the system remains invariant under the transformation or, formally, if the corresponding operator  $\hat{U}$  commutes with the Hamiltonian  $\hat{H}$  of the system, i.e.  $\hat{H}\hat{U} = \hat{U}\hat{H}$ . As a consequence, the stationary states  $\psi_i$  are (or can be chosen as) simultaneous eigenfunctions of any mutually commuting set of symmetry operators. Formally, this is the source of all the great simplification won through symmetry:

Let  $S_i$  be the subspace of simultaneous symmetry eigenfunctions belonging to a definite set of eigenvalues  $\lambda_{1i}, \dots, \lambda_{ni}$  of the commuting symmetries  $\hat{U}_1, \dots, \hat{U}_n$ . We then know that: the subspaces  $S_i$  are mutually orthogonal; the Schrödinger equation  $\hat{H}\psi = E\psi$  of the system can be solved separately and independently in each  $S_i$ ; an arbitrary function  $\psi(\mathbf{r})$  has a unique rep-

Table 1. The Basic Symmetry Operators

S. Operation (S. Element)	S. Operator with Definition
Translation (by displacement $\mathbf{a}$ )	$\hat{T}_a g(\mathbf{r}) = g(\mathbf{r} - \mathbf{a})$
Rotation (about $z$ axis through $\alpha$ )	$\hat{R}_{z\alpha} g(r, \theta, \varphi) = g(r, \theta, \varphi - \alpha)$
Reflexion (in $xy$ plane)	$\hat{\sigma}_z g(x, y, z) = g(x, y, -z)$
Inversion (through origin as center)	$\hat{I} g(\mathbf{r}) = g(-\mathbf{r})$

Table 2. Symmetry Eigenfunctions and Eigenvalues,  $\hat{U}g_\lambda = \lambda g_\lambda$ 

Operator	Subspace = eigenfunction $S_\lambda = \{g_\lambda\}$	Eigenvalue $\lambda$
$\hat{T}_a$	$S_\lambda = \{e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}) \mid u(\mathbf{r} - \mathbf{a}) = u(\mathbf{r})\}$	$\lambda = e^{-i\mathbf{k} \cdot \mathbf{a}}$
$\hat{R}_{z\alpha}$	$S_m = \{e^{im\varphi} u(\mathbf{r}) \mid u(r, \theta, \varphi - \alpha) = u(r, \theta, \varphi)\}$	$\lambda_m = e^{-im\alpha}$ , $m = \text{integer}$
$\hat{\sigma}_z$	$S_\pm = \{g(x, y, z) \pm g(x, y, -z)\}$	$\lambda_\pm = \pm 1$
$\hat{I}$	$S_\pm = \{g(\mathbf{r}) \pm g(-\mathbf{r})\}$	$\lambda_\pm = \pm 1$

resentation  $\psi(\mathbf{r}) = \sum \phi_i(\mathbf{r})$  where  $\phi_i$  is the projection of  $\psi$  on  $S_i$ ; for a time-dependent state  $\psi(\mathbf{r}, t)$  of the system  $\langle \phi_i \mid \phi_i \rangle$  is time-independent, indicating that the dynamics of the system will never mix states with different symmetry eigenvalues and, particularly, that a symmetry eigenstate will remain an eigenstate.

Any properly chosen basis sets of the subspaces  $S_i$  form together the natural basis of representation for the system taking full advantage of the symmetry. Table 2 lists the eigenfunctions and eigenvalues of the operators of Table 1 where  $g$  denotes an arbitrary function. For a translation all numbers  $\lambda$  with  $|\lambda| = 1$  are eigenvalues, and eigenfunctions are the Bloch functions. Each value  $\mathbf{k} \cdot \mathbf{a} \in (-\pi, \pi]$  specifies one subspace  $S_\lambda$ . For rotations the situation is very much analogous, except that now the eigenvalues and subspaces are defined by an integer  $m$ . The smallest number  $n$  which makes  $n\alpha$  a multiple of  $2\pi$  defines the number of different eigenvalues, corresponding now to  $m = 0, 1, \dots, n-1$ .

The eigenfunctions of a reflexion and of the inversion are just the even and odd functions with respect to the operation with the parity as the eigenvalue.

*Complete translational symmetry* means invariance under all translations. This implies *homogeneity* of all observable properties and *momentum conservation*. All translations commute and the subspaces of their simultaneous eigenfunctions are the one-dimensional  $S_\mathbf{k} = \{Ce^{i\mathbf{k} \cdot \mathbf{r}}\}$  where  $\mathbf{k}$  runs through the whole reciprocal space. The *free particle* is therefore an extreme case where the stationary states, the momentum eigenfunctions, are uniquely defined by the symmetry. In discussions of translational symmetry the momentum representation thus forms the natural basis.

When the translational symmetry is reduced to that of an *electron in a crystal* with three basic translations  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  the homogeneity is reduced to *periodicity*. The momentum conservation is lost and replaced by conservation of *crystal momentum*. The subspaces of simultaneous eigenfunctions are now the infinite-dimensional spaces  $S_\mathbf{k} = \{e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r})\}$  of Bloch functions with arbitrary triply periodic  $u(\mathbf{r})$ . The wave vector  $\mathbf{k}$  runs through the first Brillouin zone and corresponds to the eigenvalues  $e^{-i\mathbf{k} \cdot \mathbf{a}}, e^{-i\mathbf{k} \cdot \mathbf{b}}$  and  $e^{-i\mathbf{k} \cdot \mathbf{c}}$  of the translations  $\hat{T}_a, \hat{T}_b$  and  $\hat{T}_c$ , respectively. The plane waves with the wave vectors  $\mathbf{k} + 2\pi\mathbf{H}$ , where  $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$  denotes the reciprocal-lattice vectors, form a basis of  $S_\mathbf{k}$ .

*Complete point symmetry* involves invariance under all rotations, reflections, and their combinations including inversion. This implies *isotropy* of all observable properties and conservation of *angular momentum*  $L^2$  with all its components  $L_x, L_y, L_z$  and of parity.

Point-symmetry operations in general do not commute, cf. e.g. Tinkham.<sup>1</sup> Therefore there is no complete set of simultaneous eigenfunctions for all of them. The optimum choice for basis functions is the set of angular-

momentum wave functions, which are the *complex spherical harmonics* (see footnote next page)

$$Y_l^m(\theta, \varphi) = P_l^m(\cos \theta) e^{im\varphi}; \quad (1)$$

$$l = 0, 1, \dots; m = 0, \pm 1, \dots, \pm l$$

with the normalization

$$\int_{4\pi} |Y_l^m|^2 d\Omega = \frac{4\pi}{2l+1} \frac{(l+|m|)!}{(l-|m|)!}$$

Arbitrary radial functions  $R(r)$  can be attached to them so that each function (1) creates an infinite-dimensional subspace  $S_m$  of simultaneous eigenfunctions of the mutually commuting operators  $\hat{L}^2, \hat{L}_z, \hat{R}_{z\alpha}, \hat{\sigma}_z$  and  $\hat{I}$  to the eigenvalues  $\hbar^2 l(l+1), \hbar m, e^{-im\alpha}, (-1)^{l-m}$  and  $(-1)^l$ , respectively.

A *free atom* or an electron in a free atom is a system with complete point symmetry. The angular basis (1) includes the exact symmetry requirement imposed by the symmetry on the wave functions, and the Schrödinger equation can be solved independently in each subspace  $S_m$ .

