Theoret. Chim. Acta (Berl.) 57, 267–297 (1980)

THEORETICA CHIMICA ACTA

Original Investigations

Lattice Harmonics for Graphite

C. P. Mallett

Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia

A general theory for obtaining lattice harmonics of non-symmorphic space groups is presented, and the representation theory for these groups is briefly reviewed, with particular reference to graphite (space group $D^4_{6h}[P6_3/mmc]$). The irreducible matrix representations, compatibilities and lattice harmonics for all l are listed for all symmetry points, lines and planes in the representation domain of the Brillouin zone. The extra degeneracies introduced by time reversal are also considered. An appendix gives full details of the angular momentum conventions used in this paper.

Key words: Group theory – Graphite – Lattice harmonics.

1. Introduction

Lattice harmonics, which are linear combinations of spherical harmonics that transform according to the irreducible representations of the space group of a crystal, are generally useful for a discussion of solid-state properties. Originally they were introduced to simplify the wave function expansions of the cellular method of calculating band structures [1, 2], but they are now used routinely in other band structure calculations, such as the augmented plane wave [3] and the Korringa–Kohn–Rostoker methods [4]. It has been suggested recently by Cracknell [5] that developments in computer technology have made this use of lattice harmonics obsolescent but group theory is important not only for simplifying wave function expansions, and allowing an unambiguous labelling of energy bands, but also because closely spaced energy levels, if they have different symmetries, can be more accurately calculated than if symmetry is not used. In addition, in considering covalent crystals it is necessary to use non-spherical potentials and for all the methods mentioned above the radial wave equations in this case are coupled matrix functions of l and m and the use of lattice harmonics is, for practical purposes, mandatory [6]. Lattice harmonics have also been used as basis functions to obtain the rotational energy levels of a hindered rotator in a discussion of rotational specific heats [7], for a calculation of the Hall effect [8], and in obtaining the momentum density distribution in positron annihilation experiments [9]. Thus it is evident that

0040-5744/80/0057/0267/$06.20

group theory and lattice harmonics will be very useful in discussing the physical properties of graphite, in particular those properties related to the energy band structure.

Altmann and coworkers have published tables of lattice harmonics for cubic groups [10] and for the hexagonal close-packed lattice [11], and this paper, which contains an extension of some of the work in the paper by Altmann and Bradley [11], gives the lattice harmonics for graphite. After a brief discussion of the reduction of space group representations in Sect. 2, the irreducible matrix representations for the graphite setting of D_{6h}^4 are given in Sect. 3. The general theory of obtaining lattice harmonics for non-symmorphic space groups is given in Sect. 4, as are the results for all points, lines and planes of symmetry in the representation domain of the Brillouin Zone. Finally, the simplifications introduced by time reversal symmetry are considered in Sect. 5. In order to make the paper as self-contained as possible, some results previously obtained by Altmann and Bradley [11] are included here.

2. The Reduction of Space Group Representations

This brief resumé of the reduction of space group representations owes much to the work done by Altmann [12] and the definitions and notation adopted here are the same, within typographical limitations, as those used by him.

The translation subgroup $\boldsymbol{T}$ of the space group $\boldsymbol{G}$ is made finite by using the Born–von Kármán periodic boundary conditions, where a portion of crystal is chosen large enough such that its extension to infinity does not make any difference to its physical properties, and the extension to infinity is then made periodically. An element of this space group will be denoted by the Seitz notation $\{p \mid \boldsymbol{v}\}$ where p is a point operation and $\boldsymbol{v}$ is a translation vector, which may or may not be a vector of the Bravais lattice of the crystal. The group $\boldsymbol{G}$ can be expanded in terms of left cosets with respect to the invariant subgroup $\boldsymbol{T}$, the group of pure translations of the Bravais lattice, as

$$\boldsymbol{G} = \sum \{p \mid \boldsymbol{w}\}\boldsymbol{T} \tag{1}$$

in which the sum is to be understood in the Galois, direct sum sense and where the coset representatives $\{p \mid \boldsymbol{w}\}$ contain all the point operations p of the crystal (the set of which forms a group $\boldsymbol{P}$, the isogonal point group of the lattice) combined with some uniquely associated special vector that is either the zero vector or a non-primitive lattice vector. The Abelian group $\boldsymbol{T}$ has representations given by

$$_{\boldsymbol{k}}\hat{\boldsymbol{T}}\{e \mid \boldsymbol{t}\} = \exp(-i\boldsymbol{k} \cdot \boldsymbol{t}) \tag{2}$$

where $\boldsymbol{k}$ is a vector of the reciprocal lattice

$$\boldsymbol{k} = k_1\boldsymbol{g}_1 + k_2\boldsymbol{g}_2 + k_3\boldsymbol{g}_3 \tag{3}$$

(k_1, k_2, k_3 are non-integral) and the basis vectors $\boldsymbol{g}_i$ are defined as

$$\boldsymbol{g}_1 = \frac{2\pi(\boldsymbol{t}_2 \times \boldsymbol{t}_3)}{\boldsymbol{t}_1 \cdot (\boldsymbol{t}_2 \times \boldsymbol{t}_3)} \tag{4}$$

with $\boldsymbol{g}_2$ and $\boldsymbol{g}_3$ obtained by cyclic permutation of the basis vectors of the Bravais lattice. It is evident from Eqs. (2)–(4) that a vector $\boldsymbol{k}+\boldsymbol{g}$, where $\boldsymbol{g}$ is a reciprocal lattice vector with integral coefficients in (3), will have the same representative as that for the vector $\boldsymbol{k}$. For this reason it is only necessary to consider $\boldsymbol{k}$ vectors in the first unit cell of reciprocal space, and this unit cell is normally taken to be a centred unit cell, the Brillouin zone, in order to display the full symmetry of the crystal. The irreducible representations (*IR*s) of $\boldsymbol{G}$ are obtained from its invariant subgroup $\boldsymbol{T}$ by induction, although to obtain all the *IR*s this process must be carried out via a third group, the little group ${}_k\boldsymbol{K}$, containing all the elements of $\boldsymbol{G}$ that transform the wave vector $\boldsymbol{k}$ into an equivalent one, $\boldsymbol{k}+\boldsymbol{g}$. Altmann has shown that the i^{th} *IR* of $\boldsymbol{G}$ for a particular wave vector $\boldsymbol{k}$ is given by

$$\begin{aligned} {}^i_k\hat{\boldsymbol{G}}\{p \mid \boldsymbol{v}\}_{[\{p_r \mid \boldsymbol{w}_r\}\{p_s \mid \boldsymbol{w}_s\}]} &= {}^i_k\hat{\boldsymbol{K}}(\{p_r \mid \boldsymbol{w}_r\}^{-1}\{p \mid \boldsymbol{v}\}\{p_s \mid \boldsymbol{w}_s\}) \\ &\quad \text{if } \{p_r \mid \boldsymbol{w}_r\}^{-1}\{p \mid \boldsymbol{v}\}\{p_s \mid \boldsymbol{w}_s\} \in {}_k\boldsymbol{K} \\ &= 0 \quad \text{otherwise} \end{aligned} \tag{5}$$

(here representations are denoted by carets). The elements labelling the rows and columns of the *IR* of $\boldsymbol{G}$ are the generators of the star, the set of non-equivalent $\boldsymbol{k}$ vectors, which are the coset representatives in the expansion of $\boldsymbol{G}$ in left cosets of ${}_k\boldsymbol{K}$

$${}_k\boldsymbol{S} = \{p\boldsymbol{k} \mid p \quad \text{in} \quad \boldsymbol{G} = \sum \{p \mid \boldsymbol{w}\}_k\boldsymbol{K}\}. \tag{6}$$

The representation given in Eq. (5) for $\boldsymbol{G}$ is an IR if the representation ${}^i_k\hat{\boldsymbol{K}}$ is an IR of ${}_k\boldsymbol{K}$. If this process of induction, ${}_k\hat{\boldsymbol{T}} \uparrow {}_k\boldsymbol{K} \uparrow \boldsymbol{G}$, is carried out for all permitted *IR*s of ${}_k\boldsymbol{K}$ (the small representations) for all little groups ${}_k\boldsymbol{K}$ then the set of *IR*s so obtained for $\boldsymbol{G}$ is complete. A representation of ${}_k\boldsymbol{K}$ is permitted if on subduction (restriction) to $\boldsymbol{T}$, ${}^i_k\hat{\boldsymbol{K}} \downarrow \boldsymbol{T}$, it gives the correct representation (2):

$${}^i_k\hat{\boldsymbol{K}}\{e \mid \boldsymbol{t}\} = \mathbf{1} \exp(-i\boldsymbol{k} \cdot \boldsymbol{t}) \tag{7}$$

where the unit matrix $\mathbf{1}$ has the same dimension as ${}^i_k\boldsymbol{K}$.

The *IR*s in (5) are uniquely determined by a single prong of the star and therefore only the volume of the Brillouin zone that contains one prong for each star need be considered. This volume, the representation domain, generates the entire Brillouin zone when operated on by the elements of $\boldsymbol{P}$, the isogonal point group of $\boldsymbol{G}$.

From Eq. (5) it is evidently necessary to find the *IR*s of the little group ${}^i_k\hat{\boldsymbol{K}}$, and this can be done by using the little factor group ${}_k\bar{\boldsymbol{K}}$ defined as

$${}_k\bar{\boldsymbol{K}} = {}_k\boldsymbol{K}/\boldsymbol{T} = \sum [\{p \mid \boldsymbol{w}\}\boldsymbol{T}]. \tag{8}$$

For symmorphic space groups the vectors $\boldsymbol{w}$ in (8) are zero, and the little group

can be written as a semi-direct product of ${}_k\bar{\boldsymbol{K}}$ and $\boldsymbol{T}$,

$$ {}_k\boldsymbol{K} = \boldsymbol{T} \circledS {}_k\bar{\boldsymbol{K}} \tag{9} $$

($\circledS$ denotes a semi-direct product in which the invariant group $\boldsymbol{T}$ is conventionally written first). In this case the little factor group is isomorphic to a point group and its *IR*s are readily obtained. For non-symmorphic groups, however the $\boldsymbol{w}$ are not zero and it is not possible to write ${}_k\boldsymbol{K}$ in the same semi-direct product form because the set of coset representatives do not close to form a group. It is still possible to use the little factor group, but now the representations are projective rather than vector representations. To avoid this problem, which is produced by mapping $\boldsymbol{T}$ in (8) on to the identity of the little factor group, an alternative method due to Herring [17] is usually employed in which a subgroup $\boldsymbol{T}_k$ of $\boldsymbol{T}$ is defined such that the elements have representatives of unity:

$$ \boldsymbol{T}_k = \{\{e \mid \boldsymbol{t}\} \text{ such that } \exp(-i\boldsymbol{k}\cdot\boldsymbol{t}) = 1\}. \tag{10} $$

In analogy to Eq. (8) the little Herring factor group ${}_k\bar{\boldsymbol{\kappa}}$ is defined as

$$ {}_k\bar{\boldsymbol{\kappa}} = {}_k\boldsymbol{K}/\boldsymbol{T}_k = \sum [\{p \mid \boldsymbol{v}\}\boldsymbol{T}_k]. \tag{11} $$

Furthermore, the *IR*s of ${}_k\boldsymbol{K}$ can be obtained from those of ${}_k\bar{\boldsymbol{\kappa}}$ directly

$$ {}^{i}_{k}\hat{\boldsymbol{K}}\{p \mid \boldsymbol{v}\} = {}^{i}_{k}\hat{\bar{\boldsymbol{\kappa}}}[\{p \mid \boldsymbol{v}\}\boldsymbol{T}_k]. \tag{12} $$

To obviate the necessity of working with cosets, a new group, the little Herring co-group is defined as

$$ {}_k\mathscr{C} = \{\{p \mid \boldsymbol{v}\} \text{ for all } \{p \mid \boldsymbol{v}\} \text{ in (11)}\} \tag{13} $$

and where the usual Seitz multiplication rules apply, except that for all elements of $\boldsymbol{T}_k$ $\{e \mid \boldsymbol{t}\}$ is taken to be the identity. Under this rule all translations $\{e \mid \boldsymbol{t}\} \in \boldsymbol{T}$ commute with all the operations $\{p \mid \boldsymbol{v}\}$ of the little group ${}_k\boldsymbol{K}$. The structure of this new co-group can be obtained by expanding $\boldsymbol{T}$ in left cosets with respect to $\boldsymbol{T}_k$

$$ \boldsymbol{T} = \sum_{\{e \mid \boldsymbol{t}\}} \{e \mid \boldsymbol{t}\}\boldsymbol{T}_k \tag{14} $$

and substituting the result in the coset expansion of ${}_k\boldsymbol{K}$ with respect to $\boldsymbol{T}$ (cf. Eq. (8))

$$ {}_k\boldsymbol{K} = \sum_{\{p \mid \boldsymbol{w}\}} \{p \mid \boldsymbol{w}\}\boldsymbol{T} \tag{15} $$

$$ = \sum_{\{p \mid \boldsymbol{w}\}} \sum_{\{e \mid \boldsymbol{t}\}} \{p \mid \boldsymbol{w}\}\{e \mid \boldsymbol{t}\}\boldsymbol{T}_k \tag{16} $$

and so, comparing Eqs. (11) and (16)

$$ {}_k\mathscr{C} = \sum_{\{p \mid \boldsymbol{w}\}} \sum_{\{e \mid \boldsymbol{t}\}} \{p \mid \boldsymbol{w}\}\{e \mid \boldsymbol{t}\} \qquad \begin{matrix} \forall\{p \mid \boldsymbol{w}\} \text{ in (15)} \\ \forall\{e \mid \boldsymbol{t}\} \text{ in (14)} \end{matrix} \tag{17} $$

where the fact that the coset representatives in (14) form a group $\boldsymbol{\tau}_k$ has been used implicitly. The set of $\{p \mid \boldsymbol{w}\}$ in (17) (henceforth denoted as $\mathcal{P}_k$) is not in general a group, but if the $\boldsymbol{w}$ are so chosen that, if possible, the coset representatives do close, then the set product

$$_k\mathcal{C} = \boldsymbol{\tau}_k \cdot \mathcal{P}_k \tag{18}$$

will have one of the following forms:

A) the set $\mathcal{P}_k$ form a group, the elements of which, under the Herring multiplication rules mentioned above, commute with those of $\boldsymbol{\tau}_k$ and so $_k\mathcal{C}$ is a direct product:

$$_k\mathcal{C} = \boldsymbol{\tau}_k \otimes \mathcal{P}_k \tag{19}$$

where $\otimes$ is the direct product symbol.

B) It is possible to choose the $\boldsymbol{w}$'s in (17) so that the product of two elements of $\mathcal{P}_k$ never belongs to $\boldsymbol{T}_k$ but there are products of the form

$$\{p_r \mid \boldsymbol{w}_r\}\{p_s \mid \boldsymbol{w}_s\} = \{p \mid \boldsymbol{w} + \boldsymbol{t}\}. \tag{20}$$

Closure can then be obtained by replacing $\{p \mid \boldsymbol{w}\}$ in (17) by $\{p \mid \boldsymbol{w} + \boldsymbol{t}\}$ and obtaining a new set $\mathcal{P}'_k$ which gives, in analogy to A above

$$_k\mathcal{C} = \boldsymbol{\tau}_k \otimes \mathcal{P}'_k. \tag{21}$$

C) Finally it may not be possible to form a group from the $\{p \mid \boldsymbol{w}\}$ and the set product given in Eq. (18) is the simplest form for the little Herring co-group.

In cases A and B the groups $\mathcal{P}_k$ and $\mathcal{P}'_k$ are isomorphic to a point group and so their representations are readily found. For case A the class structure of $\mathcal{P}_k$ will be the same as that for the point group to which it is isomorphic, but for cases B and C this will not be so.

3. The Graphite Lattice

The normal structure of the graphite lattice is shown in Fig. 1, and consists of parallel sheets of interlinked hexagons with a carbon–carbon bond length of 1.42 Å and an interlayer separation of 3.34 Å. The sheets are oriented with respect to each other, the atoms of one sheet being translated by half a hexagon diagonal with respect to the sheets above and below. Consequently there are two sets of atoms (see Fig. 1) – A type atoms, which have neighbours directly above and below them in adjacent sheets, and B type atoms which have neighbours above and below at every other sheet. There has been some controversy about the structure of graphite [19, 20], particularly over whether the atoms in a particular sheet are coplanar and whether all the intralayer carbon–carbon bonds are equivalent. Recent evidence, both from neutron diffraction [21] and electron diffraction [22], suggests the structure described above is the correct one. The space group symmetry is $D^4_{6h}(P6_3/mmc)$, the same as that of the hexagonal close-packed lattice – in fact graphite can be

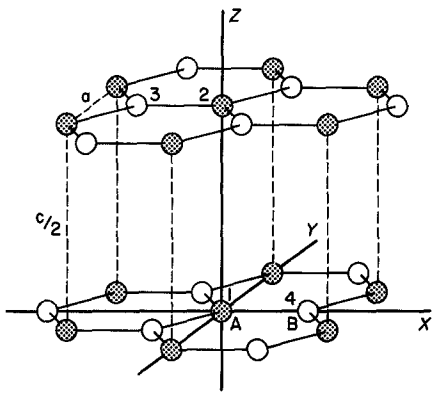

Fig. 1. The graphite lattice (after McClure [18])

considered to be made up of two interpenetrating h.c.p. lattices, each having an atom of type A and B as bases and a lattice constant of a and related by a non-Bravais lattice vector $(-\frac{1}{3}\boldsymbol{t}_1 - \frac{2}{3}\boldsymbol{t}_2)$. The lattice dimensions of graphite are [20]

$$\begin{aligned} a &= 2.461\ \text{Å} \pm 0.002 \\ c &= 6.709\ \text{Å} \pm 0.001 \\ \frac{c}{a} &= 2.725 \quad \pm 0.005 \end{aligned} \tag{22}$$

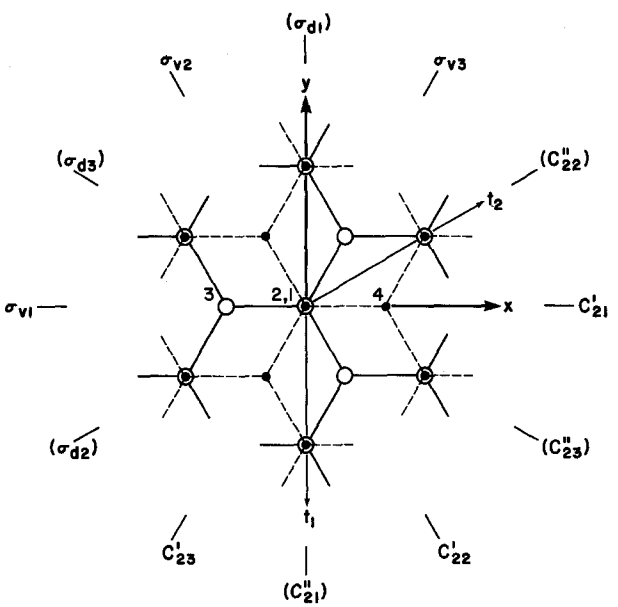

Fig. 2. The direct lattice with basis vectors $\boldsymbol{t}_1$ and $\boldsymbol{t}_2 : \boldsymbol{t}_3$ is perpendicular to the plane of the drawing. The setting of the operations for the axis system is also given. Those operations with brackets around them are not by themselves symmetry operations of the lattice and are associated with the non-primitive translation vector f

and the Bravais lattice primitive vectors are

$$\begin{aligned} \boldsymbol{t}_1 &= (0, -a, 0) \\ \boldsymbol{t}_2 &= \tfrac{1}{2}(a\sqrt{3}, a, 0) \\ \boldsymbol{t}_3 &= (0, 0, c). \end{aligned} \tag{23}$$

The unit cell contains four atoms, two of type A and two of type B, and is shown in Figs. 1 and 2. The centre of symmetry operations is atom 1 and Fig. 2 shows the symmetry operations and their setting. The solid circles in Fig. 2 refer to carbon atoms in one plane and the open ones to atoms above and below this plane. Symmetry operations enclosed in brackets are associated with a non-Bravais lattice translation vector $(0, 0, \frac{1}{2}c)$. The isogonal point group of the lattice, D_{6h}, can be written as $D_{3h} \otimes C_i$ where $C_i = \{E \mid \mathbf{0}\} \oplus \{I \mid \mathbf{0}\}$. For graphite the operations of D_{3h} are space group operations $\{p \mid \mathbf{0}\}$ but the operation $\{I \mid \mathbf{0}\}$ is replaced by $\{I \mid \boldsymbol{f}\}$ where $\boldsymbol{f} = \frac{1}{2}\boldsymbol{t}_3$. The space group $\boldsymbol{G}$ is then the product of this set with the translation subgroup $\boldsymbol{T}$. The reciprocal lattice has the basis vectors

$$\begin{aligned} \boldsymbol{g}_1 &= \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, -1, 0\right) \\ \boldsymbol{g}_2 &= \frac{2\pi}{a}\left(\frac{2}{\sqrt{3}}, 0, 0\right) \\ \boldsymbol{g}_3 &= \frac{2\pi}{a}\left(0, 0, \frac{a}{c}\right) \end{aligned} \tag{24}$$

and the Brillouin zone (BZ) constructed from these vectors is shown in Fig. 3, together with the orientation of the BZ with respect to the direct space lattice. The symmetry points and symmetry lines are labelled using the conventional notation [14].

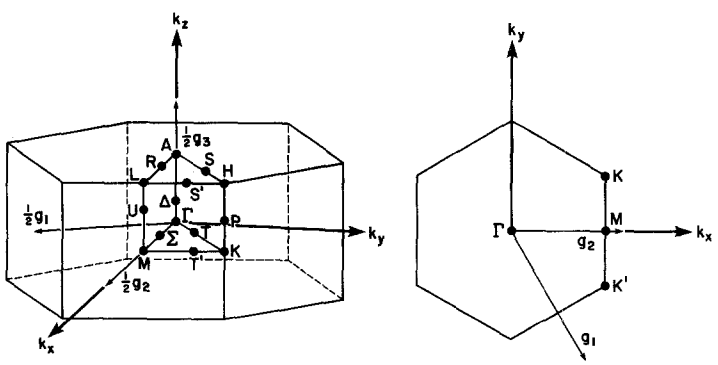

Fig. 3. (a) The Brillouin zone for hexagonal space groups (after Ref. [14]) with the conventional labelling for points and lines of symmetry. **(b)** The orientation of the reciprocal lattice with respect to the direct lattice. The vector $\mathbf{g}_3$ is perpendicular to the plane of the drawing. The scale is arbitrary

In order to obtain the *IR*s of the D_{6h}^4 space group it is necessary to carry out the procedure outlined in Sect. 2. However the D_{6h}^4 space group for the hexagonal close-packed lattice has already been reduced [11, 12, 14] and because the two space groups are isomorphic only a very brief example will be given here.

Consider the point K, with coordinates in reciprocal space of $(-\frac{1}{3}\boldsymbol{g}_1+\frac{2}{3}\boldsymbol{g}_2)$. The star has two prongs K and K' (shown in Fig. 3(b)) and the coset representatives labelling the small representations in Eq. (5) are thus $\{E\,|\,\mathbf{0}\}$ and $\{I\,|\,\boldsymbol{f}\}$ – the rotational parts of these operators generate the star of K. The operations $\{p\,|\,\mathbf{w}\}$ in (17) that constitute the non-translational part of the little Herring co-group are

$$\mathscr{P}_{\mathbf{K}}=\{E\,|\,\mathbf{0}\}\oplus\{C_3^{\pm}\,|\,\mathbf{0}\}\oplus\{\sigma_h\,|\,\mathbf{0}\}\oplus\{S_3^{\pm}\,|\,\mathbf{0}\}\oplus\{\sigma_{di}\,|\,\boldsymbol{f}\}\oplus\{C_{2i}\,|\,\boldsymbol{f}\}$$
$$i=1,2,3. \quad (25)$$

A vector of the Bravais lattice $\boldsymbol{t}=m\boldsymbol{t}_1+n\boldsymbol{t}_2+p\boldsymbol{t}_3$ will be in $\boldsymbol{T}_{\mathbf{K}}$ if

$$\exp(-i\boldsymbol{k}\cdot\boldsymbol{t})=1 \quad \text{i.e.} \quad 2\pi\nu=2\pi(-\tfrac{1}{3}m+\tfrac{2}{3}n)[\nu \text{ integral}].$$

Thus,

$$\begin{aligned}&\boldsymbol{t}\in\boldsymbol{T}_{\mathbf{K}} \quad \text{if} \quad 2n-m=3\nu\\ &\in\boldsymbol{\tau}_{\mathbf{K}} \quad \text{if} \quad 2n-m=3\nu+1 \quad \text{or} \quad 3\nu+2.\end{aligned} \quad (26)$$

For $\boldsymbol{t}$ with $2n-m=3\nu+1$, the translation has the form

$$\{E\,|\,(2n-3\nu-1)\boldsymbol{t}_1+n\boldsymbol{t}_2+p\boldsymbol{t}_3\}=\{E\,|\,(2n-3(\nu+1))\boldsymbol{t}_1+n\boldsymbol{t}_2+n\boldsymbol{t}_3\}\{E\,|\,2\boldsymbol{t}_1\} \quad (27)$$

where the first translation in (27) is, by (26), a member of $\boldsymbol{T}_{\mathbf{K}}$ and the second a member of $\boldsymbol{\tau}_{\mathbf{K}}$. For translations such that $2n-m=3\nu+2$ the result is $\{E\,|\,\boldsymbol{t}_1\}$ and so

$$\boldsymbol{\tau}_{\mathbf{K}}=\{E\,|\,\mathbf{0}\}\oplus\{E\,|\,\boldsymbol{t}_1\}\oplus\{E\,|\,2\boldsymbol{t}_1\}. \quad (28)$$

It is evident that the elements of the set $\mathscr{P}_{\mathbf{K}}$ in (25) close to form a group and thus ${}_{\mathbf{K}}\mathscr{C}$ is of the first type in the Herring classification

$${}_{\mathbf{K}}\mathscr{C}=\boldsymbol{\tau}_{\mathbf{K}}\otimes\mathscr{P}_{\mathbf{K}}. \quad (29)$$

Since the group $\mathscr{P}_{\mathbf{K}}$ is isomorphic to D_{3h} its representations are readily obtained. $\boldsymbol{\tau}_{\mathbf{K}}$, an Abelian group of order 3, has 3 *IR*s with characters given by the 3 roots of unity, but only one of them is, from Eq. (7), permitted. The characters for the permitted representation are 1 for $\{E\,|\,\mathbf{0}\}$, $\exp(-2\pi i/3)$ for $\{E\,|\,\boldsymbol{t}_1\}$ and $\exp(-4\pi i/3)$ for $\{E\,|\,2\boldsymbol{t}_1\}$.

The structure of the little Herring co-group for the point K for the graphite lattice is different from that obtained for the hexagonal close packed lattice (where ${}_{\mathbf{K}}\mathscr{C}$ has type B structure) because of the different form of the vector $\boldsymbol{f}$ associated with the glides and screw axes. A similar change in structure occurs for the representations of the line P, and the form of the operations for H

change. These three differences, apart from the change in the form of the non-primitive lattice vector from $-\frac{1}{3}\boldsymbol{t}_1-\frac{2}{3}\boldsymbol{t}_2+\frac{1}{2}\boldsymbol{t}_3$ to $\frac{1}{2}\boldsymbol{t}_3$, are the main changes between the *IR*s of D_{6h}^4 for graphite and hexagonally close-packed materials. For completeness the *IR*s are given for all points and symmetry lines [see Ref. 11] in Table 2, which should be used in conjunction with Table 1 which gives the star generators, the structure of the little Herring co-group and the elements of $\boldsymbol{\tau}_k$ for all points in the BZ. Because of the importance of Fermi surface studies in the neighbourhood of the K–P–H line, the five planes of symmetry have been included in the Tables in addition to the symmetry points and lines considered by Altmann and Bradley [11]. Table 3 gives the matrix representatives for the multi-dimensional *IR*s which are required for the projection operators (see Sect. 4) and Table 4 gives the compatibility relationships for all points, lines and planes of symmetry in the BZ. These relationships are obtained by subducing the *IR* of a supergroup (for instance at a symmetry point) onto its subgroup (for instance at a symmetry line) and decomposing the resulting representation into *IR*s of the subgroup. Character tables for the symmetry points only have been given by Bassani and Pastori Parravicini [23] who have also considered the double groups for the symmetry points which are required for relativistic work.

4. The Lattice Harmonics

A cellular expansion of a function, such as an electronic wave function, can be obtained by dividing the crystal lattice into centred unit cells, the Wigner–Seitz cells, and making a spherical harmonic expansion in each cell. For graphite the Wigner–Seitz cell comprises four subcells, each determined by one of the four basis atoms. There are two kinds of subcell (Fig. 4(a)), one for atoms of type A and one for atoms of type B, with the same sides but different ends because type A atoms have neighbours directly above and below them whereas type B atoms do not. The subcells for atoms 1 and 2 (type A atoms) have 3 octagonal faces, 2 hexagonal faces and 6 triangular faces; the subcells for atoms 1 and 2 have six diamond faces in place of the hexagonal faces. The four subcells fit together to give an irregular 52 faced polyhedron with 5 interfaces (Fig. 4(b)).

The cellular expansion in the central field approximation for a Bloch function $\Psi_{\boldsymbol{k}}(\boldsymbol{r})$ has the form

$$\Psi_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{lm} {}^1C_{lm} R_l(r_1)\, Y_l^m(\hat{\boldsymbol{r}}_1)\,\delta(\boldsymbol{r}_1, \boldsymbol{r}) + \sum_{lm} {}^2C_{lm} R_l(\bar{r}_2)\, Y_l^m(\bar{\hat{\boldsymbol{r}}}_2)\,\delta(\bar{\boldsymbol{r}}_2, \boldsymbol{r}) + \sum_{lm} {}^3C_{lm} R_l(r_3)\, Y_l^m(\hat{\boldsymbol{r}}_3)\,\delta(\boldsymbol{r}_3, \boldsymbol{r}) + \sum_{lm} {}^4C_{lm} R_l(\bar{r}_4)\, Y_l^m(\bar{\hat{\boldsymbol{r}}}_4)\,\delta(\bar{\boldsymbol{r}}_4, \boldsymbol{r}) \tag{30}$$

where the ${}^iC_{lm}$ are the cellular coefficients, which are $\boldsymbol{k}$ dependent, but whose $\boldsymbol{k}$ dependence will be left implicit, the $R_l(r_i)$ are radial functions and $\delta(\boldsymbol{r}_i, \boldsymbol{r})$ is one if $\boldsymbol{r}$ is in cell i but zero otherwise. The bar over the coordinates for cells 2 and 4 indicates that the axes for cells 2 and 4 are inverted with respect to those for 1 and 3 and the reasons for this procedure will be explained shortly.