*Complete axial symmetry*, the symmetry of a *linear molecule*, is an infinite symmetry involving all rotations  $\hat{R}_{z\alpha}$  and possibly  $\hat{\sigma}_z$  plus their combinations including  $\hat{I}$ , which all commute. Conservation of angular momentum is reduced to conservation of  $L_z$ . The subspaces  $S_{m+}$  and  $S_{m-}$  to the eigenvalues  $e^{-im\alpha}$  and  $\pm 1$  are spanned by the subspaces  $S_m$  with  $l = m, m+2, \dots$  and  $l = m+1, m+3, \dots$ , respectively. When point symmetry is reduced in any other way we come to the *finite point symmetries*. Particularly, the *site symmetry* of a bound crystal atom is one of the 32 crystal point symmetries. (The site symmetries occurring in each of the 230 crystallographic space groups are listed in the International Tables.<sup>2</sup>) Conservation of angular momentum is now lost, leaving behind just the conservation of the symmetry eigenvalues. Still the basis (1) gives the optimum starting point, first, since it corresponds to the approximate symmetry, and, second, because the relevant subspaces of symmetry eigenfunctions are easily obtained by symmetrization within each  $l$  separately and consequent direct summation over  $l$ .

Translations do not commute with point-symmetry operations, except for translations parallel to the axis of rotation or to the plane of reflexion. In crystals the choice of basis functions can therefore follow only one of them according to which one is found more important.

#### SYMMETRIC REPRESENTATION OF SPATIAL OBSERVABLES

In a discussion of wave functions all symmetry eigenfunctions are equally important. Non-commuting symmetries complicate the treatment because stationary states can obey at the same time the requirements of one

commuting set of symmetries only. Different sets yield different wave functions for the energies, which are degenerate to a degree defined by the number of existing different commuting sets. Systematic treatment of this situation can best be done using group theory, cf. e.g. Bradley and Cracknell.<sup>3</sup>

For real physical observables the problem of symmetry is far simpler. Any spatial observable, say the charge density  $\rho(\mathbf{r})$ , is invariant under all symmetry operations  $\hat{U}_i$  of the system. This means that  $\hat{U}_i\rho(\mathbf{r}) = \rho(\mathbf{r})$  or that  $\rho$  is a symmetry eigenfunction to the eigenvalue 1 of all symmetry operations of the system. The same is true for both the static and dynamic density (see Chapter XIV), for the electronic and the nuclear potential, the thermal smearing function, etc. We need work just in the subspace of completely symmetric functions of the symmetry of the system. In presence of commuting symmetries only, this is just the subspace of simultaneous eigenfunctions with all symmetry eigenvalues equal to 1. In case of non-commuting symmetries it can be found by a simple symmetrization procedure.

Thus, in complete translational symmetry the plane wave with  $\mathbf{k} = 0$ , i.e.  $\rho = \text{constant}$ , is the only possible function. This reflects the homogeneity of the free-particle system. In case of the translational symmetry of a crystal the subspace of Bloch functions with  $\mathbf{k} = 0$  is the relevant subspace. This says that the charge density must be triply periodic

$$\begin{aligned} \rho(\mathbf{r} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}) &= \rho(\mathbf{r}); \\ n_1, n_2, n_3 &= 0, \pm 1, \pm 2, \dots \end{aligned} \quad (2)$$

In terms of the plane-wave basis of this subspace the allowed functions are the Fourier series

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} F_{\mathbf{H}} e^{-2m\mathbf{H} \cdot \mathbf{r}} \quad (3)$$

with arbitrary coefficients  $F_{\mathbf{H}}$ .

Similarly, rotational symmetry  $\hat{R}_{z\alpha}$  requires  $\rho(\mathbf{r})$  to be periodic in  $\varphi$  with the period  $\alpha$ , or  $\rho \in S_0$ . Reflexion and inversion allow only even functions with respect to the corresponding symmetry element, or  $\rho \in S_+$  etc. Symmetrization means that the requirements imposed by all symmetries are taken into account simultaneously. For any specific point group the symmetric subspace can be obtained, for instance, by symmetrization of the basis (1), as shown in the next section.

In general the symmetrization of a given basis goes as follows. Let  $\{\varphi_n\}$  be the basis and  $\hat{U}_i$ ;  $i = 1, \dots, N$  the set of all symmetry operators of the system. Then  $\{\hat{S}\varphi_n\}$  with the symmetrization operator  $\hat{S} = (1/N) \sum_{i=1}^N \hat{U}_i$  is a basis in the subspace of completely symmetric functions. In fact  $\hat{S}$  is a projection operator projecting any function onto the symmetric subspace. In general the symmetric basis obtained will be overcomplete, the functions  $\hat{S}\varphi_n$  being non-orthogonal and linearly dependent. Often the symmetrization will be easier if performed in successive steps with respect to each of the generators of the group.

#### THE SITE-SYMMETRIZED HARMONICS

The partition of a crystal into atoms or molecules is ambiguous. Bound atoms or molecules cannot be defined uniquely, but, whatever the definition, it must for each atom follow the relevant site symmetry. All spatial observables of the bound atom/molecule must belong to

the completely site-symmetric subspace of functions. Thus, they must be representable as an expansion in terms of the site-symmetrized spherical harmonics which form a basis of this subspace. Since physical variables are real, it is convenient to take as the starting point instead of the complex basis (1) the real spherical harmonics\*

$$y_{lm\pm} = P_l^m(\cos\theta) \frac{\cos m\varphi}{\sin m\varphi}, \quad l = 0, 1, \dots; \quad m = 0, 1, \dots, l \quad (4)$$

with the normalization

$$N_{lm\pm}^2 = \int |y_{lm\pm}|^2 d\Omega = (1 + \delta_{m0}) \frac{2\pi}{2l+1} \frac{(l+m)!}{(l-m)!} \quad (5)$$

The site symmetrization of the spherical harmonics (1) or (4) is easily established, because any point-symmetry operation transforms a spherical harmonic into another one of the same order  $l$ . Thus, each of the symmetrized  $\hat{S}y_{lm\pm}$  is either a spherical harmonic of order  $l$  or identically zero. This simplifies the question of overcompleteness since  $\hat{S}y_{lm\pm}$  and  $\hat{S}y_{l'm'\pm}$  with  $l' \neq l$  are automatically orthogonal and the linear dependences of the symmetrized basis need be checked only within each order separately.

The harmonics  $Y_l^m$  are eigenfunctions of  $\hat{R}_{z2\pi/n}$ ,  $\hat{\sigma}_z$ ,  $\hat{I}$  and the rotatory inversion  $\hat{I}\hat{R}_{z2\pi/n}$ . Symmetrization of  $Y_l^m$  with respect to any of them conserves those with the eigenvalue 1 and destroys the others. Because  $Y_l^m$  and  $Y_l^{-m}$  are always conserved together, the resulting "index picking rules" apply for  $y_{lm\pm}$  as well.

The Cartesian representations

$$r^l Y_l^m = \frac{d^m P_l(z)}{dz^m} (x \pm iy)^m, \quad (6)$$

$$r^l y_{lm\pm} = \frac{d^m P_l(z)}{dz^m} \begin{cases} \text{Re}(x + iy)^m \\ \text{Im}(x + iy)^m \end{cases} \quad (7)$$

show that  $y_{lm\pm}$  are all even or odd polynomials with respect to each variable with

$$z\text{-parity} = (-1)^{l-m},$$

$$y\text{-parity} = \pm 1 \text{ for } (l, m, \pm) \text{ and}$$

$x\text{-parity} = (-1)^m$  and  $(-1)^{m+1}$  for  $(l, m, +)$  and  $(l, m, -)$ , respectively. Thus, they are eigenfunctions of  $\hat{\sigma}_x$ ,  $\hat{\sigma}_y$ ,  $\hat{\sigma}_z$ ,  $\hat{R}_{x\pi}$ ,  $\hat{R}_{y\pi}$ ,  $\hat{R}_{z\pi}$  and  $\hat{I}$  which only affect the signs of the coordinates. In symmetrization those with the eigenvalue +1 are preserved.