Table 1. Stars and group structure for D_{6h}^4 in graphite

Point	Coordinates	Coset representatives	Star order	τ_k	$\sum\{p \mid w\}$	Type
Γ	$(0, 0, 0)$	$\{E \mid \mathbf{0}\}$	1	$\{E \mid \mathbf{0}\}$	$D_{3h}\otimes J$	A
M	$(0, \frac{1}{2}, 0)$	C_3	3	$\{E \mid \mathbf{0}\}\oplus\{E \mid \boldsymbol{t}_2\}$	$C_{2v}\otimes J$	A
K	$(-\frac{1}{3}, \frac{2}{3}, 0)$	J	2	$\{E \mid \mathbf{0}\}\oplus\{E \mid \boldsymbol{t}_1\}\oplus\{E \mid 2\boldsymbol{t}_1\}$	$C_{3h}\otimes J$	A
A	$(0, 0, \frac{1}{2})$	as Γ	1	$\{E \mid \mathbf{0}\}\oplus\{E \mid \boldsymbol{t}_3\}$	$D_{3h}\otimes J$	C
L	$(0, \frac{1}{2}, \frac{1}{2})$	as M	3	$\{E \mid \mathbf{0}\}\oplus\{E \mid \boldsymbol{t}_2\}\oplus\{E \mid \boldsymbol{t}_3\}\oplus\{E \mid \boldsymbol{t}_2+\boldsymbol{t}_3\}$	$C_{2v}\otimes J$	C
H	$(-\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$	as K	2	$\{E \mid \mathbf{0}\}\oplus\{E \mid \boldsymbol{t}_1\}\oplus\{E \mid 2\boldsymbol{t}_1\}\oplus\{E \mid \boldsymbol{t}_3\}\oplus\{E \mid \boldsymbol{t}_3+\boldsymbol{t}_1\}$ $\oplus\{E \mid \boldsymbol{t}_3+2\boldsymbol{t}_1\}$	$C_{3h}\otimes J$	C
Δ	$(0, 0, \gamma)$	J	2	$\{E \mid \mathbf{0}\}\oplus\{E \mid p\boldsymbol{t}_3\}$; $p\gamma \neq \nu$	$C_{3v}\cdot[\{E \mid \mathbf{0}\}\oplus\{C_2 \mid \boldsymbol{f}\}]$	C
U	$(0, \frac{1}{2}, \gamma)$	$C_3\otimes J$	6	$\{E \mid \mathbf{0}\}\oplus\{E \mid \boldsymbol{t}_2\}\oplus\{E \mid p\boldsymbol{t}_3\}\oplus\{E \mid \boldsymbol{t}_2+p\boldsymbol{t}_3\}$; $p\gamma \neq \nu$	$C_s\cdot[\{E \mid \mathbf{0}\}\oplus\{C_2 \mid \boldsymbol{f}\}]$ $C_s = E\oplus\sigma_{v1}$	C
P	$(-\frac{1}{3}, \frac{2}{3}, \gamma)$	$C_s\otimes J$ $C_s = E\oplus\sigma_h$	4	$\{E \mid \mathbf{0}\}\oplus\{E \mid \boldsymbol{t}_1\}\oplus\{E \mid 2\boldsymbol{t}_1\}\oplus\{E \mid p\boldsymbol{t}_3\}$ $\oplus\{E \mid \boldsymbol{t}_1+p\boldsymbol{t}_3\}\oplus\{E \mid 2\boldsymbol{t}_1+p\boldsymbol{t}_3\}$; $p\gamma \neq \nu$	$C_3\cdot[\{E \mid \mathbf{0}\}\oplus\{\sigma_{d1} \mid \boldsymbol{f}\}]$	C
Σ	$(0, \beta, 0)$	$C_3\otimes J$	6	$\{E \mid \mathbf{0}\}\oplus\{E \mid n\boldsymbol{t}_2\}$; $n\beta \neq \nu$	C_{2v}	A
T	$(-\alpha, 2\alpha, 0)$	$C_3\otimes J$	6	$\{E \mid \mathbf{0}\}\oplus\{E \mid m\boldsymbol{t}_1\}$; $2\alpha n - \alpha m \neq \nu$	$C_s\otimes[\{E \mid \mathbf{0}\}\oplus\{C_{22}'' \mid \boldsymbol{t}\}]$ $C_s = E\oplus\sigma_h$	A
T'	$(-\alpha, \frac{1}{2}(1+\alpha), 0)$	$C_3\otimes J$	6	$\{E \mid \mathbf{0}\}\oplus\{E \mid n\boldsymbol{t}_2\}$; $(1+\alpha)n - 2\alpha m \neq 2\nu$	$C_s\otimes[\{E \mid \mathbf{0}\}\oplus\{C_{21}'' \mid \boldsymbol{f}\}]$ $C_s = E\oplus\sigma_h$	A
R	$(0, \beta, \frac{1}{2})$	as Σ	6	$\{E \mid \mathbf{0}\}\oplus\{E \mid n\boldsymbol{t}_2\}\oplus\{E \mid \boldsymbol{t}_3\}\oplus\{E \mid n\boldsymbol{t}_2+\boldsymbol{t}_3\}$: $n\beta \neq \nu$	as $\sum$	A
S	$(-\alpha, 2\alpha, \frac{1}{2})$	as T	6	$\{E \mid \mathbf{0}\}\oplus\{E \mid m\boldsymbol{t}_1\}\oplus\{E \mid \boldsymbol{t}_3\}\oplus\{E \mid m\boldsymbol{t}_1+\boldsymbol{t}_3\}$; $2\alpha n - \alpha m \neq \nu$	as T	C
S'	$(-\alpha, \frac{1}{2}(1+\alpha), \frac{1}{2})$	as T'	6	$\{E \mid \mathbf{0}\}\oplus\{E \mid n\boldsymbol{t}_2\}\oplus\{E \mid \boldsymbol{t}_3\}\oplus\{E \mid n\boldsymbol{t}_2+\boldsymbol{t}_3\}$; $(1+\alpha)n - 2\alpha m \neq 2\nu$	as T'	C
V_1	$(\alpha, \beta, 0)$	$D_3\otimes J$	12	$\{E \mid \boldsymbol{t}\}$ where $\boldsymbol{t} = m\boldsymbol{t}_1 + n\boldsymbol{t}_2$ such that $\alpha m + \beta n \neq \nu$	$C_s = E\oplus\sigma_h$	A
V_2	$(\alpha, \beta, \frac{1}{2})$	$D_3\otimes J$	12	$\{E \mid \boldsymbol{t}\}$ where $\boldsymbol{t} = m\boldsymbol{t}_1 + n\boldsymbol{t}_2$ such that $\alpha m + \beta n \neq \nu$; $\{E \mid \boldsymbol{t}_3\}$; $\{E \mid \boldsymbol{t}+\boldsymbol{t}_3\}$	$C_s = E\oplus\sigma_h$	A
V_3	$(0, \beta, \gamma)$	$D_3\otimes J$	12	$\{E \mid \boldsymbol{t}\}$ where $\boldsymbol{t} = n\boldsymbol{t}_2 + p\boldsymbol{t}_3$ such that $\beta n + \gamma p \neq \nu$	$C_s = E\oplus\sigma_{v1}$	A
V_4	$(-\alpha, 2\alpha, \gamma)$	$D_3\otimes J$	12	$\{E \mid \boldsymbol{t}\}$ where $\boldsymbol{t} = m\boldsymbol{t}_1 + n\boldsymbol{t}_2 + p\boldsymbol{t}_3$ such that $-\alpha m + 2\alpha n + \gamma p \neq \nu$	$C_s = E\oplus\sigma_{d1}$	C
V_5	$(-\alpha, \frac{1}{2}(1+\alpha), \gamma)$	$D_3\otimes J$	12	$\{E \mid \boldsymbol{t}\}$ where $\boldsymbol{t} = m\boldsymbol{t}_1 + n\boldsymbol{t}_2 + p\boldsymbol{t}_3$ such that $-\alpha m + \frac{1}{2}(1+\alpha)n + \gamma p \neq \nu$	$C_s = E\oplus\sigma_{d2}$	C

Explanatory Notes for Table 1

(i) The first column gives the symmetry point, line or plane and the second its coordinates (relative to $\boldsymbol{g}_1$, $\boldsymbol{g}_2$ and $\boldsymbol{g}_3$). $0<\alpha<\frac{1}{3}$; $0<\beta, \gamma<\frac{1}{2}$. The points and lines can be identified from Fig. 3 – the planes are

V_1 bounded by $\Gamma-\Sigma-M-T'-K-T-\Gamma$
V_2 bounded by $A-R-L-S'-H-S-A$
V_3 bounded by $\Gamma-\Sigma-M-U-L-R-A-\Delta-\Gamma$
V_4 bounded by $M-T'-K-P-H-S'-L-U-M$
V_5 bounded by $\Gamma-T-K-P-H-S-A-\Delta-\Gamma$.

(ii) The coset representatives, which label the rows and columns of the *IR*s (Eq. (5)) and whose rotational parts generate the stars, are given in column 3. The star order is given in column 4.

(iii) The groups $\boldsymbol{\tau}_k$ of translations not represented by unity are given in column 5. For symmetry lines and planes there is a restriction that, e.g. for Σ $n\alpha \neq \nu$; this means that n can take any value except one that, for a particular value of α, gives an integral result. Other, similar, restrictions hold for other $\boldsymbol{k}$ points. As was shown for K, it is often possible to reduce the restriction on two translations to one involving one only – e.g. T and S give a restriction on $\boldsymbol{t}_1$ alone, whereas T' and S' have a restriction on $\boldsymbol{t}_2$ only.

(iv) The group operation sum $\boldsymbol{\mathcal{P}}_k = \Sigma\{p \mid \boldsymbol{w}\}$ is given in column 6 and the structure of the little Herring co-group (see Sect. 2) in column 7. Only those little co-groups with structure type A have $\boldsymbol{\mathcal{P}}_k$ forming a group – those of type C have $\boldsymbol{\mathcal{P}}_k$ that do not close. There are no groups with type B structure.

(v) $J=\{E \mid \boldsymbol{0}\}\oplus\{I \mid \boldsymbol{f}\}$; $C_3=\{E \mid \boldsymbol{0}\}\oplus\{C_3^+ \mid \boldsymbol{0}\}\oplus\{C_3^- \mid \boldsymbol{0}\}$; $D_3=\{E \mid \boldsymbol{0}\}\oplus\{C_3^{\pm} \mid \boldsymbol{0}\}\oplus\{C_{2i} \mid \boldsymbol{0}\}$ $(i=1,2,3)$.

The groups D_{3h}, C_{2v}, C_{3h} can be identified from the character tables, Table 2.

If the projection operator

$$W_{ts}^i \propto \sum_{\substack{\{p \mid \boldsymbol{v}\} \\ \in {}_k\boldsymbol{K}}} {}_k^i\boldsymbol{K}(\{p \mid \boldsymbol{v}\})_{ts}^* \{p \mid \boldsymbol{v}\} \tag{31}$$

is applied to the generator $\boldsymbol{\Psi}_k$ given in (30) then it will produce a function symmetry adapted to the t^{th} column of the i^{th} small representation. From Eq. (16) the expansion (31) can be simplified:

$$W_{ts}^i \propto \sum_{\substack{\{p \mid \boldsymbol{w}\} \\ \in \\ \boldsymbol{\mathcal{P}}_k}} \sum_{\substack{\{e \mid \boldsymbol{t}\} \\ \in \\ \boldsymbol{\tau}_k}} \sum_{\substack{\{e \mid \boldsymbol{t}'\} \\ \in \\ \boldsymbol{T}_k}} {}_k^i\boldsymbol{\mathcal{C}}(\{p \mid \boldsymbol{w}\})^* {}_k^i\boldsymbol{\mathcal{C}}(\{e \mid \boldsymbol{t}\})^* \{p \mid \boldsymbol{w}\}\{e \mid \boldsymbol{t}+\boldsymbol{t}'\} \tag{32}$$

where $\{p \mid \boldsymbol{v}\}$ in (31) has been written as $\{p \mid \boldsymbol{w}\}\{e \mid \boldsymbol{t}\}\{e \mid \boldsymbol{t}'\}$ in which $\{p \mid \boldsymbol{w}\}\in\boldsymbol{\mathcal{P}}_k$, $\{e \mid \boldsymbol{t}\}\in\boldsymbol{\tau}_k$ and $\{e \mid \boldsymbol{t}'\}\in\boldsymbol{T}_k$ and Eqs. (7), (10), (12) and (13) have been used. In order to obtain the lattice harmonics from (32) and (30) it is necessary to calculate the effect of the symmetry operators, centred at atom 1, on the cellular expansions. For translations

$$\{e \mid \boldsymbol{t}\} Y_l^m(\hat{\boldsymbol{r}}_i) = {}^{\boldsymbol{t}}Y_l^m(\hat{\boldsymbol{r}}_i) \qquad i=1,2,3,4 \tag{33}$$

where ${}^{\boldsymbol{t}}Y_l^m(\hat{\boldsymbol{r}}_i)$ is identical to $Y_l^m(\hat{\boldsymbol{r}}_i)$ but centred about an origin translated by $\boldsymbol{t}$.

Table 2. Character tables for the little Herring co-groups for all $\boldsymbol{k}$ vectors

Representation / operation	Γ						A†			K			H†			Δ			P		
	A'_{1+}	A'_{2+}	A''_{1+}	A''_{2+}	E'_{+}	E''_{+}				A'_1	A''_1	E'				A_{1p}	A_{2p}	E	A_p		
	A'_{1-}	A'_{2-}	A''_{1-}	A''_{2-}	E'_{-}	E''_{-}	$A_1^{(2)}$	$A_2^{(2)}$	$E^{(4)}$	A'_2	A''_2	E''	$A_2^{(2)}$	E	E^*	A_{1m}	A_{2m}	E_m	A_m	E	
$\{E \mid \mathbf{0}\}$	1	1	1	1	2	2	2	2	4	1	1	2	2	2	2	1	1	2	1	2	$\tau_{\boldsymbol{k}}$:
$\{E \mid \boldsymbol{t}_3\}$							−2	−2	−4				−2	−2	−2						K, H, P:
$\{C_3^{\pm} \mid \mathbf{0}\}$	1	1	1	1	−1	−1	2	2	−2	1	1	−1	2	−1	−1	1	1	−1	1	−1	$\chi(\{E \mid \boldsymbol{t}_1\}) = \omega$
$\{C_3^{\pm} \mid \boldsymbol{t}_3\}$							−2	−2	2				−2	1	1						$\chi(\{E \mid 2\boldsymbol{t}_1\}) = \omega^*$
$\{C'_{2i} \mid \mathbf{0}\}\{C'_{2i} \mid \boldsymbol{t}_3\}$	1	−1	1	−1	0	0	0	0	0												Δ, P:
$\{\sigma_h \mid \mathbf{0}\}\{\sigma_h \mid \boldsymbol{t}_3\}$	1	1	−1	−1	2	−2	0	0	0	1	−1	±2	0	0	0						$\chi(\{E \mid p\boldsymbol{t}_3\}) = \exp(-ip\boldsymbol{k}\cdot\boldsymbol{t}_3)$
$\{S_3^{\pm} \mid \mathbf{0}\}\{S_3^{\pm} \mid \boldsymbol{t}_3\}$[a]	1	1	−1	−1	−1	1	0	0	0	1	−1	∓1	0	$-i\sqrt{3}$ $i\sqrt{3}$	$i\sqrt{3}$ $-i\sqrt{3}$[a]						
$\{\sigma_{vt} \mid \mathbf{0}\}$	1	−1	−1	1	0	0	2	−2	0							1	−1	0			
$\{\sigma_{vt} \mid \boldsymbol{t}_3\}$							−2	2	0												
$\{I \mid \boldsymbol{f}\}\{I \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	±1	±1	±1	±2	±2	0	0	0												
$\{S_6^{\pm} \mid \boldsymbol{f}\}\{S_6^{\mp} \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	±1	±1	±1	∓1	∓1	0	0	0												
$\{\sigma_{di} \mid \boldsymbol{f}\}\{\sigma_{di} \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	∓1	±1	∓1	0	0	0	0	0	±1	∓1	0	0	0	0	$\pm v$	$\mp v$	0	$\pm v$	0	
$\{C_2 \mid \boldsymbol{f}\}\{C_2 \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	±1	∓1	∓1	±2	∓2	0	0	0							$\pm v$	$\pm v$	$\pm 2v$			
$\{C_6^{\mp} \mid \boldsymbol{f}\}\{C_6^{\mp} \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	±1	∓1	∓1	∓1	±1	0	0	0							$\pm v$	$\pm v$	$\mp v$			
$\{C''_{2i} \mid \boldsymbol{f}\}\{C''_{2i} \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	∓1	∓1	±1	0	0	0	0	0	±1	±1	0	0	0	0						
Herring [17]	1^+	2^+	4^+	3^+	5^+	6^+				1	2	5				1	3	5	1		
							1	2	3				1	2	3					3	
	4^-	3^-	1^-	2^-	6^-	5^-				3	4	6				2	4	6	2		
Bassani & Pastori	$1g^+$	$2g^+$	$1g^-$	$2g^-$	$3g^+$	$3g^-$				1^+	1^-	3^+									
							1	2	3				1	3	2						
Parravicini [23]	$1u^+$	$2u^+$	$1u^-$	$2u^-$	$3u^+$	$3u^-$				2^+	2^-	3^-									

[a] NOTE: $\{S_3^{\pm} \mid \mathbf{0}\}$ and $\{S_3^{\pm} \mid \boldsymbol{t}_3\}$ are in different classes for H (H has nine classes) – the upper line in the entry $\{S_3^{\pm} \mid \mathbf{0}\}\{S_3 \mid \boldsymbol{t}_3\}$ refers to $\{S_3^{\pm} \mid \mathbf{0}\}$, and the lower line $\{S_3^{\pm} \mid \boldsymbol{t}_3\}$.

Representation / operation	M				U		$L\dagger$		R		Σ		$S\dagger$	T		$S'\dagger$	T'		V_1	V_2	V_3	V_4	V_5	
	$\mathscr{A}'_+$	$\mathscr{B}'_+$	$\mathscr{A}''_+$	$\mathscr{B}''_+$	$\mathscr{A}_p$	$\mathscr{B}_p$			$\mathscr{A}'$	$\mathscr{A}''$	$\mathscr{A}'$	$\mathscr{A}''$		$\mathscr{A}'$	$\mathscr{A}''$		$\mathscr{A}'$	$\mathscr{A}''$	A'	A''	$\mathscr{A}$	A_p	A_p	
	$\mathscr{A}'_-$	$\mathscr{B}'_-$	$\mathscr{A}''_-$	$\mathscr{B}''_-$	$\mathscr{A}_m$	$\mathscr{B}_m$	ε_1	ε_2	$\mathscr{B}'$	$\mathscr{B}''$	$\mathscr{B}'$	$\mathscr{B}''$	ε	$\mathscr{B}'$	$\mathscr{B}''$	ε	$\mathscr{B}'$	$\mathscr{B}''$	A''	A''	$\mathscr{B}$	A_m	A_m	
$\{E \mid \mathbf{0}\}$	1	1	1	1	1	1	2	2	1	1	1	1	2	1	1	2	1	1	1	1	1	1	1	τ_k:
$\{E \mid \boldsymbol{t}_3\}$							−2	−2					−2			−2								T, S, V_1, V_2, V_4, V_5:
$\{C_{21} \mid \mathbf{0}\}\{C_{21} \mid \boldsymbol{t}_3\}$	1	−1	1	−1			0	0	±1	±1	±1	±1												$\chi(\{E \mid m\boldsymbol{t}_1\}) = \exp(-im\boldsymbol{k}\cdot\boldsymbol{t}_1)$
$\{\sigma_h \mid \mathbf{0}\}\{\sigma_h \mid \boldsymbol{t}_3\}$	1	1	−1	−1			0	0	1	−1	1	−1	0	1	−1	0	1	−1	±1	±1				M, U, L:
$\{\sigma_{v1} \mid \mathbf{0}\}$	1	−1	−1	1	1	−1	2	−2	±1	∓1	±1	∓1									±1			$\chi(\{E \mid \boldsymbol{t}_2\}) = -1$
$\{\sigma_{v1} \mid \boldsymbol{t}_3\}$							−2	2																$\Sigma, T', R, S', V_1, V_2, V_3, V_4, V_5$:
$\{I \mid \boldsymbol{f}\}\{I \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	±1	±1	±1			0	0																$\chi(\{E \mid n\boldsymbol{t}_2\}) = \exp(-in\boldsymbol{k}\cdot\boldsymbol{t}_2)$
$\{\sigma_{d1} \mid \boldsymbol{f}\}\{\sigma_{d1} \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	∓1	±1	∓1	$\pm v$	$\mp v$	0	0								0	±1	∓1				±1		R, V_2:
$\{\sigma_{d2} \mid \boldsymbol{f}\}\{\sigma_{d2} \mid \boldsymbol{f}+\boldsymbol{t}_3\}$													0	±1	∓1								±1	$\chi(\{E \mid \boldsymbol{t}_3\}) = -1$
$\{C_2 \mid \boldsymbol{f}\}\{C_2 \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	±1	∓1	∓1	$\pm v$	$\pm v$	0	0																U, V_3, V_4, V_5:
$\{C''_{21} \mid \boldsymbol{f}\}\{C''_{21} \mid \boldsymbol{f}+\boldsymbol{t}_3\}$	±1	∓1	∓1	±1			0	0								0	±1	±1						$\chi(\{E \mid p\boldsymbol{t}_3\}) = \exp(-ip\boldsymbol{k}\cdot\boldsymbol{t}_3)$
$\{C''_{22} \mid \boldsymbol{f}\}\{C''_{22} \mid \boldsymbol{f}+\boldsymbol{t}_3\}$													0	±1	±1									
Herring [17]	1^+	4^+	2^+	3^+	1	4			1	2	1	2		1	2		1	2						
							1	2					1			1								
	2^-	3^-	1^-	4^-	2	3			4	3	4	3		4	3		4	3						
Bassani & Pastori	$1g^+$	$2g^+$	$1g^-$	$2g^-$																				
							1	2																
Parravicini [23]	$1u^+$	$2u^+$	$1u^-$	$2u^-$																				

Time reversal symmetry introduces extra degeneracy between $\mathscr{A}'$ and $\mathscr{B}''$ and between $\mathscr{A}''$ and $\mathscr{B}'$ for R and between A' and A'' for V_2.

Explanatory Notes for Table 2

(i) This table should be read in conjunction with Table 1. The subscript i takes the values 1, 2 and 3 and thus σ_{di} is shorthand for $\sigma_{d1}, \sigma_{d2}, \sigma_{d3}$.

(ii) The groups listed below are the full little Herring co-groups, ${}_{k}\mathscr{G}$ which have as a subgroup $\boldsymbol{\tau}_k$, the elements of which are given in Table 1, as is the type of group product. Only permitted representations are listed.

(iii) The operations are to be identified from the first column of the tables. The operations involving $\boldsymbol{t}_3$ are only to be included for points marked with a dagger (†) when two operations are given (i.e. are in the same class). For most groups the names of two representations appear, one above the other, and the upper sign is used for the upper of the two representations and the lower sign with the lower of the listed representations. e.g. for K the character of $\{\sigma_{di} \mid \boldsymbol{f}\}$ for representation A_1'' is -1 and for A_2'' it is $+1$.

(iv) The nomenclature is that of Altmann and Bradley [11]. An alternative notation due to Herring [17] is listed at the foot of the tables, as is one due to Bassani and Pastori Parravicini [23].

(v) The characters of the elements of $\boldsymbol{\tau}_k$ for permitted representations are also given in the table. In order to find the character of a general operation in ${}_{k}\boldsymbol{K}$, it is written (cf. Eq. (16)) as a product of three operations $\{p \mid \boldsymbol{w}\}\{e \mid \boldsymbol{t}\}\{e \mid \boldsymbol{t}'\}$ where $\{p \mid \boldsymbol{w}\}$ is a member of $\mathscr{P}_k$, $\{e \mid \boldsymbol{t}\}$ of $\boldsymbol{\tau}_k$ and $\{e \mid \boldsymbol{t}'\}$ of $\boldsymbol{T}_k$. Since the character of $\{e \mid \boldsymbol{t}'\}$ is unity, the character of the operation is obtained by multiplying the characters of $\{p \mid \boldsymbol{w}\}$ and $\{e \mid \boldsymbol{t}\}$ obtained from the table. For symmetry lines and planes the conditions for a translation to be in $\boldsymbol{\tau}_k$ should be carefully noted; for fractional, rather than irrational values of α and β in Table 1, a translation may be in $\boldsymbol{T}_k$, if the representative becomes unity.

(vi) Time reversal symmetry (see Sect. 5) introduces extra degeneracies for R and V_2.

(vii) The following abbreviations have been used:

$$\omega = \exp(-2\pi i/3)$$
$$\omega^* = \exp(2\pi i/3)$$
$$v = \exp(-i\boldsymbol{k} \cdot \boldsymbol{t}_3/2).$$

The operations $\{p \mid \boldsymbol{w}\}$ in (32) are such that operations with $\boldsymbol{w} = \boldsymbol{0}$ (i.e. in D_{3h}) either leave $Y_l^m(\hat{\boldsymbol{r}}_i)$ centred at atom i or move it to another centre related by a Bravais lattice vector to the original centre. However the operations with $\boldsymbol{w} = \boldsymbol{f}$, which are a product of $\{I \mid \boldsymbol{f}\}$ with an operation from D_{3h}, move $Y_l^m(\hat{\boldsymbol{r}}_1)$ to $Y_l^m(\hat{\boldsymbol{r}}_2)$ and move $Y_l^m(\hat{\boldsymbol{r}}_2)$ to a centre at atom 1 or one directly above or below it. Similarly, $Y_l^m(\hat{\boldsymbol{r}}_3)$ is moved to a centre related to atom 4 by a Bravais lattice vector and conversely for $Y_l^m(\hat{\boldsymbol{r}}_4)$. Since

$$\begin{aligned} Y^m(\bar{\hat{\boldsymbol{r}}}_2) &= \{I \mid \boldsymbol{f}\} Y_l^m(\hat{\boldsymbol{r}}_1) \\ Y^m(\bar{\hat{\boldsymbol{r}}}_4) &= \{I \mid \boldsymbol{f}\} Y_l^m(\hat{\boldsymbol{r}}_3) \end{aligned} \tag{34}$$

the coordinate axes at centres 2 and 4 are inverted with respect to those at centres 1 and 3 to avoid the factor of $(-1)^l$ that would otherwise occur because of the transformation properties of the spherical harmonics under inversion. In addition.

$$Y_l^m(\hat{\boldsymbol{r}}_3) = \{e \mid \boldsymbol{\tau}\} Y_l^m(\hat{\boldsymbol{r}}_1) \tag{35}$$

Table 3. Matrices for the multidimensional representations

	Γ				K		A			L		H			Δ		P	S	S'
	E_+'	E_-'	E_+''	E_-''	E'	E''	$A_1^{(2)}$	$A_2^{(2)}$	$E^{(4)}$	ε_1	ε_2	$A^{(2)}$	E	E^*	E_p	E_m	E	ε	ε
E	ε	ε	ε	ε	ε	ε	ε	ε	ε'	ε	ε	ε	ε	ε	ε	ε	ε	ε	ε
C_3^+	β	β	β	β	β	β	ε	ε	β'			ε	ω^*	ω^*	β	β	β		
C_3^-	α	α	α	α	α	α	ε	ε	α'			ε	ω	ω	α	α	α		
C_{21}'	λ	λ	$\bar{\lambda}$	$\bar{\lambda}$			λ	$\bar{\lambda}$	λ''	λ	$\bar{\lambda}$								
C_{22}'	μ	μ	$\bar{\mu}$	$\bar{\mu}$			λ	$\bar{\lambda}$	μ''										
C_{23}'	ν	ν	$\bar{\nu}$	$\bar{\nu}$			λ	$\bar{\lambda}$	ν''										
σ_h	ε	ε	$\bar{\varepsilon}$	$\bar{\varepsilon}$	ε	$\bar{\varepsilon}$	λ	λ	ε''	λ	λ	λ	λ	$\bar{\lambda}$				λ	λ
S_3^+	β	β	$\bar{\beta}$	$\bar{\beta}$	β	$\bar{\beta}$	λ	λ	β''			λ	$\lambda\omega^*$	$\bar{\lambda}\omega^*$					
S_3^-	α	α	$\bar{\alpha}$	$\bar{\alpha}$	α	$\bar{\alpha}$	λ	λ	α''			λ	$\lambda\omega$	$\bar{\lambda}\omega$					
σ_{v1}	λ	λ	λ	λ			ε	$\bar{\varepsilon}$	λ'	ε	$\bar{\varepsilon}$				λ	λ			
σ_{v2}	μ	μ	μ	μ			ε	$\bar{\varepsilon}$	μ'						μ	μ			
σ_{v3}	ν	ν	ν	ν			ε	$\bar{\varepsilon}$	ν'						ν	ν			
I	ε	$\bar{\varepsilon}$	ε	$\bar{\varepsilon}$			$i\bar{\rho}$	$i\rho$	$\eta\varepsilon'$	$i\bar{\rho}$	$i\rho$								
S_6^-	β	$\bar{\beta}$	β	$\bar{\beta}$			$i\bar{\rho}$	$i\rho$	$\eta\beta'$										
S_6^+	α	$\bar{\alpha}$	α	$\bar{\alpha}$			$i\bar{\rho}$	$i\rho$	$\eta\alpha'$										
σ_{d1}	λ	$\bar{\lambda}$	$\bar{\lambda}$	λ	λ	λ	$i\kappa$	$i\kappa$	$\eta\lambda''$	$i\kappa$	$i\kappa$	$i\kappa$	$i\bar{\kappa}$	$i\bar{\kappa}$	$\upsilon\lambda$	$\upsilon\bar{\lambda}$	$\upsilon\lambda$		$i\kappa$
σ_{d2}	μ	$\bar{\mu}$	$\bar{\mu}$	μ	μ	μ	$i\kappa$	$i\kappa$	$\eta\mu''$			$i\kappa$	$i\bar{\kappa}\omega^*$	$i\bar{\kappa}\omega^*$	$\upsilon\mu$	$\upsilon\bar{\mu}$	$\upsilon\mu$	$i\kappa$	
σ_{d3}	ν	$\bar{\nu}$	$\bar{\nu}$	ν	ν	ν	$i\kappa$	$i\kappa$	$\eta\nu''$			$i\kappa$	$i\bar{\kappa}\omega$	$i\bar{\kappa}\omega$	$\upsilon\nu$	$\upsilon\bar{\nu}$	$\upsilon\nu$		
C_2	ε	$\bar{\varepsilon}$	$\bar{\varepsilon}$	ε			$i\kappa$	$i\bar{\kappa}$	$\eta\varepsilon''$	$i\kappa$	$i\bar{\kappa}$				$\upsilon\varepsilon$	$\upsilon\bar{\varepsilon}$			
C_6^-	β	$\bar{\beta}$	$\bar{\beta}$	β			$i\kappa$	$i\bar{\kappa}$	$\eta\beta''$						$\upsilon\beta$	$\upsilon\bar{\beta}$			
C_6^+	α	$\bar{\alpha}$	$\bar{\alpha}$	α			$i\kappa$	$i\bar{\kappa}$	$\eta\alpha''$						$\upsilon\alpha$	$\upsilon\bar{\alpha}$			
C_{21}''	λ	$\bar{\lambda}$	λ	$\bar{\lambda}$	λ	$\bar{\lambda}$	$i\bar{\rho}$	$i\bar{\rho}$	$\eta\lambda'$	$i\bar{\rho}$	$i\bar{\rho}$	$i\bar{\rho}$	$i\rho$	$i\bar{\rho}$					$i\bar{\rho}$
C_{22}''	μ	$\bar{\mu}$	μ	$\bar{\mu}$	μ	$\bar{\mu}$	$i\bar{\rho}$	$i\bar{\rho}$	$\eta\mu'$			$i\bar{\rho}$	$i\rho\omega^*$	$i\bar{\rho}\omega^*$			$i\bar{\rho}$		
C_{23}''	ν	$\bar{\nu}$	ν	$\bar{\nu}$	ν	$\bar{\nu}$	$i\bar{\rho}$	$i\bar{\rho}$	$\eta\nu'$			$i\bar{\rho}$	$i\rho\omega$	$i\bar{\rho}\omega$					

$$\boldsymbol{\alpha}=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix} \quad \boldsymbol{\beta}=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix} \quad \boldsymbol{\varepsilon}=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \quad \boldsymbol{\kappa}=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$$

$$\boldsymbol{\lambda}=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \quad \boldsymbol{\mu}=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix} \quad \boldsymbol{\nu}=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix} \quad \boldsymbol{\rho}=\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}$$

$$\boldsymbol{\omega}=\begin{pmatrix}\omega & 0\\ 0 & \omega^*\end{pmatrix} \quad \boldsymbol{\alpha}'=\begin{pmatrix}\boldsymbol{\alpha} & \mathbf{0}\\ \mathbf{0} & \boldsymbol{\alpha}\end{pmatrix} \quad \boldsymbol{\alpha}''=\begin{pmatrix}\boldsymbol{\alpha} & \mathbf{0}\\ \mathbf{0} & -\boldsymbol{\alpha}\end{pmatrix} \quad \boldsymbol{\eta}=\begin{pmatrix}\mathbf{0} & -\boldsymbol{\varepsilon}\\ -\boldsymbol{\varepsilon} & \mathbf{0}\end{pmatrix}$$

$\omega = \exp(2\pi i/3)$, $\upsilon = \exp(-i\boldsymbol{k}, \boldsymbol{t}_3/2)$.

Explanatory Notes for Table 3

(i) The matrix representations listed here are a corrected version of those used by Altmann and Bradley [11]. The notes for the two previous tables are also relevant here.

(ii) The table contains both (2×2) matrices (denoted by Greek letters) and also (4×4) matrices (denoted by Greek letters with a prime or double prime) which are supermatrices of (2×2) matrices.

(iii) To find a matrix representative for a general operation, write it (cf. note (v) to Table 2) as $\{p \mid \boldsymbol{w}\}\{e \mid \boldsymbol{t}\}\{e \mid \boldsymbol{t}'\}$ where $\{p \mid \boldsymbol{w}\}$ is a member of $\mathscr{P}_{\boldsymbol{k}}$, $\{e \mid \boldsymbol{t}\}$ of $\boldsymbol{\tau}_{\boldsymbol{k}}$ and $\{e \mid \boldsymbol{t}'\}$ of $\boldsymbol{T}_{\boldsymbol{k}}$. The matrix for this operation is obtained by choosing the matrix corresponding to p in the table and multiplying it by the matrix representative of $\{e \mid \boldsymbol{t}\}$ in $\boldsymbol{\tau}_{\boldsymbol{k}}$ obtained from Table 2.

where $\boldsymbol{\tau}$ is a non-primitive lattice vector

$$\boldsymbol{\tau} = -\tfrac{1}{3}\boldsymbol{t}_1 - \tfrac{2}{3}\boldsymbol{t}_2 + \tfrac{1}{2}\boldsymbol{t}_3. \tag{36}$$

It is also necessary to obtain the effect of the rotational operator p of $\{p \mid \boldsymbol{w}\}$ on

Table 4. Compatibilities for the irredicible representations of D_{6h}^4

Symmetry line						
Γ	$A'_{1\pm}, E'_{\pm}$	$A'_{2\pm}, E'_{\pm}$	$A''_{1\pm}, E''_{\pm}$	$A''_{2\pm}, E''_{\pm}$		
Σ	$\mathscr{A}'$	$\mathscr{B}'$	$\mathscr{A}''$	$\mathscr{B}''$		
M	$\mathscr{A}'_{\pm}$	$\mathscr{B}'_{\pm}$	$\mathscr{A}''_{\pm}$	$\mathscr{B}''_{\pm}$		
M	$\mathscr{A}'_{+}, \mathscr{B}'_{-}$	$\mathscr{A}'_{-}, \mathscr{B}'_{+}$	$\mathscr{A}''_{-}, \mathscr{B}''_{+}$	$\mathscr{A}''_{+}, \mathscr{B}''_{-}$		
T'	$\mathscr{A}'$	$\mathscr{B}'$	$\mathscr{A}''$	$\mathscr{B}''$		
K	A'_1, E'	A'_2, E'	A''_1, E''	A''_2, E''		
K	A'_1, E'	A'_2, E'	A''_1, E''	A''_2, E''		
T	$\mathscr{A}'$	$\mathscr{B}'$	$\mathscr{A}''$	$\mathscr{B}''$		
Γ	$A'_{1+}, A'_{2-}, E'_{\pm}$	$A'_{1-}, A'_{2+}, E'_{\pm}$	$A''_{1-}, A''_{2+}, E''_{\pm}$	$A''_{1+}, A''_{2-}, E''_{\pm}$		
Γ	A'_{1+}, A''_{2-}	A'_{1-}, A''_{2+}	A'_{2+}, A''_{1-}	A'_{2-}, A''_{1+}	E'_{+}, E''_{-}	E'_{-}, E''_{+}
Δ	A_{1p}	A_{1m}	A_{2p}	A_{2m}	E_p	E_m
A	$A_1^{(2)}$	$A_1^{(2)}$	$A_2^{(2)}$	$A_2^{(2)}$	$E^{(4)}$	$E^{(4)}$
A	$A_1^{(2)}, E^{(4)}$	$A_2^{(2)}, E^{(4)}$	$A_2^{(2)}, E^{(4)}$	$A_1^{(2)}, E^{(4)}$		
R	$\mathscr{A}'$	$\mathscr{B}'$	$\mathscr{A}''$	$\mathscr{B}''$		
L	ε_1	ε_2	ε_2	ε_1		
L	ε_1	ε_1	ε_2	ε_2		
U	$\mathscr{A}_p$	$\mathscr{A}_m$	$\mathscr{B}_p$	$\mathscr{B}_m$		
M	$\mathscr{A}'_{+}, \mathscr{B}''_{-}$	$\mathscr{A}'_{-}, \mathscr{B}''_{+}$	$\mathscr{B}'_{+}, \mathscr{A}''_{-}$	$\mathscr{B}''_{-}, \mathscr{A}''_{+}$		
K	A'_1, A''_2	A'_2, A''_1	E', E''			
P	A_p	A_m	E			
H	$A^{(2)}$	$A^{(2)}$	E, E^*			

Symmetry plane			Symmetry plane		
Σ	$\mathscr{A}', \mathscr{B}'$	$\mathscr{A}'', \mathscr{B}''$	R	$\mathscr{A}', \mathscr{B}'$	$\mathscr{A}'', \mathscr{B}''$
V_1	A'	A''	V_2	A'	A''
T	$\mathscr{A}', \mathscr{B}'$	$\mathscr{A}'', \mathscr{B}''$	S	ε	ε
V_1	A'	A''	V_2	A'	A''
T'	$\mathscr{A}', \mathscr{B}'$	$\mathscr{A}'', \mathscr{B}''$	S'	ε	ε
Σ	$\mathscr{A}', \mathscr{B}''$	$\mathscr{A}'', \mathscr{B}'$	T'	$\mathscr{A}', \mathscr{B}''$	$\mathscr{A}'', \mathscr{B}'$
V_3	$\mathscr{A}$	$\mathscr{B}$	V_4	A_p	A_m
U	$\mathscr{A}_p, A_m$	$\mathscr{B}_p, \mathscr{B}_m$	U	$\mathscr{A}_p, \mathscr{B}_m$	$\mathscr{A}_m, \mathscr{B}_p$
V_3	$\mathscr{A}$	$\mathscr{B}$	V_4	A_p	A_m
R	$\mathscr{A}', \mathscr{B}''$	$\mathscr{A}'', \mathscr{B}'$	S'	ε	ε
V_3	$\mathscr{A}$	$\mathscr{B}$	V_4	A_p	A_m
Δ	A_{1p}, A_{1m}, E_p, E_m	A_{2p}, A_{2m}, E_p, E_m	P	A_p, E	A_m, E
T	$\mathscr{A}', \mathscr{B}''$	$\mathscr{A}'', \mathscr{B}'$			
V_5	A_p	A_m			
P	A_p, E	A_m, E			
V_5	A_p	A_m			
S	ε	ε			
V_5	A_p	A_m			
Δ	A_{1p}, A_{2m}, E_p, E_m	A_{1p}, A_{2m}, E_p, E_m			

Explanatory Note for Table 4

(i) The table lists, under one column, all the compatible *IR*s for each of the seven symmetry lines and five symmetry planes in the BZ. When more than one sign subscript appears in a particular column, either can be used. Along the lines *ASH* and *LS'H* all the representations are compatible.