Table 3 summarizes the picking rules based on these eigenfunction properties of  $Y_l^m$  and  $y_{lm\pm}$ . The operators listed here are sufficient for generation of any of the 27 non-cubic site symmetries. The completely symmetrized spherical-harmonics basis for any of these symmetries is

\* The nomenclature varies. In general the solutions of the Laplace equation  $\nabla^2 f = 0$  are *harmonics*. In spherical coordinates it has the solutions  $r^l Y_l^m$ ,  $r^{-l-1} Y_l^m$  where  $Y_l^m = Y_l(\theta, \varphi)$  is any combination  $Y_l^m = \sum_{m'} C_{m'} y_{lm'}$ . Both the solutions and their angular dependence  $Y_l^m$  are generally called *spherical harmonics*. To make a distinction one sometimes calls them *spherical volume harmonics* and *spherical surface harmonics* or just *surface harmonics*. Further, the name spherical harmonics is often used specifically either for the functions  $Y_l^m$ , (1) or  $y_{lm\pm}$ , (4). The more specific names *zonal*, *tesseral* and *sectoral* harmonics are used for these sets with  $m = 0$ ;  $0 < m < l$  and  $m = l$ , respectively.<sup>4</sup>

Table 3. Effect of Symmetrization on Real Spherical Harmonics ( $\lambda, \mu, j$  are integers)

Symmetry element	Operation	Index picking rule for $y_{lmp}$
Center of symmetry	$\hat{I} (xyz \rightarrow -x, -y, -z)$	$(2\lambda, m, \pm)$
$p$ -fold axis $\parallel z$ -axis	$\hat{R}_z^{2\pi/p}$	$(l, p\mu, \pm)$
$p$ -fold inversion axis $\parallel z$	$\hat{I}\hat{R}_z^{2\pi/p}$ $p$ even $p$ odd	$(2\lambda, p\mu, \pm)$ $(2\lambda + 1, p(\mu + \frac{1}{2}), \pm)$ $(2\lambda, p\mu, \pm)$
2-fold axis $\parallel y$ -axis	$\hat{R}_{y\pi} (xz \rightarrow -x, -z)$	$(2\lambda, m, +)$ $(2\lambda + 1, m, -)$
2-fold axis $\parallel x$ -axis	$\hat{R}_{x\pi} (yz \rightarrow -y, -z)$	$(l, l - 2j, +)$ $(l, l - 2j + 1, -)$
Symmetry plane $\perp z$ -axis	$\hat{\sigma}_z (z \rightarrow -z)$	$(l, l - 2j, \pm)$
$\perp y$ -axis	$\hat{\sigma}_y (y \rightarrow -y)$	$(l, m, +)$
$\perp x$ -axis	$\hat{\sigma}_x (x \rightarrow -x)$	$(l, 2\mu, +)$ $(l, 2\mu + 1, -)$

Table 4. Index Picking Rules of Site-Symmetric Spherical Harmonics

Symmetry	Choice of coordinate axes	Indices of symmetric $y_{lmp}$
$\frac{1}{1}$	any	all $(l, m, \pm)$
$\frac{1}{1}$	any	$(2\lambda, m, \pm)$
2	$2 \parallel z$	$(l, 2\mu, \pm)$
$m$	$m \perp z$	$(l, l - 2j, \pm)$
$2/m$	$2 \parallel z, m \perp z$	$(2\lambda, 2\mu, \pm)$
222	$2 \parallel z, 2 \parallel y, (2 \parallel x)$	$(2\lambda, 2\mu, +), (2\lambda + 1, 2\mu, -)$
$mm2$	$2 \parallel z, m \perp y, (m \perp x)$	$(l, 2\mu, +)$
$mmm$	$m \perp z, m \perp y, m \perp x$	$(2\lambda, 2\mu, +)$
4	$4 \parallel z$	$(l, 4\mu, \pm)$
$\bar{4}$	$4 \parallel z$	$(2\lambda, 4\mu, \pm), (2\lambda + 1, 4\mu + 2, \pm)$
$4/m$	$4 \parallel z, m \perp z$	$(2\lambda, 4\mu, \pm)$
422	$4 \parallel z, 2 \parallel y, (2 \parallel x)$	$(2\lambda, 4\mu, +), (2\lambda + 1, 4\mu, -)$
$4mm$	$4 \parallel z, m \perp y, (m \perp x)$	$(l, 4\mu, +)$
$\bar{4}2m$	$4 \parallel z, 2 \parallel x, (m \perp xy \rightarrow yx)$ $m \perp y, (2 \perp xyz \rightarrow yxz)$	$(2\lambda, 4\mu, +), (2\lambda + 1, 4\mu + 2, -)$ $(2\lambda, 4\mu, +), (2\lambda + 1, 4\mu + 2, +)$
$4/mmm$	$4 \parallel z, m \perp z, m \perp x, (m \perp xy \rightarrow yx)$	$(2\lambda, 4\mu, +)$
$\frac{3}{3}$	$3 \parallel z$	$(l, 3\mu, \pm)$
$\frac{3}{3}$	$3 \parallel z$	$(2\lambda, 3\mu, \pm)$
32	$3 \parallel z, 2 \parallel y$ $2 \parallel x$	$(2\lambda, 3\mu, +), (2\lambda + 1, 3\mu, -)$ $(3\mu + 2j, 3\mu, +), (3\mu + 2j + 1, 3\mu, -)$
$3m$	$3 \parallel z, m \perp y$ $m \perp x$	$(l, 3\mu, +)$ $(l, 6\mu, +), (l, 6\mu + 3, -)$
$\bar{3}m$	$3 \parallel z, m \perp y$ $m \perp x$	$(2\lambda, 3\mu, +)$ $(2\lambda, 6\mu, +), (2\lambda, 6\mu + 3, -)$
6	$6 \parallel z$	$(l, 6\mu, \pm)$
$\bar{6}$	$6 \parallel z = (3 \parallel z, m \perp z)$	$(2\lambda, 6\mu, \pm), (2\lambda + 1, 6\mu + 3, \pm)$
$6/m$	$6 \parallel z, m \perp z$	$(2\lambda, 6\mu, \pm)$
622	$6 \parallel z, 2 \parallel y, (2 \parallel x)$	$(2\lambda, 6\mu, +), (2\lambda + 1, 6\mu, -)$
$6mm$	$6 \parallel z, m \perp y, (m \perp x)$	$(l, 6\mu, +)$
$\bar{6}m2$	$6 \parallel z, m \perp y, (2 \parallel x)$ $m \perp x, (2 \parallel y)$	$(2\lambda, 6\mu, +), (2\lambda + 1, 6\mu + 3, +)$ $(2\lambda, 6\mu, +), (2\lambda + 1, 6\mu + 3, -)$
$6/mmm$	$6 \parallel z, m \perp z, m \perp y, (m \perp x)$	$(2\lambda, 6\mu, +)$

therefore a set of functions  $y_{lmp}$ . It is obtained by simultaneous application of the picking rules corresponding to the group generators. The results are listed in Table 4. For this table to be applicable one has to define for each atom a local Cartesian coordinate system adapted to its site symmetry as indicated in the table.