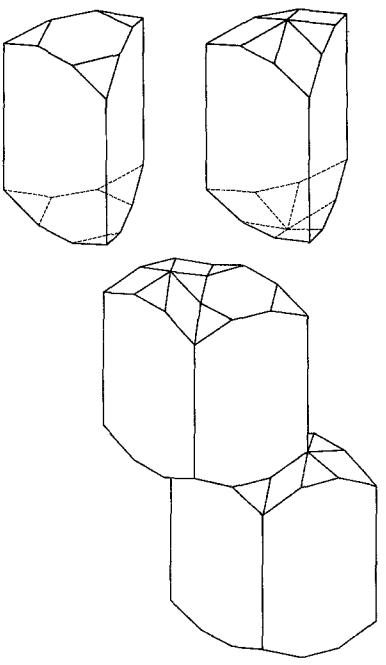

Fig. 4. (a) The Wigner–Seitz subcells for atoms type A and B in graphite. **(b)** The full Wigner–Seitz cell with its four subcells

the spherical harmonics, and this can be done using the properties of the 3-dimensional rotation group and parametrising p into Euler angles. The detailed procedure for doing this, and an explanation of the conventions used, are given in the Appendix.

The effect of the operator (32) on the generator (30) will be to produce a multicentre expansion (a lattice harmonic) consisting of linear combinations of spherical harmonics at different lattice sites. However it is sufficient to treat only the four atoms of the basis because the expansions for other centres can be obtained by Bloch periodicity from that for the basis. Thus it is only necessary to consider the terms in (32) that interchange the atoms of the basis, though it must be emphasized that these operations are in general a product of a point operation and a translation. Consider, as an example, the effect of $\{\sigma_h \mid \mathbf{0}\}$ on $Y_l^m(\hat{\mathbf{r}}_2)$, which moves it from a centre directly above atom 1 to a centre directly below it; that is to a new centre $\boldsymbol{t}_3$ below the centre at atom 2. If, however, the operation $\{e \mid -\boldsymbol{t}_3\}$ is first applied to $Y_l^m(\hat{\mathbf{r}}_2)$ followed by $\{\sigma_h \mid \mathbf{0}\}$ then the net result is to leave the spherical harmonic centred on atom 2. Thus the operational procedure is as follows: write the effect of the operations in (32) on a spherical harmonic as

$$\{p \mid \boldsymbol{w}\}\{e \mid \boldsymbol{t}\} Y_l^m(\hat{\mathbf{r}}_i) = \{p \mid \boldsymbol{w}\}\{e \mid \boldsymbol{t}\}\{r \mid \boldsymbol{u}\} Y_l^m(\hat{\mathbf{r}}_1) \tag{37}$$

where $\{r \mid \boldsymbol{u}\}$ is one of the operations in (34) or (35) and $\{e \mid \boldsymbol{t}\}$ is a translation of the lattice (which may be in $\boldsymbol{\tau}_k$ or $\boldsymbol{T}_k$). Because the symmetry operations $\{p \mid \boldsymbol{w}\}$ centred at atom 1 move the cellular expansion at atoms 2, 3 and 4 from these centres into different Wigner–Seitz cells it is necessary to choose $\{e \mid \boldsymbol{t}\}$ so that

this effect is cancelled. There are two cases to consider:

(i) $\{p \mid \boldsymbol{w}\} \in D_{3h}, \qquad \boldsymbol{w} = \boldsymbol{0}$

$$\{p \mid \boldsymbol{0}\}\{e \mid \boldsymbol{t}\}\{r \mid \boldsymbol{u}\} Y_l^m(\hat{\boldsymbol{r}}_1) = \{pr \mid p\boldsymbol{t} + p\boldsymbol{u}\} Y_l^m(\hat{\boldsymbol{r}}_1) \tag{38}$$

$$= \{r \mid p\boldsymbol{t} + p\boldsymbol{u}\}\{p \mid \boldsymbol{0}\} Y_l^m(\hat{\boldsymbol{r}}_1) \tag{39}$$

$$= \{r \mid p\boldsymbol{t} + p\boldsymbol{u}\} \sum_n Y_l^n(\hat{\boldsymbol{r}}_1) \mathfrak{D}^l(p)_{nm} \tag{40}$$

$$= \{e \mid p\boldsymbol{t} + p\boldsymbol{u} - \boldsymbol{u}\}\{r \mid \boldsymbol{u}\} \sum_n Y_l^n(\hat{\boldsymbol{r}}_1) \mathfrak{D}^l(p)_{nm} \tag{41}$$

$$= \{e \mid p\boldsymbol{t} + p\boldsymbol{u} - \boldsymbol{u}\} \sum_n Y_l^n(\hat{\boldsymbol{r}}_i) \mathfrak{D}^l(p)_{nm} \tag{42}$$

where $\mathfrak{D}^l(p)_{nm}$ is a matrix element of the representative of p for the rotation group (see the Appendix). For the translation in (42) to be zero, and for the combined operation $\{p \mid \boldsymbol{0}\}\{e \mid \boldsymbol{t}\}$ to leave $Y_l^m(\hat{\boldsymbol{r}}_i)$ at centre i then

$$\boldsymbol{t} = p^{-1}\boldsymbol{u} - \boldsymbol{u} \tag{43}$$

(ii) $\{p \mid \boldsymbol{w}\} \in D_{3h} \cdot \{I \mid \boldsymbol{f}\}, \qquad \boldsymbol{w} = \boldsymbol{f}$

$$\{p \mid \boldsymbol{w}\} = \{I \mid \boldsymbol{f}\}\{q \mid \boldsymbol{0}\} \qquad (Iq = p) \tag{44}$$

$$\{p \mid \boldsymbol{w}\}\{e \mid \boldsymbol{t}\} Y_l^m(\hat{\boldsymbol{r}}_i) = \{I \mid \boldsymbol{f}\}\{q \mid \boldsymbol{0}\}\{e \mid \boldsymbol{t}\}\{r \mid \boldsymbol{u}\} Y_l^m(\hat{\boldsymbol{r}}_1) \tag{45}$$

$$= \{Iqr \mid \boldsymbol{f} - q\boldsymbol{t} - q\boldsymbol{u}\} Y_l^m(\hat{\boldsymbol{r}}_1) \tag{46}$$

$$= \{e \mid -q\boldsymbol{t} - q\boldsymbol{u} + \boldsymbol{u}\}\{I \mid \boldsymbol{f}\}\{r \mid \boldsymbol{u}\}\{q \mid \boldsymbol{0}\} Y_l^m(\hat{\boldsymbol{r}}_1) \tag{47}$$

$$= \{e \mid -q\boldsymbol{t} - q\boldsymbol{u} + \boldsymbol{u}\}\{I \mid \boldsymbol{f}\}\{r \mid \boldsymbol{u}\} \sum_n Y_l^m(\hat{\boldsymbol{r}}_1) \mathfrak{D}^l(q)_{nm} \tag{48}$$

$$= \{e \mid -q\boldsymbol{t} - q\boldsymbol{u} + \boldsymbol{u}\} \sum_n (\{I \mid \boldsymbol{f}\} Y_l^n(\hat{\boldsymbol{r}}_i)) \mathfrak{D}^l(q)_{nm} \tag{49}$$

and so for $Y_l^m(\hat{\boldsymbol{r}}_i)$ to go into a centre related to one at atom i by $\{I \mid \boldsymbol{f}\}$, then

$$\boldsymbol{t} = q^{-1}\boldsymbol{u} - \boldsymbol{u}. \tag{50}$$

Evidently $\boldsymbol{t}$ can be different for each operation $\{p \mid \boldsymbol{w}\}$ in (32), though in practice several operations have the same translation vector. The representatives of $\{p \mid \boldsymbol{w}\}$ required in (32) are given in Tables 2 and 3 (see especially footnote (iii) to Table 3).

As an example of this procedure, consider the result for the representation A_2'' of K. The method outlined above gives the result

$$\begin{aligned}\boldsymbol{\Psi}_{\boldsymbol{k}}(\boldsymbol{r}) = {} & \sum_{lm}^{l} {}^1C_{lm} R_l(r_1) Y_l^m(\hat{\boldsymbol{r}}_1) + \sum_{lm}^{l} {}^2C_{l-m} R_l(\bar{r}_2) Y_l^{-m}(\hat{\bar{\boldsymbol{r}}}_2) + \sum_{lm}^{n} {}^3C_{lm} R_l(r_3) Y_l^m(\hat{\boldsymbol{r}}_3) \\ & + \sum_{lm}^{n} {}^4C_{l-m} R_l(\bar{r}_4) Y_l^{-m}(\hat{\bar{\boldsymbol{r}}}_4) \\ & - (-1)^m \Big\{ \sum_{lm}^{l} {}^1C_{lm} R_l(\bar{r}_2) Y_l^{-m}(\hat{\bar{\boldsymbol{r}}}_2) + \sum_{lm} {}^2C_{l-m} R_l(r_1) Y_l^m(\hat{\boldsymbol{r}}_1) \\ & + \sum_{lm}^{n} {}^3C_{lm} R_l(\bar{r}_4) Y_l^{-m}(\hat{\bar{\boldsymbol{r}}}_4) + \sum_{lm}^{n} {}^4C_{l-m} R_l(r_3) Y_l^m(\hat{\boldsymbol{r}}_3) \Big\}. \end{aligned} \tag{51}$$

The delta functions have been dropped for convenience: the single prime denotes summation over those values of l and m such that l is odd, $m=0$ (modulo 6) and l even, $m=3$ (modulo 6) whereas the double prime indicates that the summation is over l and m values of l even, $m=5$ (modulo 6) and l odd, $m=2$ (modulo 6). The first four terms in (51) come from the effect of operations in D_{3h} and the second from operations of the form (44). The expression in (51) simplifies to give

$$\sum_{lm}{}' {}^1B_{lm}R_l(r_1)\{Y_l^m(\hat{\boldsymbol{r}}_1)-Y_l^{-m}(\bar{\hat{\boldsymbol{r}}}_2)(-1)^m\}$$

$$+\sum_{lm}{}'' {}^3B_{lm}R_l(r_3)\{Y_l^m(\hat{\boldsymbol{r}}_3)-Y_l^{-m}(\bar{\hat{\boldsymbol{r}}}_4)(-1)^m\} \tag{52}$$

where

$${}^1B_{lm}(r_1)={}^1C_{lm}(r_1)-{}^2C_{l-m}(\bar{r}_2)(-1)^m$$

and

$${}^3B_{lm}(r_3)={}^3C_{lm}(r_3)-{}^4C_{l-m}(\bar{r}_4)(-1)^m \tag{53}$$

and

$$R_l(r_1)=R_l(\bar{r}_2); \qquad R_l(r_3)=R_l(\bar{r}_4). \tag{54}$$

This work has been carried out for all the small representations for all symmetry points, lines and planes in the representation domain of the BZ. The results, which are given in Table 5, have been checked using the empty lattice test version of the cellular method for band structure calculations. This test provides a necessary and sufficient condition for the correctness not only of the numerical analysis and programming of the method but also of the lattice harmonics [2]. The importance of the lattice harmonics is evident from the form of (52) – in, for instance, a band structure calculation, it is only necessary to solve for two different sets of coefficients for certain restricted values of l and m, instead of solving for four different coefficients for all values of l and m, as in Eq. (30).

5. Time Reversal

The symmetry operation of time reversal can introduce extra degeneracies in addition to those that result from spatial symmetry. The full symmetry group to be considered is the grey space group $\boldsymbol{G}\otimes(E+\theta)$ where θ is the time reversal operator, which in this spin-free case is the complex conjugation operator [5, 13, 14]. Following the discussion of Bradley and Cracknell [14] these extra degeneracies are obtained by forming the corepresentations of the grey space group $\boldsymbol{M}=\boldsymbol{G}+\theta\boldsymbol{G}$. In analogy to the simple space group, these corepresentations can be obtained by induction from the small representations of the little group of $\boldsymbol{M}, {}_k\boldsymbol{K}^m$. The space group D_{6h}^4 contains the inversion operator and because the effect of $\{I\,|\,\boldsymbol{f}\}$ on a Bloch function $\boldsymbol{\Psi}_{\boldsymbol{k}}$ gives $\boldsymbol{\Psi}_{-\boldsymbol{k}}$, $\boldsymbol{k}$ and $-\boldsymbol{k}$ will always be in the same star and the spectra of eigenvalues for $\boldsymbol{k}$ and $-\boldsymbol{k}$ will be

Table 5. Lattice harmonics for the graphite lattice

Symmetry point	Representation		l	m	l	m	Harmonics
Γ	A'_{1+}, A'_{1-}		0	0	3	3	$x_1(c_1 \oplus \bar{c}_2)+x_3(c_3 \oplus \bar{c}_4)$
m mod (+6)	A'_{2+}, A'_{2-}		3	3	6	6	$x_1(s_1 \oplus \bar{s}_2)+x_3(s_3 \oplus \bar{s}_4)$
	A''_{1+}, A''_{1-}		4	3	7	6	$x_1(s_1 \oplus \bar{s}_2)+x_3(s_3 \oplus \bar{s}_4)$
	A''_{2+}, A''_{2-}		1	0	4	3	$x_1(c_1 \oplus \bar{c}_2)+x_3(c_3 \oplus \bar{c}_4)$
	E'_+, E'_-	row 1	1	1	4	4	$x_1(c_1 \oplus \bar{c}_2)+x_3(c_3 \oplus \bar{c}_4)$
			2	2	5	5	$y_1(c_1 \oplus \bar{c}_2)+y_3(c_3 \oplus \bar{c}_4)$
		row 2	1	1	4	4	$x_1(s_1 \oplus \bar{s}_2)+x_3(s_3 \oplus \bar{s}_4)$
			2	2	5	5	$y_1\{-(s_1 \oplus \bar{s}_2)\}+y_3\{-(s_3 \oplus \bar{s}_4)\}$
	E''_+, E''_-	row 1	2	1	5	4	$x_1(c_1 \oplus \bar{c}_2)+x_3(c_3 \oplus \bar{c}_4)$
			3	2	6	5	$y_1(c_1 \oplus \bar{c}_2)+y_3(c_3 \oplus \bar{c}_4)$
		row 2	2	1	5	4	$x_1(s_1 \oplus \bar{s}_2)+x_3(s_3 \oplus \bar{s}_4)$
			3	2	6	5	$y_1\{-(s_1 \oplus \bar{s}_2)\}+y_3\{-(s_3 \oplus s_4)\}$
M	$\mathscr{A}'_+, \mathscr{A}'_-$		0	0	1	1	$x_1(c_1 \oplus \bar{c}_2)+x_3(c_3 \oplus \bar{c}_4)$
m mod (+2)	$\mathscr{B}'_+, \mathscr{B}'_-$		1	1	2	2	$x_1(s_1 \oplus \bar{s}_2)+x_3(s_3 \oplus \bar{s}_4)$
	$\mathscr{A}''_+, A''_-$		2	1	3	2	$x_1(s_1 \oplus \bar{s}_2)+x_3(s_3 \oplus \bar{s}_4)$
	$\mathscr{B}''_+, \mathscr{B}''_-$		1	0	2	1	$x_1(c_1 \oplus \bar{c}_2)+x_3(c_3 \oplus \bar{c}_4)$
K	A'_1, A'_2		0	0	3	3	$x_1\{m_1 \pm \oplus(-\bar{m}_2)\}+$
m mod (6)			2	2	5	5	$x_3\{m_3 \pm \oplus(-\bar{m}_4)\}$
	A''_1, A''_2		1	0	4	3	$x_1\{m_1 \pm \oplus(-\bar{m}_2)\}+$
			3	2	6	5	$x_3\{m_3 \pm \oplus(-\bar{m}_4)\}$
	E'	row 1	1	1	4	4	$x_1\{m_1 \mp(-\bar{m}_2)\}+$
			2	2	5	5	$y_1\{m_1 \pm(-\bar{m}_2)\}+$
			0	0	3	3	$x_3\{m_3 \pm(-\bar{m}_4)\}+$
			1	1	4	4	$y_3\{m_3 \mp(-\bar{m}_4)\}$
		row 2	1	1	4	4	$x_1[-i\{m_1 \pm(-\bar{m}_2)\}]+$
			2	2	5	5	$y_1[i\{m_1 \pm(-\bar{m}_2)\}]+$
			0	0	3	3	$x_3[-i\{m_3 \mp(-\bar{m}_4)\}]+$
			1	1	4	4	$y_3[i\{m_3 \pm(-\bar{m}_4)\}]$
	E''	row 1	2	1	5	4	$x_1\{m_1 \mp(-\bar{m}_2)\}+$
			3	2	6	5	$y_1\{m_1 \pm(-\bar{m}_2)\}+$
			1	0	4	3	$x_3\{m_3 \pm(-\bar{m}_4)\}+$
			2	1	5	4	$y_3\{m_3 \mp(-\bar{m}_4)\}$
		row 2	2	1	5	4	$x_1[-i\{m_1 \pm(-\bar{m}_2)\}]+$
			3	2	6	5	$y_1[i\{m_1 \mp(-\bar{m}_2)\}]+$
			1	0	4	3	$x_3[-i\{m_3 \mp(-\bar{m}_4)\}]+$
			2	1	5	4	$y_3[i\{m_3 \pm(-\bar{m}_4)\}]$
A	$A_1^{(2)}$	row 1	0	0	3	3	$x_1c_1+x_4\bar{c}_4+$
m mod (+6)			1	0	4	3	$x_2\bar{c}_2+x_3c_3$
		row 2	0	0	3	3	$x_2(-i\bar{c}_2)+x_3(-ic_3)+$
			1	0	4	3	$x_1(-ic_1)+x_4(-i\bar{c}_4)$
	$A_2^{(2)}$	row 1	3	3	6	6	$x_1s_1+x_4\bar{s}_4+$
			4	3	7	6	$x_2\bar{s}_2+x_3s_3$
		row 2	3	3	6	6	$x_2(-i\bar{s}_2)+x_3(-is_3)+$
			4	3	7	6	$x_1(-is_1)+x_4(-i\bar{s}_4)$
	$E^{(4)}$	row 1	1	1	4	4	$x_1c_1+x_4\bar{c}_4+$
			2	2	5	5	$y_1c_1+y_4\bar{c}_4+$
			2	1	5	4	$x_2\bar{c}_2+x_3c_3+$
			3	2	6	5	$y_2\bar{c}_2+y_3c_3$

Table 5 (continued)

Symmetry point	Representation		l	m	l	m	Harmonics
A (cont.)		row 2	1	1	4	4	$x_1 s_1 + x_4 \bar{s}_4 +$
m mod (+6)			2	2	5	5	$y_1(-s_1) + y_4(-\bar{s}_4) +$
			2	1	5	4	$x_2 \bar{s}_2 + x_3 s_3 +$
			3	2	6	5	$y_2(-\bar{s}_2) + y_3(-s_3)$
	$E^{(4)}$	row 3	1	1	4	4	$x_2(-\bar{c}_2) + x_3(-c_3) +$
			2	2	5	5	$y_2(-\bar{c}_2) + y_3(-c_3) +$
			2	1	5	4	$x_1(-c_1) + x_4(-\bar{c}_4) +$
			3	2	6	5	$y_1(-c_1) + y_4(-\bar{c}_4)$
		row 4	1	1	4	4	$x_2(-\bar{s}_2) + x_3(-s_3) +$
			2	2	5	5	$y_2 \bar{s}_2 + y_3 s_3 +$
			2	1	5	4	$x_1(-s_1) + x_4(-\bar{s}_4) +$
			3	2	6	5	$y_1 s_1 + y_4 \bar{s}_4$
L	ε_1	row 1	0	0	1	1	$x_1 c_1 + x_4 \bar{c}_4 +$
m mod (+2)			1	0	2	1	$x_2 \bar{c}_2 + x_3 c_3$
		row 2	0	0	1	1	$x_2(-i\bar{c}_2) + x_3(-ic_3) +$
			1	0	2	1	$x_1(-ic_1) + x_4(-i\bar{c}_4)$
	ε_2	row 1	1	1	2	2	$x_1 s_1 + x_4 \bar{s}_4 +$
			2	1	3	2	$x_2 \bar{s}_2 + x_3 s_3$
		row 2	1	1	2	2	$x_2(-i\bar{s}_2) + x_3(-is_3) +$
			2	1	3	2	$x_1(-is_1) + x_4(-i\bar{s}_4)$
H	$A^{(2)}$	row 1	0	0	3	3	$x_1 m_1 +$
m mod (6)			1	0	4	3	$x_2\{i(-\bar{m}_2)\} +$
			3	2	6	5	$x_3 m_3 +$
			2	2	5	5	$x_4\{i(-\bar{m}_4)\}$
		row 2	0	0	3	3	$x_2\{-i(-\bar{m}_2)\} +$
			1	0	4	3	$x_1 m_1 +$
			3	2	6	5	$x_4\{-i(-\bar{m}_4)\} +$
			2	2	5	5	$x_3 m_3$
	E	row 1	1	1	4	4	$x_1 m_1 +$
			3	2	6	5	$x_2\{-i(-\bar{m}_2)\} +$
			1	0	4	3	$x_3 m_3 +$
			1	1	4	4	$x_4\{-i(-\bar{m}_4)\}$
		row 2	1	1	4	4	$x_2\{i(-\bar{m}_2)\} +$
			3	2	6	5	$x_1 m_1 +$
			1	0	4	3	$x_4\{i(-\bar{m}_4)\} +$
			1	1	4	4	$x_3 m_3$
	E^*	row 1	2	1	5	4	$x_1 m_1 +$
			2	2	5	5	$x_2\{i(-\bar{m}_2)\}$
			0	0	3	3	$x_3 m_3$
			2	1	5	4	$x_4\{i(-\bar{m}_4)\}$
		row 2	2	1	5	4	$x_2\{(-i(-\bar{m}_2)\} +$
			2	2	5	5	$x_1 m_1 +$
			0	0	3	3	$x_4\{-i(-\bar{m}_4)\} +$
			2	1	5	4	$x_3 m_3$
Symmetry line							
Δ	A_{1p}, A_{1m}		0	0	3	3	$x_1(c_1 \oplus q\bar{c}_2) + x_3(c_3 \oplus q^*\bar{c}_4) +$
m mod (+6)			1	0	4	3	$y_1(c_1 \ominus q\bar{c}_2) + y_3(c_3 \ominus q^*\bar{c}_4)$

Table 5 (continued)

Symmetry line	Representation		l	m	l	m	Harmonics
Δ (cont.)	A_{2p}, A_{2m}		3	3	6	6	$x_1(s_1 \oplus q\bar{s}_2) + x_3(s_3 \oplus q^*\bar{s}_4) +$
m mod (+6)			4	3	7	6	$y_1(s_1 \ominus q\bar{s}_2) + y_3(s_3 \ominus q^*\bar{s}_4)$
	E_p, E_m	row 1	1	1	4	4	$w_1(c_1 \oplus q\bar{c}_2) + w_3(c_3 \oplus q^*\bar{c}_4) +$
			2	2	5	5	$x_1(c_1 \oplus q\bar{c}_2) + x_3(c_3 \oplus q^*\bar{c}_4) +$
			2	1	5	4	$y_1(c_1 \ominus q\bar{c}_2) + y_3(c_3 \ominus q^*\bar{c}_4) +$
			3	2	6	5	$z_1(c_1 \ominus q\bar{c}_2) + z_3(c_3 \ominus q^*\bar{c}_4)$
	E_p, E_m	row 2	1	1	4	4	$w_1(s_1 \oplus q\bar{s}_2) + w_3(s_3 \oplus q^*\bar{s}_4) +$
			2	2	5	5	$x_1\{-(s_1 \oplus q\bar{s}_2)\} + x_3\{-(s_3 \oplus q^*\bar{s}_4)\} +$
			2	1	5	4	$y_1(s_1 \ominus q\bar{s}_2) + y_3(s_3 \ominus q^*\bar{s}_4) +$
			3	2	6	5	$z_1\{-(s_1 \ominus q\bar{s}_2)\} + z_3\{-(s_3 \ominus q^*\bar{s}_4)\}$
U	$\mathscr{A}_p, \mathscr{A}_m$		0	1	1	1	$x_1(c_1 \oplus q\bar{c}_2) + x_3(c_3 \oplus q^*\bar{c}_4) +$
m mod (+2)			1	0	2	1	$y_1(c_1 \ominus q\bar{c}_2) + y_3(c_3 \oplus q^*\bar{c}_4) +$
	$\mathscr{B}_p, \mathscr{B}_m$		1	1	2	2	$x_1(s_1 \oplus q\bar{s}_2) + x_3(s_3 \oplus q^*\bar{s}_4) +$
			2	1	3	2	$y_1(s_1 \ominus q\bar{s}_2) + y_3(s_3 \ominus q^*\bar{s}_4)$
P	A_p, A_m		0	0	3	3	$x_1\{m_1 \pm \oplus q(-\bar{m}_2)\} +$
m mod (6)			1	0	4	3	$y_1\{m_1 \pm \ominus q(-\bar{m}_2)\} +$
			2	2	5	5	$x_3\{m_3 \pm \oplus q^*(-\bar{m}_4)\} +$
			3	2	6	5	$y_3\{m_3 \pm \ominus q^*(-\bar{m}_4)\}$
	E	row 1	1	1	4	4	$w_1\{m_1 \mp q(-\bar{m}_2)\} +$
			2	1	5	4	$x_1\{m_1 \pm q(-\bar{m}_2)\} +$
			2	2	5	5	$y_1\{m_1 \pm q(-\bar{m}_2)\} +$
			3	2	6	5	$z_1\{m_1 \mp q(-\bar{m}_2)\} +$
			0	0	3	3	$w_3\{m_3 \pm q^*(-\bar{m}_4)\} +$
			1	0	4	3	$x_3\{m_3 \mp q^*(-\bar{m}_4)\} +$
			1	1	4	4	$y_3\{m_3 \mp q^*(-\bar{m}_4)\} +$
			2	1	5	4	$z_3\{m_3 \pm q^*(-\bar{m}_4)\}$
		row 2	1	1	4	4	$w_1[-i\{m_1 \pm q(-\bar{m}_2)\}] +$
			2	1	5	4	$x_1[-i\{m_1 \mp q(-\bar{m}_2)\}] +$
			2	2	5	5	$y_1[i\{m_1 \mp q(-\bar{m}_2)\}] +$
			3	2	6	5	$z_1[i\{m_1 \pm q(-\bar{m}_2)\}] +$
			0	0	3	3	$w_3[-i\{m_3 \mp q^*(-\bar{m}_4)\}] +$
			1	0	4	3	$x_3[-i\{m_3 \pm q^*(-\bar{m}_4)\}] +$
			1	1	4	4	$y_3[i\{m_3 \pm q^*(-\bar{m}_4)\}] +$
			2	1	5	4	$z_3[i\{m_3 \mp q^*(-\bar{m}_4)\}]$
Σ	$\mathscr{A}'$		0	0	1	1	$x_1c_1 + x_2\bar{c}_2 + x_3c_3 + x_4\bar{c}_4$
m mod (+2)	$\mathscr{B}'$		1	1	2	2	$x_1s_1 + x_2\bar{s}_2 + x_3s_3 + x_4\bar{s}_4$
	$\mathscr{A}''$		2	1	3	2	$x_1s_1 + x_2\bar{s}_2 + x_3s_3 + x_4\bar{s}_4$
	$\mathscr{B}''$		1	0	2	1	$x_1c_1 + x_2\bar{c}_2 + x_3c_3 + x_4\bar{c}_4$
T	$\mathscr{A}', \mathscr{B}'$		0	0	3	3	$x_1[\{m_1 \pm \oplus(-\bar{m}_2)\}] + x_3[\{m_3 \pm \oplus a(-\bar{m}_4)\}]$
m mod (6)			1	1	4	4	$y_1[\{m_1 \mp \oplus\omega^*(-\bar{m}_2)\}] + y_3[\{m_3 \mp \oplus a\omega^*(-\bar{m}_4)\}]$
			2	2	5	5	$z_1[\{m_1 \pm \oplus\omega(-\bar{m}_2)\}] + z_3[\{m_3 \pm \oplus a\omega(-\bar{m}_4)\}]$
	$\mathscr{A}'', \mathscr{B}''$		1	0	4	3	$x_1[\{m_1 \pm \oplus(-\bar{m}_2)\}] + x_3[\{m_3 \pm \oplus a(-\bar{m}_4)\}]$
			2	1	5	4	$y_1[\{m_1 \mp \oplus\omega^*(-\bar{m}_2)\}] + y_3[\{m_3 \mp \oplus a\omega^*(-\bar{m}_4)\}]$
			3	2	6	5	$z_1[\{m_1 \pm \oplus\omega(-\bar{m}_2)\}] + z_3[\{m_3 \pm \oplus a\omega(-\bar{m}_4)\}]$
T'	$\mathscr{A}', \mathscr{B}'$		0	0	1	1	$x_1[\{m_1 \pm \oplus(-\bar{m}_2)\}] + x_3[\{m_3 \pm \oplus(-\bar{m}_4)\}]$
m mod (2)	$\mathscr{A}'', \mathscr{B}''$		1	0	2	1	$x_1[\{m_1 \pm \oplus(-\bar{m}_2)\}] + x_3[\{m_3 \pm \oplus(-\bar{m}_4)\}]$

Table 5 (continued)

Symmetry line	Representation		l	m	l	m	Harmonics
R	$\mathscr{A}'$		0	0	1	1	$x_1c_1+x_4\bar{c}_4+$
m mod (+2)			1	0	2	1	$x_2\bar{c}_2+x_3c_3$
	$\mathscr{B}'$		1	1	2	2	$x_1s_1+x_4\bar{s}_4+$
			2	1	3	2	$x_2\bar{s}_2+x_3s_3$
	$\mathscr{A}''$		2	1	3	2	$x_1s_1+x_4\bar{s}_4+$
			1	1	2	2	$x_2\bar{s}_2+x_3s_3$
	$\mathscr{B}''$		1	0	2	1	$x_1c_1+x_4\bar{c}_4+$
			0	0	1	1	$x_2\bar{s}_2+x_3s_3$
S	ε	row 1	0	0	3	3	x_1m_1+
m mod (6)			1	0	4	3	$x_2\{i(-\bar{m}_2)\}+$
			1	0	4	3	x_3m_3+
			0	0	3	3	$x_4\{ia(-\bar{m}_4)\}+$
			1	1	4	4	y_1m_1+
			2	1	5	4	$y_2\{i\omega^*(-\bar{m}_2)\}+$
			2	1	5	4	y_3m_3+
			1	1	4	4	$y_4\{i\omega^*a(-\bar{m}_4)\}+$
			2	2	5	5	z_1m_1+
			3	2	6	5	$z_2\{i\omega(-\bar{m}_2)\}+$
			3	2	6	5	z_3m_3+
			2	2	5	5	$z_4\{i\omega a(-\bar{m}_4)\}+$
	ε	row 2	0	0	3	3	$x_2\{-i(-\bar{m}_2)\}+$
			1	0	4	3	x_1m_1+
			1	0	4	3	$x_4\{-ia(-\bar{m}_4)\}+$
			0	0	3	3	x_3m_3+
			1	1	4	4	$y_2\{-i\omega^*(-\bar{m}_2)\}+$
			2	1	5	4	y_1m_1+
			2	1	5	4	$y_4\{-i\omega^*a(-\bar{m}_4)\}+$
			1	1	4	4	y_3m_3+
			2	2	5	5	$z_2\{-i\omega a(-\bar{m}_2)\}+$
			3	2	6	5	z_1m_1+
			3	2	6	5	$z_4\{-i\omega(-\bar{m}_4)\}+$
			2	2	5	5	z_3m_3
S'	ε	row 1	0	0	1	1	$x_1m_1+x_4\{i(-\bar{m}_4)\}+$
m mod (2)			1	0	2	1	$x_2\{i(-\bar{m}_2)\}+x_3m_3$
		row 2	0	0	1	1	$x_2\{-i(-\bar{m}_2)\}+x_3m_3+$
			1	0	2	1	$x_1m_1+x_4\{-i(-\bar{m}_4)\}$
Symmetry plane							
V_1	A'		0	0	1	1	$x_1m_1+x_2\bar{m}_2+x_3m_3+x_4\bar{m}_4$
m mod (2)	A''		1	0	2	1	$x_1m_1+x_2\bar{m}_2+x_3m_3+x_4\bar{m}_4$
V_2	A'		0	0	1	1	$x_1m_1+x_4\bar{m}_4$
m mod (2)			1	0	2	1	$x_2\bar{m}_2+x_3m_3$
	A''		1	0	2	1	$x_1m_1+x_4\bar{m}_4$
			0	0	1	1	$x_2\bar{m}_2+x_3m_3$
V_3	$\mathscr{A}$		0	0	1	0	$x_1c_1+x_2\bar{c}_2+x_3c_3+x_4\bar{c}_4$
m mod (+2)			1	1	2	1	$x_1c_1+x_2\bar{c}_2+x_3c_3+x_4\bar{c}_4$