To obtain the symmetrized harmonics for the five cubic site symmetries we need one more symmetrization. The groups  $23, m\bar{3}, 432, \bar{4}3m$  and  $m3m$  are obtained from  $222, mmm, 422, \bar{4}2m$  and  $4/mmm$ , respectively by

introducing a 3-fold axis in the  $[111]$  direction. This requires the further symmetrization under cyclic permutation of the coordinates defined as  $\hat{S}f(x, y, z) = \frac{1}{3}[f(x, y, z) + f(y, z, x) + f(z, x, y)]$ , which yields sets of cubic harmonics  $K_{ij}$  as given in Tables 5 and 6 up to the 10<sup>th</sup> order. Several  $y_{lmp}$  lead to the same function  $K_{ij}$ , reflecting the overcompleteness of symmetrized bases in general. However, since the functions  $K_{ij}$  listed contain each  $y_{lmp}$  just once, they are orthogonal. The normalized functions  $K_{ij}/N_{ij}$  are identical with cubic harmonics of

Table 5. Symmetrization of  $y_{imp}$  with Respect to a 3-axis in [111] Direction

$(l, m, p) \longrightarrow$	$\hat{S}y_{imp}$	belongs to	23	$m\bar{3}$	432	$\bar{4}3m$	$m\bar{3}m$
(0, 0, +)	$K_0$		×	×	×	×	×
(2, 0, +), (2, 2, +)	0						
(3, 2, -)	$K_3$		×			×	
(4, 0, +), (4, 4, +)	$K_4$		×	×	×	×	×
(4, 2, +)	0						
(5, 2, -), (5, 4, -)	0						
(6, 0, +), (6, 4, +)	$K_{6,1}$		×	×	×	×	×
(6, 2, +), (6, 6, +)	$K_{6,2}$		×	×			
(7, 2, -), (7, 6, -)	$K_7$		×			×	
(7, 4, -)	0						
(8, 0, +), (8, 4, +), (8, 8, +)	$K_8$		×	×	×	×	×
(8, 2, +), (8, 6, +)	0						
(9, 2, -), (9, 6, -)	$K_{9,1}$		×			×	
(9, 4, -), (9, 8, -)	$K_{9,2}$		×		×		
(10, 0, +), (10, 4, +), (10, 8, +)	$K_{10,1}$		×	×	×	×	×
(10, 2, +), (10, 6, +), (10, 10, +)	$K_{10,2}$		×	×			

Table 6. Expressions for Cubic Harmonics

Unnormalized $K_{ij}(\theta, \varphi)$	Normalization constant $N_{ij}^2$
$K_0 = y_{00+} = 1$	$\frac{4\pi}{240\pi}$
$K_3 = y_{32-}$	$\frac{7}{7}$
$K_4 = y_{40+} + \frac{1}{168}y_{44+}$	$\frac{16\pi}{21}$
$K_{6,1} = y_{60+} - \frac{1}{360}y_{64+}$	$\frac{32\pi}{13}$
$K_{6,2} = y_{62+} - \frac{1}{792}y_{66+}$	$\frac{512\pi}{13} \cdot \frac{105}{11}$
$K_7 = y_{72-} + \frac{1}{1560}y_{76-}$	$\frac{256\pi}{15} \cdot \frac{567}{13}$
$K_8 = y_{80+} + \frac{1}{5940} \left( y_{84+} + \frac{1}{672}y_{88+} \right)$	$\frac{256\pi}{17 \cdot 33}$
$K_{9,1} = y_{92-} - \frac{1}{2520}y_{96-}$	$\frac{512\pi}{19} \cdot 165$
$K_{9,2} = y_{94-} - \frac{1}{4080}y_{98-}$	$\frac{2048\pi}{19} \cdot \frac{243 \cdot 5005}{17}$
$K_{10,1} = y_{10,0+} - \frac{1}{5460} \left( y_{10,4+} + \frac{1}{4320}y_{10,8+} \right)$	$\frac{512\pi}{21} \cdot \frac{3}{65}$
$K_{10,2} = y_{10,2+} + \frac{1}{43680} \left( y_{10,6+} - \frac{1}{456}y_{10,10+} \right)$	$\frac{2048\pi}{21} \cdot \frac{4455}{247}$

the types  $\alpha, \alpha', \beta, \beta'$  ( $K_{2\lambda,1}, K_{2\lambda,2}, K_{2\lambda+1,1}, K_{2\lambda+1,2}$ , respectively) of von der Lage and Bethe<sup>5</sup> and with the one-dimensional real representations of the cubic groups as given e.g. by Bradley and Cracknell.<sup>3</sup>

#### THE MULTIPOLE EXPANSION

Once the position of an atom in a crystal is known the crystal symmetry determines its site symmetry and, hence, the form of the site-symmetrized harmonic expansion of the atomic charge density. If the origin is put at the atomic position and if a local Cartesian coordinate system adapted to the site symmetry is used, this expansion can be written in the form

$$\rho(\mathbf{r}) = \sum_{imp} \frac{1}{N_{imp}} \rho_{imp}(\mathbf{r}) y_{imp}(\theta, \varphi) \quad (8)$$

for any of the 27 non-cubic site symmetries and in the form

$$\rho(\mathbf{r}) = \sum_{ij} \frac{1}{N_{ij}} \rho_{ij}(\mathbf{r}) K_{ij}(\theta, \varphi) \quad (8')$$

for any of the five cubic site symmetries, where the indices  $l, m, p$  and  $l, j$  run through the values indicated by Tables 4 and 5, respectively. The same form of expansion is valid for all other spatial observables of the atom. Since the bound atom cannot be uniquely defined, neither the radial densities  $\rho_{imp}(\mathbf{r})$  nor  $\rho_{ij}(\mathbf{r})$  are unique, but the form of the expansion is. If we have by some means defined the atomic charge density  $\rho(\mathbf{r})$  then the radial densities are obtained from

$$\rho_{imp}(\mathbf{r}) = \frac{1}{N_{imp}} \int_{4\pi} \rho(\mathbf{r}) y_{imp}(\theta, \varphi) d\Omega \quad (9)$$

or

$$\rho_{ij}(\mathbf{r}) = \frac{1}{N_{ij}} \int_{4\pi} \rho(\mathbf{r}) K_{ij}(\theta, \varphi) d\Omega, \quad (9')$$

corresponding to the general way of calculating coefficients of an orthogonal series.

The expansion (8) or (8') is called the *multipole expansion* since its terms have a close relation to the multipole moments of the charge distribution  $\rho(\mathbf{r})$ . The quantities

$$q_{lmp} = \frac{1}{N_{lmp}} \int \rho(\mathbf{r}) r^l y_{lmp}(\theta, \varphi) d^3r = \int_0^{(\infty)} \rho_{lmp}(r) r^{l+2} dr, \quad (10)$$

$$q_{ij} = \frac{1}{N_{ij}} \int \rho(\mathbf{r}) r^l K_{ij}(\theta, \varphi) d^3r = \int_0^{(\infty)} \rho_{ij}(r) r^{l+2} dr \quad (10')$$

are called multipole moments in spherical coordinates. According to the polynomial representation (7) they are simple linear combinations of the conventional Cartesian multipole moments of order  $l$ . In the lowest three orders we get, in terms of the monopole moment or the total charge  $Q$ , of the components  $p_x, p_y, p_z$  of the dipole vector and of the components of the quadrupole tensor  $Q_{ij} = \int (3x_i x_j - r^2 \delta_{ij}) \rho(\mathbf{r}) d^3r$ ,

$$q_{00+} = Q/2\sqrt{\pi} \quad (11)$$

$$q_{10+} = \frac{1}{2} \sqrt{3/\pi} p_z \quad (12)$$

11+	x
11-	y

$$q_{20+} = \frac{1}{4} \sqrt{5/\pi} Q_{zz}; \quad q_{21+} = \frac{1}{2} \sqrt{5/3\pi} Q_{xz};$$

21-	yz
22-	xy

(13)

$$q_{22+} = \frac{1}{4} \sqrt{5/3\pi} (Q_{xx} - Q_{yy}).$$

The terms with  $l = 0, 1, 2, 3, 4, 5, 6$ , etc. of the multipole expansion are correspondingly called monopole or scalar, dipole or vector, quadrupole, octopole, hexadecapole, triacontadipole, hexecontatetrapole, etc. terms, respectively.