V_3 (cont.)	$\mathscr{B}$	1	1	2	1	$x_1 s_1 + x_2 \bar{s}_2 + x_3 s_3 + x_4 \bar{s}_4$
m mod (+2)		2	2	3	2	$x_1 s_1 + x_2 \bar{s}_2 + x_3 s_3 + x_4 \bar{s}_4$
V_4	A_p	0	0	1	0	$x_1\{m_1 + q(-\bar{m}_2)\} + x_3\{m_3 + q^*(-\bar{m}_4)\}$
m mod (2)	A_m	1	1	2	1	$x_1\{m_1 + q(-\bar{m}_2)\} + x_3\{m_3 + q^*(-\bar{m}_4)\}$
V_5	$\mathscr{A}$, $\mathscr{B}$	0	0	1	0	$u_1\{m_1 \oplus q(-\bar{m}_2)\} + u_3\{m_3 \oplus q^* a(-\bar{m}_4)\}$
m mod (6)		3	3	4	3	$v_1\{m_1 \ominus q(-\bar{m}_2)\} + v_3\{m_3 \ominus q^* a(-\bar{m}_4)\}$
		1	1	2	1	$w_1\{m_1 \oplus \omega^* q(-\bar{m}_2)\} + w_3\{m_3 \oplus \omega^* q^* a(-\bar{m}_4)\}$
		4	4	5	4	$x_1\{m_1 \ominus \omega^* q(-\bar{m}_2)\} + x_3\{m_3 \ominus \omega^* q^* a(-\bar{m}_4)\}$
		2	2	3	2	$y_1\{m_1 \ominus \omega q(-\bar{m}_2)\} + y_3\{m_3 \ominus \omega q^* a(-\bar{m}_4)\}$
		5	5	6	5	$z_1\{m_1 \oplus \omega q(-\bar{m}_2)\} + z_3\{m_3 \oplus \omega q^* a(-\bar{m}_4)\}$
General point		0	0	1	0	$k_1\{m_1 + (-\bar{m}_2)\} + k_3\{m_3 + (-\bar{m}_4)\}$
m mod (2)		0	0	1	0	$in_1\{m_1 - (-\bar{m}_2)\} + in_3\{m_3 - (-\bar{m}_4)\}$
		1	1	2	1	$p_1\{m_1 - (-\bar{m}_2)\} + p_3\{m_3 - (-\bar{m}_4)\}$
		1	1	2	1	$ir_1\{m_1 + (-\bar{m}_2)\} + ir_3\{m_3 + (-\bar{m}_4)\}$

Explanatory Notes for Table 5

(i) The values of l and m to be used with the harmonics are given in column three of the table. The l value is given mod (+2) except for K, H, P, T, S and V_5 when the values are mod (2) – i.e. any multiple of 2 can be added to or subtracted from that listed. The accompanying values of m are given in an analogous fashion, either as mod $(+s)$ or mod (s), and are listed in column one under the $\boldsymbol{k}$ point label. The permitted values of l and m are obtained by forming a succession of values using the modulo conditions. Thus, for K, with l mod (2) and m mod (6) the allowed l and m values for A_1'' are

(1, 0)(3, 0)(4, 3)(4, −3)(5, 0)(6, 3)(6, −3)(7, 0)(7, 6)(7, −6) etc.

for cells 1 and 2 and

(2, −1)(3, 2)(4, −1)(5, 2)(5, −4)(6, −1)(6, 5)(7, 2)(7, −4)(8, −1)(8, 5)(8, −7) etc.

for cells 3 and 4.

(ii) The notation for the spherical harmonics (see Appendix) is $m = Y_l^m(\theta, \phi)$, $(-m) = Y_l^{-m}(\theta, \phi)$, $c = Y_l^{m,c}(\theta, \phi)$, $s = Y_l^{m,s}(\theta, \phi)$. Subscripts refer to the atom about which a spherical harmonic is centred and bars for atoms 2 and 4 indicate that the axes for these centres are inverted with respect to those for 1 and 3.

(iii) There are two different sets of ± signs in the table – the signs with the circumscribing circle, ⊜ and ⊜, are used for $\boldsymbol{k}$ points where two different representations are listed in column 2 and the upper sign refers to the first representation listed and the lower sign the second. The other signs, ± and ∓ without the circle, refer to the m value – the upper sign is to be taken for the first m value of the two listed on a particular line, and the lower sign the second.

(iv) The expansions can be obtained by associating, for a particular representation of a $\boldsymbol{k}$ point, the permitted values of l and m (see (i)) with the functions listed under harmonics. The resulting four centre expansions can be used with Bloch periodicity to form the multicentred lattice harmonics. For degenerate representations the basis is to be understood as a row vector, whose transformation properties are obtained by postmultiplication with the appropriate matrix representative from Table 3.

(v) The following coefficients are used: u_i, v_i, w_i, x_i, y_i, z_i $(i = 1, 2, 3, 4)$ arbitrary complex coefficients (such as a product of a cellular coefficient and a radial function). k_i, n_i, p_i, r_i $(i = 1, 2, 3)$

arbitrary real coefficients.

$i = \sqrt{-1}$

$q = \exp(\pi i\gamma)$ $\quad q^* = \exp(-\pi i\gamma)$ $\quad [\gamma = \boldsymbol{T}_3$ component of the $\boldsymbol{k}$ vector]

$a = \exp(4\pi i\alpha)$ $\quad [2\alpha = \boldsymbol{T}_2$ component of the $\boldsymbol{k}$ vector]

$\omega = \exp(-2\pi i/3)$ $\quad \omega^* = \exp(2\pi i/3)$.

(vi) Examples: the following are suitable cellular expansions:

a) $\Gamma E_-''$ second row:

$$
\begin{aligned}
&{}^1B_{21}R_2(1)\{Y_2^{1,s}(1) - Y_2^{1,s}(\bar{2})\} + {}^2B_{21}R_2(3)\{Y_2^{1,s}(3) - Y_2^{1,s}(\bar{4})\} + \\
&{}^1B_{32}R_3(1)[-\{Y_3^{2,s}(1) - Y_3^{2,s}(\bar{2})\}] + {}^2B_{32}R_3(3)[-\{Y_3^{2,s}(3) - Y_3^{2,s}(\bar{4})\}] + \\
&{}^1B_{41}R_4(1)\{Y_4^{1,s}(1) - Y_4^{1,s}(\bar{2})\} + {}^2B_{41}R_4(3)\{Y_4^{1,s}(3) - Y_4^{1,s}(\bar{4})\} + \\
&{}^1B_{52}R_5(1)[-\{Y_5^{2,s}(1) - Y_5^{2,s}(\bar{2})\} + {}^2B_{52}R_5(3)[-\{Y_5^{2,s}(3) - Y_5^{2,s}(\bar{4})\}] + \\
&{}^1B_{54}R_5(1)\{Y_5^{4,s}(1) - Y_5^{4,s}(\bar{2})\} + {}^2B_{54}R_5(3)\{Y_5^{4,s}(3) - Y_5^{4,s}(\bar{4})\} + \\
&{}^1B_{61}R_6(1)\{Y_6^{1,s}(1) - Y_6^{1,s}(\bar{2})\} + {}^2B_{61}R_6(3)\{Y_6^{1,s}(3) - Y_6^{1,s}(\bar{4})\} + \\
&{}^1B_{65}R_6(1)[-\{Y_6^{5,s}(1) - Y_6^{5,s}(\bar{2})\} + {}^2B_{65}R_6(3)[-\{Y_6^{5,s}(3) - Y_6^{5,s}(\bar{4})\}] + \cdots .
\end{aligned}
$$

The form for the expansions for other *IR*s of Γ, M, Δ and U is similar.

b) KA_2' – see Eqs. (52) and (53). The form of the expansion for P, T, T', V_4 and V_5 is similar. For a general point the expansion coefficients are real.

c) for $AA_1^{(2)}$ first row:

$$
\begin{aligned}
&{}^1B_{00}R_0(1)Y_0^0(1) + {}^2B_{10}R_1(\bar{2})Y_1^0(\bar{2}) + {}^3B_{10}R_1(3)Y_1^0(3) + {}^4B_{00}R_0(\bar{4})Y_0^0(\bar{4}) + \\
&{}^1B_{20}R_0(1)Y_2^0(1) + {}^2B_{30}R_3(\bar{2})Y_3^0(\bar{2}) + {}^3B_{30}R_3(3)Y_3^0(3) + {}^4B_{20}R_2(\bar{4})Y_2^0(\bar{4}) + \\
&{}^1B_{33}R_3(1)Y_3^{3,c}(1) + {}^2B_{43}R_4(\bar{2})Y_4^{3,c}(\bar{2}) + {}^3B_{43}R_4(3)Y_4^{3,c}(3) + {}^4B_{33}R_3(\bar{4})Y_3^{3,c}(\bar{4}) + \\
&{}^1B_{40}R_4(1)Y_4^0(1) + {}^2B_{50}R_5(\bar{2})Y_5^0(\bar{2}) + {}^3B_{50}R_5(3)Y_5^0(3) + {}^4B_{40}R_4(\bar{4})Y_4^0(\bar{4}) + \\
&{}^1B_{53}R_5(1)Y_5^{3,c}(1) + {}^2B_{63}R_6(\bar{2})Y_6^{3,c}(\bar{2}) + {}^3B_{63}R_6(3)Y_6^{3,c}(3) + {}^4B_{63}R_6(\bar{4})Y_6^{3,c}(\bar{4}) + \\
&{}^1B_{60}R_6(1)Y_6^0(1) + {}^2B_{70}R_7(\bar{2})Y_7^0(\bar{2}) + {}^3B_{70}R_7(3)Y_7^0(3) + {}^4B_{60}R_6(\bar{4})Y_6^0(\bar{4}) + \\
&{}^1B_{66}R_6(1)Y_6^{6,c}(1) + {}^2B_{76}R_7(\bar{2})Y_7^{6,c}(\bar{2}) + {}^3B_{76}R_7(3)Y_7^{6,c}(3) + {}^4B_{66}R_6(\bar{4})Y_6^{6,c}(\bar{4}) + \cdots .
\end{aligned}
$$

The expansions for L and R are similar.

d) $HA^{(2)}$ first row:

$$
\begin{aligned}
&{}^1B_{00}R_0(1)Y_0^0(1) + {}^2B_{10}R_1(\bar{2})Y_1^0(\bar{2}) + {}^3B_{2-1}R_2(3)Y_2^{-1}(3) + {}^6B_{11}R_1(\bar{4})Y_1^1(\bar{4}) + \\
&{}^1B_{20}R_2(1)Y_2^0(1) + {}^2B_{30}R_3(\bar{2})Y_3^0(\bar{2}) + {}^3B_{32}R_3(3)Y_3^2(3) + {}^4B_{2-2}R_2(\bar{4})Y_2^{-2}(\bar{4}) + \\
&{}^1B_{3-3}R_3(1)Y_3^{-3}(1) + {}^2B_{4-3}R_4(\bar{2})Y_4^{-3}(\bar{2}) + {}^3B_{4-1}R_4(3)Y_4^{-1}(3) + {}^4B_{31}R_3(\bar{4})Y_3^1(\bar{4}) + \\
&{}^1B_{33}R_3(1)Y_3^3(1) + {}^2B_{43}R_4(\bar{2})Y_4^3(\bar{2}) + {}^3B_{52}R_5(3)Y_5^2(3) + {}^4B_{4-2}R_4(\bar{4})Y_4^{-2}(\bar{4}) + \\
&{}^1B_{40}R_4(1)Y_4^0(1) + {}^2B_{50}R_5(\bar{2})Y_5^0(\bar{2}) + {}^3B_{5-4}R_5(3)Y_5^4(3) + {}^4B_{44}R_4(\bar{4})Y_4^4(\bar{4}) + \\
&{}^1B_{5-3}R_5(1)Y_5^{-3}(1) + {}^2B_{6-3}R_6(\bar{2})Y_6^{-3}(\bar{2}) + {}^3B_{6-1}R_6(3)Y_6^{-1}(3) + {}^4B_{51}R_5(\bar{4})Y_5^1(\bar{4}) + \\
&{}^1B_{53}R_5(1)Y_5^3(1) + {}^2B_{63}R_6(\bar{2})Y_6^3(\bar{2}) + {}^3B_{65}R_6(3)Y_6^5(3) + {}^4B_{5-5}R_5(\bar{4})Y_5^{-5}(\bar{4}) + \cdots .
\end{aligned}
$$

e) $\sum \mathscr{A}''$

$$
\begin{aligned}
&{}^1B_{21}R_2(1)\,Y_2^{1,s}(1)+{}^2B_{21}R_2(\bar{2})\,Y_2^{1,s}(\bar{2})+{}^3B_{21}R_2(3)\,Y_2^{1,s}(3)+{}^4B_{21}R_2(\bar{4})\,Y_2^{1,s}(\bar{4})+\\
&{}^1B_{32}R_3(1)\,Y_3^{2,s}(1)+{}^2B_{32}R_3(\bar{2})\,Y_3^{2,s}(\bar{2})+{}^3B_{32}R_3(3)\,Y_3^{2,s}(3)+{}^4B_{32}R_3(\bar{4})\,Y_3^{2,s}(\bar{4})+\\
&{}^1B_{41}R_4(1)\,Y_4^{1,s}(1)+{}^2B_{41}R_4(\bar{2})\,Y_4^{1,s}(\bar{2})+{}^3B_{41}R_4(3)\,Y_4^{1,s}(3)+{}^4B_{41}R_4(\bar{4})\,Y_4^{1,s}(\bar{4})+\\
&{}^1B_{43}R_4(1)\,Y_4^{3,s}(1)+{}^2B_{43}R_4(\bar{2})\,Y_4^{3,s}(\bar{2})+{}^3B_{43}R_4(3)\,Y_4^{3,s}(3)+{}^4B_{43}R_4(\bar{4})\,Y_4^{3,s}(\bar{4})+\cdots.
\end{aligned}
$$

The expansions for V_3 have a similar form.

the same. In this case the magnetic little group ${}_k\boldsymbol{K}^m$ will have one of the following forms:

$${}_k\boldsymbol{K}^m = {}_k\boldsymbol{K} + \theta\,{}_k\boldsymbol{K} \tag{55}$$

$${}_k\boldsymbol{K}^m = {}_k\boldsymbol{K} + A\,{}_k\boldsymbol{K} \tag{56}$$

where A is the product of θ and some space group operation other than a translation. Whether the antiunitary element A introduces extra degeneracy depends on whether the components of the basis of $\boldsymbol{M}$, $\langle\boldsymbol{\Psi}|\oplus A\langle\boldsymbol{\Psi}|$ ($\langle\boldsymbol{\Psi}|$ is a row vector of Bloch functions) are linearly independent and this in turn depends on the relationship between the corresponding components of the corepresentations of ${}_k\boldsymbol{K}^m$, ${}^i_k\hat{\boldsymbol{K}}$ and $[{}^i_k\hat{\boldsymbol{K}}(A^{-1}RA)]^*$, for an element R of $\boldsymbol{G}$. First, the magnetic little group is expanded in left cosets with respect to $\boldsymbol{T}$ (cf. Eq. (8)).

$${}_k\boldsymbol{K}^m = \sum_{\{p\,|\,\boldsymbol{w}\}} \{p\,|\,\boldsymbol{w}\}\boldsymbol{T} + \sum_{\{q\,|\,\boldsymbol{x}\}} \theta\{q\,|\,\boldsymbol{x}\}\boldsymbol{T} \tag{57}$$

where the sum over the $\{p\,|\,\boldsymbol{w}\}$ and $\{q\,|\,\boldsymbol{x}\}$ includes elements obeying

$$
\begin{aligned}
p\boldsymbol{k} &= \boldsymbol{k} + \boldsymbol{g}\\
q\boldsymbol{k} &= -\boldsymbol{k} + \boldsymbol{g}
\end{aligned}
\tag{58}
$$

and $\boldsymbol{g}$ is a reciprocal lattice vector. The relationship between the two components of the corepresentation can then be established using the Frobenius–Schur test,

$$\sum_{\{q\,|\,\boldsymbol{x}\}} \chi(\{q\,|\,\boldsymbol{x}\}^2\,|\,{}^i_k\hat{\boldsymbol{K}}) = c\,|{}_k\bar{\boldsymbol{K}}| \tag{59}$$

in which $\chi(\{q\,|\,\boldsymbol{x}\}^2\,|\,{}^i_k\hat{\boldsymbol{K}})$ is the character of $\{q\,|\,\boldsymbol{x}\}^2$ in the i^{th} IR of ${}_k\boldsymbol{K}$, $|{}_k\bar{\boldsymbol{K}}|$ the order of the little factor group (cf. Eq. (8)) and c has the values $1, -1$ or zero. Extra degeneracies occur if $c = 0$ or -1. To find the $\{q\,|\,\boldsymbol{x}\}$ required in the test (59) the form of the magnetic little group is required. If the form is given by (55) then from Eqn. (58) for $\{q\,|\,\boldsymbol{x}\}$, it is the elements of ${}_k\boldsymbol{K}$ that transform $\boldsymbol{k}$ into $-\boldsymbol{k}$, and thus the two vectors are equivalent – this is the case if $\boldsymbol{k}$ is either zero or half a reciprocal lattice vector (points Γ, A and M of the BZ). If the magnetic little group has the form (56) then $\boldsymbol{k}$ and $-\boldsymbol{k}$ appear in the same star but are not equivalent and the elements $\{q\,|\,\boldsymbol{x}\}$ in (57) will be the elements of the set $\{I\,|\,\boldsymbol{f}\}_k\mathscr{K}$, where ${}_k\mathscr{K}$ is the little co-group, the isomorph of the little factor group containing the elements $\{p\,|\,\boldsymbol{w}\}$ in (8). (cf. the definition of ${}_k\mathscr{C}$, Eq.