Tables 4 and 5 indicate directly for each site symmetry how many independent components there are in each multipole tensor and, particularly, which of the multipoles vanish through symmetry.

The approximate free-atom symmetry of the bound atom corresponds to a spherical charge distribution, i.e. to the monopole term. Because of bonding the monopole term of the bound atom will be slightly different from the free-atom radial density. The arising non-spherical terms  $l > 0$  violate the approximate symmetry reflecting the nature of the symmetry reduction.

The *charge density of the whole crystal* can also be represented as a multipole expansion (8) or (8'), as first suggested by Atoji.<sup>6</sup> The form of the expansion must then correspond to the site symmetry of the origin. This charge density, contrary to the atomic one, is conceptually unique and is represented by the Fourier series (3).

Inserting Eq. (3) in (9) or (9') we get, by application of the general Fourier invariance theorem of the spherical harmonics

$$\int Y_l(\theta, \varphi) e^{2\pi i \mathbf{s} \cdot \mathbf{r}} d\Omega = 4\pi (-i)^l j_l(2\pi S r) Y_l(\theta_s, \varphi_s), \quad (14)$$

for the corresponding radial densities

$$\rho_{lmp}(r) = \frac{4\pi (-i)^l}{VN_{lmp}} \sum_{\mathbf{H}} F_{\mathbf{H}j_l}(2\pi H r) y_{lmp}(\theta_{\mathbf{H}}, \varphi_{\mathbf{H}}), \quad (15)$$

$$\rho_{ij}(r) = \frac{4\pi (-i)^l}{VN_{ij}} \sum_{\mathbf{H}} F_{\mathbf{H}j_l}(2\pi H r) K_{ij}(\theta_{\mathbf{H}}, \varphi_{\mathbf{H}}), \quad (15')$$

where  $j_l(x)$  is the spherical Bessel function of order  $l$ .<sup>7</sup> We can choose the origin at any atomic site. The phases of the structure amplitudes  $F_{\mathbf{H}}$  just depend on this choice. Then we can understand the radial densities (15) or (15') at small values of  $r$  to represent the atom at the origin. For radii  $r$  clearly less than the nearest neighbour distance, the multipole expansion of the whole crystal converges rapidly. Few terms are necessary to show the central atom accurately. The number of terms necessary for a good representation of  $\rho(\mathbf{r})$  at larger distances increases rapidly with increasing  $r$ .

#### SYMMETRY IN RECIPROCAL SPACE

In diffraction studies we deal with reciprocal-space properties of the system like the scattering amplitude or the Fourier transform

$$f(\mathbf{S}) = \int \rho(\mathbf{r}) e^{2\pi i \mathbf{s} \cdot \mathbf{r}} d^3r \quad (16)$$

of the electron charge distribution  $\rho(\mathbf{r})$ . The inverse relation

$$\rho(\mathbf{r}) = \int f(\mathbf{S}) e^{-2\pi i \mathbf{s} \cdot \mathbf{r}} d^3S \quad (17)$$

is the representation of  $\rho(\mathbf{r})$  in the plane-wave basis. Consequences of symmetry in reciprocal space can therefore also be interpreted in terms of symmetrization of the plane-wave basis.

The operator  $\hat{U}$  is uniquely defined in reciprocal space through the statement:

$$\hat{U}f(\mathbf{S}) = \int [\hat{U}\rho(\mathbf{r})] e^{2\pi i \mathbf{s} \cdot \mathbf{r}} d^3r, \quad (18)$$

for all  $f$  and  $\rho$  related through Eq. (16). By this definition all equations, e.g. commuting rules and eigenvalue equations, fulfilled in the real-space representation are valid in reciprocal space as well. Thus, reciprocal-space eigenfunctions are Fourier transforms of the real-space eigenfunctions and belong to the same eigenvalues.

According to the definition (18) the *translation* operator  $\hat{T}_a$  has the effect of multiplication by an  $\mathbf{S}$ -dependent phase factor:

$$\hat{T}_a f(\mathbf{S}) = e^{2\pi i \mathbf{a} \cdot \mathbf{S}} f(\mathbf{S}). \quad (19)$$

For such an operator the subspace of eigenfunctions to an arbitrary eigenvalue  $e^{2\pi i \mathbf{a} \cdot \mathbf{S}_0}$  is defined by all functions that vanish everywhere except on the set of equidistant parallel planes defined by the equation

$$\mathbf{a} \cdot \mathbf{S} = \mathbf{a} \cdot \mathbf{S}_0 + n; \quad n = 0, \pm 1, \pm 2, \dots \quad (20)$$

This is equivalent to stating that in the plane-wave representation of the corresponding real-space eigenfunctions only wave numbers  $\mathbf{k}$  with  $\mathbf{a} \cdot \mathbf{k} = -2\pi \mathbf{a} \cdot \mathbf{S}_0 - 2\pi n$  can be present, which just form the plane-wave basis for the subspace of the relevant Bloch functions in Table 2.

All *point-symmetry* operators preserve their nature in the Fourier transformation, i.e. rotation is a rotation about the same axis and through the same angle, reflexion is a reflexion in the same plane and inversion is an inversion in both spaces simultaneously. The meaning of this statement will be clear if we define a common Cartesian coordinate system with dimensionless unit

vectors  $i, j, k$ , writing  $\mathbf{r} = xi + yj + zk$ ,  $\mathbf{S} = hi + kj + lk$ . Then we have, corresponding to Table 1:

$$\hat{R}_{za}f(\mathbf{S}, \theta_s, \varphi_s) = f(\mathbf{S}, \theta_s, \varphi_s - \alpha);$$

$$\hat{\sigma}_z f(h, k, l) = f(h, k, -l); \hat{I}f(\mathbf{S}) = f(-\mathbf{S}).$$

Thus, the treatment of point symmetry in reciprocal space is in all details similar to that in real space. The Fourier invariance (14) of the spherical harmonics, forming the natural bases for any subspaces of point-symmetry eigenfunctions, is an expression of this invariance. The scattering amplitude (16) must belong to the eigenvalue 1 of all symmetries of the system.

According to Eq. (20) the subspace of completely symmetrized functions for the crystal translational symmetry is formed by functions which vanish everywhere except at points which lie simultaneously on the three sets of parallel planes  $\mathbf{a} \cdot \mathbf{S} = h$ ,  $\mathbf{b} \cdot \mathbf{S} = k$ ,  $\mathbf{c} \cdot \mathbf{S} = l$ , i.e. at the reciprocal-lattice points. In analytic form this is defined by

$$f(\mathbf{S}) = \sum_{\mathbf{H}} F_{\mathbf{H}} \delta(\mathbf{S} - \mathbf{H}) \quad (21)$$

with arbitrary coefficients  $F_{\mathbf{H}}$ . In terms of the plane-wave representation of real-space functions this says that the wave vectors  $\mathbf{k} = -2\pi\mathbf{H}$  form the basis of the symmetrized functions as expressed by Eq. (3).

The site-symmetrized basis for representing scattering amplitudes of bound atoms is given also in reciprocal space by the symmetrized harmonics as defined by Tables 4, 5, and 6. Thus the atomic scattering amplitude has the same type of multipole expansion as the atomic charge density:

$$f(\mathbf{S}) = \sum_{lmp} \frac{1}{N_{lmp}} f_{lmp}(\mathbf{S}) y_{lmp}(\theta_s, \varphi_s) \quad (22)$$

or

$$f(\mathbf{S}) = \sum_{ly} \frac{1}{N_{ly}} f_{ly}(\mathbf{S}) K_{ly}(\theta_s, \varphi_s), \quad (22')$$

where the *radial scattering amplitudes* are obtained from the scattering amplitude through the equation

$$f_{lmp}(\mathbf{S}) = \frac{1}{N_{lmp}} \int_{4\pi} f(\mathbf{S}) y_{lmp}(\theta_s, \varphi_s) d\Omega_s, \quad (23)$$

$$f_{ly}(\mathbf{S}) = \frac{1}{N_{ly}} \int_{4\pi} f(\mathbf{S}) K_{ly}(\theta_s, \varphi_s) d\Omega_s. \quad (23')$$

The expansion (22) or (22') is obtained by Fourier transforming the real-space expansion (8) or (8'), showing that the radial densities and the radial scattering amplitudes are related through the Fourier-Bessel transformation

$$f_{lmp}(\mathbf{S}) = 4\pi i^l \int_0^{(\infty)} \rho_{lmp}(r) j_l(2\pi Sr) r^2 dr, \quad (24)$$

$$f_{ly}(\mathbf{S}) = 4\pi i^l \int_0^{(\infty)} \rho_{ly}(r) j_l(2\pi Sr) r^2 dr. \quad (24')$$

It is worthwhile inserting for the spherical Bessel function its power expansion. This yields for  $f_{lmp}$  the power series

$$f_{lmp}(\mathbf{S}) = 4\pi i^l \frac{\sqrt{\pi}}{2} \sum_{n=0}^{\infty} \left[ \frac{(-1)^n \pi^{l+2n}}{n! \Gamma(n+j+3/2)} \int_0^{\infty} \rho_{lmp}(r) r^{l+2n+2} dr \right] S^{l+2n} \quad (25)$$

showing e.g. that the radial scattering amplitude  $f_{lmp}$  behaves at the origin like  $S^l$  with a coefficient proportional to the multipole moment  $q_{lm\hat{e}_z}$ , given by Eq. (10), of the system. Vice versa, the multipole moments are determined by the behaviour of the scattering amplitude at the origin:

$$q_{lmp} = (-i)^l \frac{1}{2} \pi^{-l-3/2} \Gamma\left(l + \frac{3}{2}\right) \frac{1}{l!} \left. \frac{d^l f_{lmp}(\mathbf{S})}{dS^l} \right|_{S=0}. \quad (26)$$

#### EQUIVALENT REFLEXIONS AND EXTINCTION RULES

Equation (21) summarizes the effect of translational symmetry on the scattering amplitude of a crystal. It is concentrated into Dirac deltas of weights  $F_{\mathbf{H}}$ , called the structure amplitudes, at the reciprocal-lattice points  $\mathbf{H}$ . This expression must further be invariant under all other operators of the crystal space-group symmetry. This involves two kinds of symmetries.

First, there are the *site symmetries* of different points of the unit cell. If  $\hat{U}_0$  is a point-symmetry operator belonging to the point  $\mathbf{r}_0$ , then  $\hat{T}_{-\mathbf{r}_0}$  is invariant under  $\hat{U}_0$  or, written in reciprocal space,

$$\hat{U}_0[e^{-2\pi i \mathbf{r}_0 \cdot \mathbf{S}} f(\mathbf{S})] = e^{-2\pi i \mathbf{r}_0 \cdot \mathbf{S}} f(\mathbf{S}).$$

When applied to Eq. (21) this says that in the operation  $\hat{U}_0$  any reciprocal-lattice point  $\mathbf{H}$  is transformed into another one  $\mathbf{K}$ , and that the corresponding structure amplitudes have the phase relationship

$$F_{\mathbf{K}} = e^{2\pi i \mathbf{r}_0 \cdot (\mathbf{K} - \mathbf{H})} F_{\mathbf{H}}. \quad (27)$$

Second, there may be *combined symmetries*  $\hat{U}_1 \hat{T}_{\mathbf{R}}$  involving a non-lattice translation and a point-symmetry operation  $\hat{U}_1$  with respect to a point  $\mathbf{r}_1$  (any point of the relevant axis or plane). This imposes invariance of  $\hat{T}_{-\mathbf{r}_0}$  under  $\hat{U}_1 \hat{T}_{\mathbf{R}}$  or, written in reciprocal space,

$$\hat{U}_1 e^{2\pi i (\mathbf{R} - \mathbf{r}_1) \cdot \mathbf{S}} f(\mathbf{S}) = e^{-2\pi i \mathbf{r}_1 \cdot \mathbf{S}} f(\mathbf{S}).$$

This again requires that  $\hat{U}_1$  bring each reciprocal-lattice point  $\mathbf{H}$  to another one  $\mathbf{K}$  and that there be the phase relationship

$$F_{\mathbf{K}} = e^{-2\pi i \mathbf{R} \cdot \mathbf{K}} \cdot e^{2\pi i \mathbf{r}_1 \cdot (\mathbf{K} - \mathbf{H})} F_{\mathbf{H}} \quad (28)$$

between the relevant structure amplitudes.

The *phase rules* (27) and (28) written for a set of generators of the space group express in full the requirements put by the symmetry on the scattering amplitude (21) of a crystal.

Each of these rules yields an *equivalence rule* of structure amplitudes such that  $|F_{\mathbf{K}}| = |F_{\mathbf{H}}|$ . The *crystal point group*, which includes all point-symmetry operators occurring in the crystal space group either as a true point-symmetry with respect to a point in crystal (type  $\hat{U}_0$ ) or as a part of a combined symmetry (type  $\hat{U}_1$ ), is thus the symmetry group of  $|F_{\mathbf{H}}|$ . (It is not necessary that the point symmetry of the crystal with respect to any single point equal the crystal point symmetry.)

Further, for any reciprocal-lattice point  $\mathbf{H}$ , which is degenerate in a point-symmetry operation involved in a combined symmetry (type  $\hat{U}_1$ ), Eq. (28) yields

$$F_{\mathbf{H}} = e^{-2\pi i \mathbf{R} \cdot \mathbf{H}} F_{\mathbf{H}}. \quad (29)$$



This expresses an *extinction rule*:  $F_{\mathbf{H}} = 0$  unless  $\mathbf{R} \cdot \mathbf{H}$  is an integer. Thus, each combined symmetry necessary to generate the space group defines a set of *strictly forbidden reflexions*.

These phase rules, equivalences and extinction rules are all consequences of the symmetry of the crystal and, hence, *exact requirements*. For each of the 230 crystal space groups that can be generated by three translations, point symmetry operators and combined symmetries, these rules are listed in the International Tables<sup>2</sup> under the title "General".