(13)). When the sums are carried out for Γ, A and M using (55), (57) and (58) and for all other points using (56), (57) and (58) it is found that degeneracies are only introduced for the line R and the symmetry plane V_2, when c in Eq. (59) is zero and ${}_{\boldsymbol{k}}\boldsymbol{K}^m$ has the form (56) with $A = \theta\{I \mid \boldsymbol{f}\}$. For these $\boldsymbol{k}$ points the representations ${}^{i}_{\boldsymbol{k}}\hat{\boldsymbol{K}}\{p \mid \boldsymbol{0}\}$ and $[{}^{i}_{\boldsymbol{k}}\hat{\boldsymbol{K}}(\theta\{I \mid \boldsymbol{f}\}\{p \mid \boldsymbol{0}\}\{I \mid \boldsymbol{f}\}\theta)]^*$ are inequivalent and the corresponding bases $\langle\boldsymbol{\Psi}_{\boldsymbol{k}}|$ and $\theta\{I \mid \boldsymbol{f}\}\langle\boldsymbol{\Psi}_{\boldsymbol{k}}|$ are mutually orthogonal. In this case $[{}^{i}_{\boldsymbol{k}}\boldsymbol{K}(\theta\{I \mid \boldsymbol{f}\}\{p \mid \boldsymbol{0}\}\{I \mid \boldsymbol{f}\}\theta)]^*$ must be equivalent to some other IR of ${}_{\boldsymbol{k}}\boldsymbol{K}$ and the extra degeneracy is thus between two sets of eigenvalues belonging to different IRs. The representation $\mathscr{A}'$ of R will be equivalent with one in which the characters for $\{E \mid \boldsymbol{0}\}$, $\{C'_{21} \mid \boldsymbol{0}\}\{\sigma_h \mid \boldsymbol{0}\}$ and $\{\sigma_{v1} \mid \boldsymbol{0}\}$ are $1, -1, -1$ and 1 respectively – that is $\mathscr{B}''$ (remember that $\{I \mid \boldsymbol{f}\}\{\sigma_h \mid \boldsymbol{0}\}\{I \mid \boldsymbol{f}\} = \{\sigma_h \mid \boldsymbol{0}\}\{E \mid \boldsymbol{t}_3\}$ and that $\chi(\{E \mid \boldsymbol{t}_3\} \mid {}^{i}_{\boldsymbol{R}}\hat{\boldsymbol{K}}) = -1$). Similarly the representations $\mathscr{A}''$ and $\mathscr{B}'$ are degenerate as are the representations A' and A'' for V_2. In each case the bases of each row are related to each other by $A = \theta\{I \mid \boldsymbol{f}\}$. This result is the same as that obtained by examining the reality of the representations of $\boldsymbol{G}$[13, 14], though with the method described above it is easier to find the bases of the representations that stick together.

Time reversal symmetry can also be used to simplify the cellular expansion for a general $\boldsymbol{k}$ point, because in this case both $\{I \mid \boldsymbol{f}\}\boldsymbol{\Psi}_{\boldsymbol{k}}$ and $\theta\boldsymbol{\Psi}_{\boldsymbol{k}}$, which give a result proportional to $\boldsymbol{\Psi}_{-\boldsymbol{k}}$, are identical because each Bloch function $\boldsymbol{\Psi}_{\boldsymbol{k}}$ appears only once in the basis of $\boldsymbol{G}$, and so, therefore, must $\boldsymbol{\Psi}_{-\boldsymbol{k}}$. With Eq. (30) for $\boldsymbol{\Psi}_{\boldsymbol{k}}$, the result

$$\{I \mid \boldsymbol{f}\}\boldsymbol{\Psi}_{\boldsymbol{k}} = \theta\boldsymbol{\Psi}_{\boldsymbol{k}} \tag{60}$$

becomes

$$\begin{aligned}
&\sum_{lm} {}^{1}C_{lm}R_l(\bar{2})\,Y_l^m(\bar{2})\delta(\bar{2}) + \sum_{lm} {}^{2}C_{lm}R_l(1)\,Y_l^m(1)\delta(1) \\
&+ \sum_{lm} {}^{3}C_{lm}R_l(\bar{4})\,Y_l^m(\bar{4})\delta(\bar{4}) + \sum_{lm} {}^{4}C_{lm}R_l(3)\,Y_l^m(3)\delta(3) \\
&= \sum_{lm} {}^{1}C^*_{lm}R_l(1)(Y_l^m(1))^*\delta(1) + \sum_{lm} {}^{2}C^*_{lm}R_l(\bar{2})(Y_l^m(\bar{2}))^*\delta(\bar{2}) \\
&+ \sum_{lm} {}^{3}C^*_{lm}R_l(3)(Y_l^m(3))^*\delta(3) + \sum_{lm} {}^{4}C_{lm}R_l(\bar{4})(Y_l^m(\bar{4}))^*\delta(\bar{4})
\end{aligned} \tag{61}$$

so, equating coefficients and using the Condon and Shortley convention for the spherical harmonics and Eq. (54)

$$\begin{aligned}
{}^{1}C^*_{l-m} &= {}^{2}C_{lm}(-1)^m \\
{}^{3}C^*_{l-m} &= {}^{4}C_{lm}(-1)^m.
\end{aligned} \tag{62}$$

The result given in Table 5 comes from (62) by expanding the complex cellular coefficients in real and imaginary parts. This result is known as the coefficient theorem in electronic band structure calculations [2].

Acknowledgements. Part of this work was carried in Oxford [25] and I wish to thank Dr. S. L. Altmann for all his kind help and encouragement. I also wish to thank Dr. C. J. Bradley for helpful discussion on time reversal symmetry.

Appendix on Conventions

The spherical harmonics used in this work are defined in the Condon and Shortley convention as [24, 26]

$$Y_l^m(\theta,\phi)=\left\{\frac{(2l+1)!\,(l-m)!}{4\pi(l+m)!}\right\}^{1/2}\frac{(-1)^{l+m}}{2^l l!}(\sin\theta)^m\left(\frac{d}{d\cos\theta}\right)^{l+m}$$
$$\times(1-\cos^2\theta)^l\exp(im\phi) \tag{A1}$$
$$=(-1)^m(2\pi)^{-1/2}\mathcal{P}_l^m(\cos\theta)\exp(im\phi) \tag{A2}$$

where $\mathcal{P}_l^m(\cos\theta)$ is a normalised Associated Legendre function

$$\mathcal{P}_l^m(\cos\theta)=\left\{\frac{(2l+1)!\,(l-m)!}{2(l+m)!}\right\}^{1/2}\frac{(-1)^l}{2^l l!}(\sin\theta)^m\left(\frac{d}{d\cos\theta}\right)^{l+m}(1-\cos^2\theta)^l \tag{A3}$$

with the properties that [Ref. 26, Appendix 3]

$$\mathcal{P}_l^m(\cos\theta)=(-1)^m\mathcal{P}_l^{-m}(\cos\theta) \tag{A4}$$

and so, under conjugation

$$[Y_l^m(\theta,\phi)]^*=(-1)^m Y_l^{-m}(\theta,\phi). \tag{A5}$$

For inversion

$$IY_l^m(\theta,\phi)=Y_l^m(\pi-\theta,\phi+\pi)=(-1)^l Y_l^m(\theta,\phi). \tag{A6}$$

In order to use the projection operator (32), it is evident from Eqs. (39) and (47) that it is necessary to obtain the effect of a point operation on the spherical harmonics (A1). This can be done by specifying a pure rotation R by its Euler angles, α, β and γ – the convention of Bradley and Cracknell [14] is adopted here. All rotation operations are carried out actively (i.e. the axes are kept fixed and the points of space are rotated) about space fixed axes and are positive in an anticlockwise direction. The full rotation is decomposed into a rotation of $\alpha(0\leqslant\alpha<2\pi)$ about the space-fixed z-axis, a rotation of $\beta(0\leqslant\beta<\pi)$ about the space fixed y-axis and finally a rotation of $\gamma(0\leqslant\gamma<2\pi)$ about the z-axis. The Euler angles for the rotations of D_{6h} (the isogonal point group of D_{6h}^4) are given in Table 6. With these conventions the spherical harmonics transform under rotations according to

$$R(\alpha,\beta,\gamma)Y_l^m(\theta,\phi)=\sum_{n=-l}^{l}Y_l^n(\theta,\phi)\mathfrak{D}^l\{R(\alpha,\beta,\gamma)\}_{nm}. \tag{A7}$$

For dihedral groups such as D_{6h} the operations have β angles of 0 or π [14, 27] and the rotation matrices then have the form

$$\mathfrak{D}^l\{R(\alpha,0,\gamma)\}_{nm}=\exp(-im\alpha)\exp(-im\gamma)\delta_{n,m} \tag{A8}$$

and

$$\mathfrak{D}^l\{R(\alpha,\pi,\gamma)\}_{nm}=\exp(-im\alpha)\exp(im\gamma)(-1)^{l+m}\delta_{n,-m}. \tag{A9}$$

Table 6. Euler angles

Proper operation R	Improper operation S	α	β	γ
E	I	0	0	0
C_3^+	S_6^-	$2\pi/3$	0	0
C_3^-	S_6^+	$4\pi/3$	0	0
C_{21}'	σ_{d1}	π	π	0
C_{22}'	σ_{d2}	$5\pi/3$	π	0
C_{23}'	σ_{d3}	$\pi/3$	π	0
C_2	σ_h	π	0	0
C_6^-	S_3^+	$5\pi/3$	0	0
C_6^+	S_3^-	$\pi/3$	0	0
C_{21}''	σ_{v1}	0	π	0
C_{22}''	σ_{v2}	$2\pi/3$	π	0
C_{23}''	σ_{v3}	$4\pi/3$	π	0

Explanatory Note for Table 6

(i) The rotations are about the axes in Fig. 2.

For an improper rotation S, written as IR, the effect on the spherical harmonics can be obtained from (A7) and (A6). The following definitions are used in Table 5:

$$\begin{aligned}\frac{1}{\sqrt{2}}(Y_l^m + Y_l^{-m}) &= \frac{1}{\sqrt{2}}(-1)^m(2\pi)^{-1/2}\{\mathcal{P}_l^m e^{im\phi} + \mathcal{P}_l^{-m} e^{-im\phi}\} \\ &= \frac{1}{\sqrt{2}}(-1)^m(2\pi)^{-1/2}\mathcal{P}_l^m\{e^{im\phi} + (-1)^m e^{-im\phi}\} \\ &= \frac{1}{\sqrt{2}}(-1)^m(2\pi)^{-1/2}\mathcal{P}_l^m 2\cos m\phi = Y_l^{m,c} \quad m \text{ even} \\ &= \frac{1}{\sqrt{2}}(-1)^m(2\pi)^{-1/2}\mathcal{P}_l^m 2i\sin m\phi = iY_l^{m,s} \quad m \text{ odd} \end{aligned} \tag{A10}$$

$$\begin{aligned}\frac{1}{\sqrt{2}}(Y_l^m - Y_l^{-m}) &= iY_l^{m,s} \quad m \text{ even} \\ &= Y_l^{m,c} \quad m \text{ odd.}\end{aligned} \tag{A11}$$

This spherical harmonic convention, the Condon and Shortley one, differs from that adopted by Altmann, Bradley and Cracknell [10, 11] as follows [24, 28]

$$\begin{aligned}Y_l^m(ABC) &= Y_l^m(CS) \qquad m \leq 0 \\ &= (-1)^m Y_l^m(CS) \qquad m > 0.\end{aligned} \tag{A12}$$

To convert the tables of Refs. [10] and [11] into spherical harmonics in the

Condon and Shortley convention, then

$$Y_l^{m,c}(ABC) = \frac{1}{\sqrt{2}}\{Y_l^m(ABC) + Y_l^{-m}(ABC)\} = Y_l^{m,c}(CS) \qquad m>0 \quad m \text{ even}$$

$$= iY_l^{m,s}(CS) \qquad m>0 \quad m \text{ odd}$$

$$Y_l^{m,s}(ABC) = \frac{-i}{\sqrt{2}}\{Y_l^m(ABC) - Y_l^{-m}(ABC)\} = Y_l^{m,s}(CS) \qquad m>0 \quad m \text{ even}$$

$$= iY_l^{m,c}(CS) \qquad m>0 \quad m \text{ odd.}$$

These changes should be made for all *IR*s in the cubic harmonics [10] and for the IRs of Γ, M, A, L, Δ, U, Σ, T, T', and R of the hexagonal close packed lattice harmonics [11].

Of the complex lattice harmonics for the h.c.p. lattice, only those for K and P need to be amended, since for H, S and S' the phase factor in (A7) can be absorbed in the cellular coefficient. For K and P the changes are

$$\frac{1}{\sqrt{2}}\{Y_l^m(ABC) \pm \bar{Y}_l^{-m}(ABC)\} = \frac{1}{\sqrt{2}}\{Y_l^m(CS) \pm \bar{Y}_l^{-m}(CS)\} \qquad m \text{ even}$$

$$= \frac{-1}{\sqrt{2}}\{Y_l^m(CS) \mp \bar{Y}_l^{-m}(CS)\} \qquad m \text{ odd}$$

where the notation of Altmann and Bradley [11] has been used. The following minor misprints in the h.c.p. harmonics should be noted in addition to those listed by Altmann [2]:

(a) Interchange the subscript labels 1 and 2 on the vectors $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$ of the reciprocal lattice.

(b) For the character table of H in Table 1 for the class of elements $\{C_3^+ \mid \boldsymbol{t}_1 + \boldsymbol{t}_0\} \oplus \{C_3^- \mid 2\boldsymbol{t}_1 + \boldsymbol{t}_0\}$ for representations E and E^* change the -1 to $+1$. The classes in H containing $\boldsymbol{\tau}$ with zero characters are $\{C_2'' \mid \boldsymbol{\tau}_r, \boldsymbol{\tau}_r + \boldsymbol{t}_0\}$, not $\{C_{2r}' \mid \boldsymbol{\tau}_r, \boldsymbol{\tau}_r + \boldsymbol{t}_0\}$.

(c) In Table II the matrix representatives for σ_{dr} and C_2'' ($r = 1, 2, 3$) for the representation KE'' should be interchanged.

(d) In Table IV the lattice harmonics for T' should read $c \pm \bar{c}$ *and* $s \mp \bar{s}$, *not* $c \pm c$ *or* $s \mp \bar{s}$.

References

1. von der Lage, F. C., Bethe, H. A.: Phys. Rev. **71,** 612 (1947)
2. Altmann, S. L.: The cellular method for metals, in: Orbital theories of molecules and solids, March, N. H. Ed. Oxford: Clarendon Press 1974
3. Neckel, A., Rastl, P., Eibler, R., Weinberger, P., Schwarz, K.: J. Phys. C: Solid State **9,** 579 (1976)
4. Weinberger, P., Podloucky, R., Mallett, C. P., Neckel, A.: J. Phys. C: Solid State **12,** 801 (1979)

5. Cracknell, A. P.: Group theory in solid state physics. London: Taylor and Francis 1975
6. Altmann, S. L., Barton, W. B., Mallett, C. P.: J. Phys. C: Solid State, **11,** 1801 (1978)
7. Bartolemé, J., Navarro, R., Gonzalez, D., de Jongh, L. J.: Chem. Phys. Letters **48,** 536 (1977)
8. Hasegawa, A.: J. Phys. F: Metals **4,** 1024 (1974)
9. Kontrym-Sznajd, G., Stachowiak, H., Wieszchowski, W., Petersen, K., Thrane, N., Trumpy, G.: Appl. Phys. **8,** 151 (1975)
10. Altmann, S. L., Cracknell, A. P.: Rev. Mod. Phys. **37,** 19 (1965)
11. Altmann, S. L., Bradley, C. J.: Rev. Mod. Phys. **37,** 33 (1965)
12. Altmann, S. L.: Induced representations in crystals and molecules. London: Academic Press 1977
13. Streitwolf, H. W.: Group theory in solid state physics. London: MacDonald 1971
14. Bradley, C. J., Cracknell, A. P.: The mathematical theory of symmetry in solids. Oxford: Clarendon Press 1972
15. Janssen, T.: Crystallographic groups. Amsterdam: North Holland 1973
16. Lax, M.: Symmetry principles in solid state and molecular physics. New York: Wiley (Interscience) 1974
17. Herring, C.: J. Franklin Inst. **233,** 525 (1942)
18. McClure, J. W.: IBM Jl. Res. Dev. **8,** 255 (1964)
19. Ergun, S.:Nature, **241,** 65 (1973)
20. Donohue, J.: The structure of the elements. New York: Wiley 1974
21. Trucano, P., Chen, R.: Nature **258,** 136 (1975)
22. Goodman, P.: Acta Cryst. **A32,** 793 (1976)
23. Bassani, F., Pastori Parravicini, G.: Nuovo Cimento **50,** 95 (1967)
24. Mallett, C. P.: Report No. 45. Institut für Technische Elektrochemie, Technische Universität, Vienna (1978)
25. Mallett, C. P.: D.Phil Thesis, Oxford University 1977. (Unpublished)
26. Rose, M. E.: Elementary theory of angular momentum. New York: John Wiley and Sons, Inc. 1957
27. Altmann, S. L.: Proc. Cambridge Phil. Soc. **53,** 343 (1957)
28. Altmann, S. L., Bradley, C. J.: Phil. Trans. Roy. Soc. **A255,** 199 (1963)

Received January 15, 1980