Representation of the crystal as a superposition of atoms does not bring any new aspects of the exact symmetry of the crystal. Let us for simplicity consider one kind of atom only. The number  $p$  of equivalent atoms depends on the crystal symmetry and on the degeneracy of the atomic site in the symmetry. They are all obtained from one of them, taken as number 1, through a set of translations and point-symmetry operations  $\hat{U}_n$  as defined by the space group. Their contribution to  $F_{\mathbf{H}}$  can thus be written in the form

$$F_{\mathbf{H}_1} = \sum_{n=1}^p e^{2\pi i \mathbf{R}_n \cdot \mathbf{H}} \hat{U}_n f_i(\mathbf{H}). \quad (30)$$

Now, the whole crystal symmetry is built in this expression through the site symmetry of  $f_i(\mathbf{S})$ , the positions  $\mathbf{R}_n$ , the symmetry operations  $\hat{U}_n$  which form a subgroup of the crystal point symmetry, and the reciprocal lattice  $\{\mathbf{H}\}$ . Therefore, if the scattering amplitude  $f_i(\mathbf{S})$  follows the site symmetry without any further assumptions, i.e. if it can be written in the form of the relevant multipole expansion (22) or (22'), then Eq. (30) does exhibit exactly those phase relations, equivalences and extinction rules which were obtained generally from the space-group symmetry, no less and no more. This is obvious, since in principle we can just divide the total crystal charge density arbitrarily into equivalent site symmetric contributions and call such a symmetric unit the "atom" in our example.

However, if we assume the approximate free-atom symmetry, then we have a spherical  $f_i(\mathbf{S})$  and  $\hat{U} f_i(\mathbf{S}) = f_i(\mathbf{S})$  for all point-symmetry operations  $\hat{U}$ . Equation (30) is then reduced to

$$F_{\mathbf{H}_1} \approx f_i(\mathbf{H}) \cdot \sum_{n=1}^p e^{2\pi i \mathbf{R}_n \cdot \mathbf{H}}. \quad (31)$$

The difference between Eqs. (31) and (30) tells the effect of approximate symmetry.

Particularly, for special positions  $\mathbf{R}_n$  the sum of exponentials in Eq. (31) may have equal absolute value for some  $F_{\mathbf{H}}$  and  $F_{\mathbf{K}}$  with  $\mathbf{K} = \mathbf{H}$  but which are not related through the crystal point symmetry. This is trivially true if  $p = 1$ . As a consequence we may get additional *approximate equivalences* of structure amplitudes.

Secondly, the sum of exponentials in Eq. (31) may vanish systematically in a set of reciprocal-lattice points. Thus, we get additional *approximate extinction rules*. They refer to the contribution of one kind of atom and are specific for each kind. They are all listed in International Tables<sup>2</sup> under the title "Special". They are never exactly true. In simple structures they may give rise to the occurrence of very weak, *almost forbidden reflexions*, like the famous  $F_{222}$  in the diamond structure.

Conventional talk about reflexions that depend just on one kind of atom, e.g. Cu reflexions and O reflexions in  $\text{Cu}_2\text{O}$ , is always based on the approximate extinction

rules and may lead to erroneous conclusions in charge-density analysis.<sup>8,9</sup>

If violation of the approximate extinction rules (or equivalences) can be observed, they give a direct measure of bonding effects or anharmonicity of thermal motion.<sup>10-12</sup>

#### REALITY AS A SYMMETRY

If  $\rho(\mathbf{r})$  is a *real* function and  $f(\mathbf{S})$  its Fourier transform (16), then the complex conjugate  $f^*(\mathbf{S})$  is the Fourier transform of  $\hat{I}\rho(\mathbf{r})$ . Because inversion is inversion also in reciprocal space, this yields

$$\hat{I}f(\mathbf{S}) = f^*(\mathbf{S}). \quad (32)$$

The reality of the charge density therefore appears as a symmetry of  $|f(\mathbf{S})|$  under inversion, known as Friedel's law.

If our system has a center of symmetry and we choose it as the origin, then  $\hat{I}f(\mathbf{S}) = f(\mathbf{S})$  by symmetry. Combined with the reality condition (32) this yields  $f^* = f$  showing that  $f(\mathbf{S})$  is also real.

For a non-centrosymmetric crystal, reality of the charge density gives an additional equivalence rule  $|F_{-\mathbf{H}}| = |F_{\mathbf{H}}|$ . For a centrosymmetric one this is already true due to symmetry. This adds  $\hat{I}$  as a new generator to the symmetry group of  $|f(\mathbf{S})|$ . If  $\{\hat{U}_1, \dots, \hat{U}_n\}$  is the crystal point group then the *Laue group*  $\{\hat{U}_n, \hat{I}\hat{U}_n\}$  of the crystal is the point group of  $|f(\mathbf{S})|$ . For a centrosymmetric crystal the two groups are identical. For a non-centrosymmetric one the number of elements is double in the Laue group. In this way the set of equivalent reflexions consists of two partial sets  $\{\hat{S}\mathbf{H}\}$  and  $\{\hat{I}\hat{S}\mathbf{H}\} = \{-\hat{S}\mathbf{H}\}$ .<sup>13</sup> The equivalence within each is due to symmetry; the equivalence of the two sets is due to reality.

The *anomalous dispersion* causes the coherent scattering power  $\rho'(\mathbf{r})$  to differ from the charge density  $\rho(\mathbf{r})$ . Since it causes a phase change in the scattering process  $\rho'(\mathbf{r})$  is complex. Its imaginary component corresponds physically to a current density rather than a charge density. All genuine symmetry conditions are still exactly valid for  $\rho'(\mathbf{r})$  and the corresponding effective structure amplitudes  $F'_{\mathbf{H}}$  obey the corresponding phase rules, equivalences and extinction rules. Only the *reality* is no longer accurate for  $\rho'$ —as it is for  $\rho$ —but appears as an approximate symmetry. Particularly, Eq. (32) is violated and the two groups of equivalent reflexions are only approximately equivalent. The difference  $|F'_{\mathbf{K}}| - |F'_{\mathbf{H}}|$  where  $\mathbf{K} \in \{-\hat{S}\mathbf{H}\}$  differs therefore from zero, and its value is a direct measure of the violation of the reality of  $\rho'$ .

#### SYMMETRIC AND ANTISYMMETRIC COMPONENTS

The connection of complex conjugation with the inversion gives the eigenfunctions of inversion a special role. The charge density  $\rho(\mathbf{r})$ , like any function, can be represented as a sum of a symmetric and an antisymmetric component:

$$\rho(\mathbf{r}) = \rho_s(\mathbf{r}) + \rho_a(\mathbf{r}); \quad \hat{I}\rho_s = \rho_s, \quad \hat{I}\rho_a = -\rho_a. \quad (33)$$

The Fourier transform of Eq. (33) represents the corresponding division of the scattering amplitude. It is conventional to write

$$f(\mathbf{S}) = f_s(\mathbf{S}) + if_a(\mathbf{S}). \quad (34)$$

As a consequence of reality of  $\rho$  both  $f_s$  and  $f_a$  are real, as seen from Eq. (32).



In the multipole expansions (8) or (8') and (22) or (22') for the charge density and the scattering amplitude, respectively, the terms with even and odd  $l$  are all symmetric and antisymmetric, respectively. The division into even and odd  $l$  series thus corresponds directly to the divisions (33) and (34). Note that according to Eq. (24) or (24') the radial scattering amplitudes of the even and odd terms are real and pure imaginary, respectively, in accordance with Eq. (34).

The site-symmetric structure factor formalism was, in fact, first presented in terms of symmetric and antisymmetric components by Dawson.<sup>14</sup>

When applied to bound atoms the symmetric component includes the spherical term corresponding to the approximate free-atom symmetry, and the antisymmetric part can occur only because of bonding effects or anharmonicity of thermal motion.

The best known type of almost forbidden reflexions is caused just by the antisymmetric components of off-center atoms in centrosymmetric structures. Let such an atom lie at the position  $\mathbf{R}_1$  and have the scattering amplitude  $f_1(\mathbf{S}) = f_s + if_A$ . It has a counterpart at  $\mathbf{R}_2 = -\mathbf{R}_1$  with  $f_2(\mathbf{S}) = if_1(\mathbf{S}) = f_1^*(\mathbf{S}) = f_s - if_A$ . Their combined contribution to the structure amplitude  $F_{\mathbf{H}}$  is thus, according to Eq. (30),

$$\begin{aligned} f_1(\mathbf{H})e^{2\pi i\mathbf{R}_1 \cdot \mathbf{H}} + f_2(\mathbf{H})e^{2\pi i\mathbf{R}_2 \cdot \mathbf{H}} &= \\ = 2f_s(\mathbf{H})\cos 2\pi\mathbf{R}_1 \cdot \mathbf{H} - 2if_A(\mathbf{H})\sin 2\pi\mathbf{R}_1 \cdot \mathbf{H} \end{aligned} \quad (35)$$

while the approximate Eq. (31) would give just the first term. For reflexions with  $\cos 2\pi\mathbf{R}_1 \cdot \mathbf{H} = 0$  this yields  $\pm 2if_A(\mathbf{H})$  while Eq. (31) would give zero. Therefore, if  $f_A(\mathbf{H})$  does not vanish due to symmetry, the extinction is only approximate. For instance, the almost forbidden reflexions of the hcp<sup>8,11</sup> and diamond<sup>10</sup> structures and of tetragonal tin<sup>12</sup> are all of this type.

If we take the anomalous dispersion into account, we naturally can still write Eqs. (33) and (34) for the scattering power  $\rho'$  and the effective scattering amplitude  $f'$ . But now  $\rho'_s$ ,  $\rho'_A$ ,  $f'_s$  and  $f'_A$  will all be complex. Conventionally we write for each atom  $f'_n = f_n + \Delta'_n + i\Delta''_n$  where  $f_n$  is the true atomic scattering factor (16) corresponding to atomic charge density and  $\Delta'_n$ ,  $\Delta''_n$  are the real and imaginary parts of the dispersion correction. Each of the three terms in  $f'_n$  must obey the atomic site symmetry. In a non-centrosymmetric case we should thus write  $\Delta' = \Delta'_s + \Delta'_A$  and  $\Delta'' = \Delta''_s + \Delta''_A$ . In fact, the antisymmetric  $\Delta'_A$  and  $\Delta''_A$  are in practice negligible, because the effect is almost exclusively due to the core part. At least, their occurrence would require very large anomalous dispersion combined with very strong anharmonicity of the thermal motion. With this in mind we can write for a Friedel pair of effective structure amplitudes

$$\begin{aligned} F'_{\pm\mathbf{H}} = \sum_n e^{\pm 2\pi i\mathbf{R}_n \cdot \mathbf{H}} [(f_{ns}(\mathbf{H}) + \Delta'_{ns}(\mathbf{H}) \pm \Delta'_{nA}(\mathbf{H})) + \\ + i(\pm f_{nA}(\mathbf{H}) + \Delta''_{ns}(\mathbf{H}) \pm \Delta''_{nA}(\mathbf{H}))]. \end{aligned} \quad (36)$$

Writing explicitly the expressions for the real and imaginary parts

$$\begin{aligned} X'_{\pm\mathbf{H}} = \sum_n [\cos(2\pi\mathbf{R}_n \cdot \mathbf{H})(f_{ns} + \Delta'_{ns} \pm \Delta'_{nA}) - \\ - \sin(2\pi\mathbf{R}_n \cdot \mathbf{H})(f_{nA} \pm \Delta''_{ns} + \Delta''_{nA})], \end{aligned} \quad (37)$$

$$\begin{aligned} Y'_{\pm\mathbf{H}} = \sum_n [\cos(2\pi\mathbf{R}_n \cdot \mathbf{H})(\pm f_{nA} + \Delta''_{ns} \pm \Delta''_{nA}) + \\ + \sin(2\pi\mathbf{R}_n \cdot \mathbf{H})(\pm f_{ns} \pm \Delta'_{ns} + \Delta'_{nA})] \end{aligned}$$

of  $F' = X' + iY'$  we see more clearly the role of different components. The terms with double sign in  $X'$  and those with single sign in  $Y'$ , i.e.  $\Delta''_s$  and  $\Delta'_A$ , cause deviations from the Friedel law  $F'_{-\mathbf{H}} = F'^*_{\mathbf{H}}$ . On the other hand, we can note how in a centrosymmetric structure all double-sign terms in (37) cancel in summation over a pair of inversion-related atoms at the positions  $\pm\mathbf{R}$ , producing the relation  $F'_{-\mathbf{H}} = F'_{\mathbf{H}}$  required by the symmetry.

Thus, normally  $\Delta''_s$  is the reason for the deviation of  $|F_{-\mathbf{H}}| - |F_{\mathbf{H}}|$  from zero. However, occasionally, the sine (or the cosine) terms in (37) may vanish for some special reflexions. Then, neglecting  $\Delta'_A$  and  $\Delta''_A$ , the corrections  $\Delta''$  with no antisymmetric components  $f_A$  from the atoms would bring about the situation  $F'_{-\mathbf{H}} = F_{\mathbf{H}}$  (or  $F_{-\mathbf{H}} = -F_{\mathbf{H}}$ ). In such cases, as McIntyre et al.<sup>15</sup> have pointed out, it is only the interplay of  $f_A$  and  $\Delta''$  which makes visible the non-equivalence of  $F'_{-\mathbf{H}}$  and  $F'_{\mathbf{H}}$ .

#### REFERENCES

1. M. Tinkham, *Group Theory and Quantum Mechanics*, §4.1, McGraw-Hill, New York, 1964.
2. *International Tables for X-ray Crystallography*, vol. I, The Kynoch Press, Birmingham, 1952.
3. C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids*, Clarendon Press, Oxford, 1972.
4. Ph. Morse and H. Feshbach, *Methods of Theoretical Physics*, vol. II, §10.3 and 11.3, McGraw-Hill, New York, 1953.
5. F. C. von der Lage and H. A. Bethe, *Phys. Rev.*, **71**, 612 (1947).
6. M. Atoji, *Acta Crystallogr.*, **11**, 827 (1958).
7. K. Kurki-Suonio, *Ann. Acad. Sci. Fenn. Ser. A6*, **263** (1967).
8. K. Kurki-Suonio, *Acta Crystallogr. Sect. A*, **26**, 458 (1970).
9. K. Kurki-Suonio and P. Salmo, *Ann. Acad. Sci. Fenn. Ser. A6*, **369** (1971).
10. R. Colella, *Phys. Scr.*, **15**, 143 (1977) and references therein.
11. M. Merisalo, M. Järvinen and J. Kurittu, *Phys. Scr.*, in press.
12. M. Merisalo and M. Järvinen, *Phil. Mag.*, in press.
13. *International Tables for X-ray Crystallography*, vol. IV, §2.3.2, The Kynoch Press, Birmingham, 1974.
14. B. Dawson, *Proc. R. Soc. London Ser. A*, **298**, 255 (1967) and in *Advances in Structure Research by Diffraction Methods*, vol. 6, §3.1, Pergamon Press, Oxford, 1975.
15. G. J. McIntyre, G. R. Moss, J. M. Boehm and Z. Barnea, *Acta Crystallogr. Sect. A*, **31**, S 223 (1975).