CRYSTAL FIELD THEORY AND MAGNETIC POINT GROUPS

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Summary

The author's previous work on the application of Wigner's theory of the coreps of non-unitary groups to the Shubnikov groups (magnetic groups) is here considered in relation to crystal field theory. Both the splitting of the energy levels and the symmetry properties of the wave function are considered in magnetic point groups. Examples of $4'mm'$ and $4m'm'$ are studied.

I. INTRODUCTION

Since the start of the systematic study of crystal field theory (Bethe 1929), it has been applied to many phenomena in substances from various point groups. A convenient review of the group-theoretical part of crystal field theory problems for the ordinary point groups is given by Herzfeld and Meijer (1961). However, neutron diffraction experiments now make it clear that there are many crystalline solids whose symmetry can only be properly described by one of the magnetic point groups or magnetic space groups whose derivation has been considered by Zamorzaev (1953), Belov, Neronova, and Smirnova (1955), Tavger and Zaitsev (1956), and Shubnikov and Belov (1964).

Some group-theoretical work on these magnetic groups has been done by Dimmock and Wheeler (1962*a*, 1964), Guccione (1963), Cracknell (1965, 1966),† and Opechowski and Guccione (1965). Dimmock and Wheeler (1962*b*) gave some consideration to the degeneracy of the energy levels in crystals whose structures have to be described by one of these magnetic point groups. Since in APCII not only the character tables but also the matrix representatives for the magnetic point groups were given, it now seems appropriate to consider the symmetry properties of the wave functions themselves.

There are two important ways in which group theory is applied to crystal field theory. Firstly, any point group is simply related to a subgroup of the rotation group in three dimensions and therefore the irreducible representations (or "reps") of the point group can be found by "subduction" of the reps of the rotation group (see Altmann and Cracknell (1965) for an explanation of the term "subduced representation"). Or, in terms of energy levels, a level that was degenerate in the case of spherical symmetry will probably split into several levels, each of which may or may not be degenerate, in the case of symmetry belonging to one of the point groups, and the qualitative nature of this splitting can be determined by group theory. Secondly, group theory can be employed to produce symmetry-adapted functions for various symmetrical situations, that is, functions belonging to the various reps of the point groups, to the totally symmetrical rep if the function describes a physical observable, such as the electrostatic potential for example, or to any specified rep if the function is to be the angular part of a wave function.

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† These two papers are henceforth referred to as APCI and APCII respectively.

II. The Rotation Group and Time Reversal

Any ordinary point group is a subgroup of $O(3)$, the rotation group in three dimensions, but a magnetic point group must be related to the group that is the direct product of the rotation group in three dimensions with the group $(E+R)$, where E is the identity element and R is the operation of time inversion. The modification of representation theory to allow for the fact that R is an anti-unitary operator was considered by Wigner (1959); here we follow his work and when dealing with the magnetic point groups we follow the same notation as in APCI and APCII.

If a rotation in three-dimensional space is denoted by $\{\alpha, \beta, \gamma\}$, where α, β, and γ are the Euler angles of the rotation, then there is a set of irreducible representations $D^l(\{\alpha, \beta, \gamma\})$ of the group of all possible rotations of this type, where l can take any integer or half-integer value and the rep $D^l(\{\alpha, \beta, \gamma\})$ is of dimension $(2l+1)$. The properties of these reps $D^l(\{\alpha, \beta, \gamma\})$ are well known (Wigner 1959). To study the application of crystal field theory in the case of the magnetic point groups we consider the group $RO(3)$, the direct product of $O(3)$ and $(E+R)$. Since R is an anti-unitary operator, half of the elements of this group are unitary operators and the other half are anti-unitary operators, the group is then called a "non-unitary" group and instead of having representations and irreducible representations it has corepresentations and irreducible corepresentations ("coreps") (see Section 3 of APCI). It is then by restricting the elements of this group to the elements of a magnetic point group that we can study crystal field theory and the splitting of energy levels in magnetic crystals. Each of the coreps of this group will, on restriction in this way, be a corepresentation (either reducible or irreducible) of the magnetic point group in question; if it is reducible, then the manner in which it splits up into coreps of the magnetic point group (see APCII) will tell us the qualitative behaviour of the crystal-field splitting of the levels in that magnetic point group. Following APCII, we neglect spin-orbit coupling, that is, we confine ourselves to integer l values and to single-valued coreps of the magnetic point groups.

The first problem then is to be able to determine the coreps of the group $RO(3)$ from the reps $D^l(\{\alpha, \beta, \gamma\})$ of $O(3)$. In the notation of APCI, $RO(3)$ is a grey group $\mathbf{M}$ given by

$$\mathbf{M} = \mathbf{G} + R\mathbf{G}, \tag{2.1}$$

where $\mathbf{G}$ is the group $O(3)$, $D^l(\{\alpha, \beta, \gamma\})$ the reps of $\mathbf{G}$ correspond to $\mathbf{\Delta(u)}$, and as the element $\mathbf{a}_0$ we choose R. The coreps of $RO(3)$ can therefore be found by considering the relationship between $\mathbf{\Delta(u)}$ and $\overline{\mathbf{\Delta}}(\mathbf{u}) = \mathbf{\Delta}(\mathbf{a}_0^{-1}\mathbf{u}\,\mathbf{a}_0)^*$, and will be one of three types according to certain conditions, which, together with the actual coreps, are given in Section 4 of APCI. For $RO(3)$, $\mathbf{\Delta(u)} = D^l(\{\alpha, \beta, \gamma\})$ so that

$$\begin{aligned} \overline{\mathbf{\Delta}}(\mathbf{u}) &= D^l(R^{-1}\{\alpha, \beta, \gamma\}R)^* \\ &= D^l(R^{-1}R\{\alpha, \beta, \gamma\})^* \\ &= D^l(\{\alpha, \beta, \gamma\})^*. \end{aligned} \tag{2.2}$$

Therefore we have to consider the relationship between $D^l(\{\alpha, \beta, \gamma\})$ and $D^l(\{\alpha, \beta, \gamma\})^*$. The result is that they are equivalent and that $\boldsymbol{\beta}\boldsymbol{\beta}^* = +\mathbf{1}$. To show this, we note

that (Wigner 1959)

$$D^l(\{\alpha,\beta,\gamma\})_{m'm} = \mathrm{e}^{\mathrm{i}m'\alpha}\, d^l(\beta)_{m'm}\, \mathrm{e}^{\mathrm{i}m\gamma}, \tag{2.3}$$

where $d^l(\beta)_{m'm}$ is real, and therefore

$$D^l(\{\alpha,\beta,\gamma\})^*_{m'm} = \mathrm{e}^{-\mathrm{i}m'\alpha}\, d^l(\beta)_{m'm}\, \mathrm{e}^{-\mathrm{i}m\gamma}. \tag{2.4}$$

This can be related to $D^l(\{\alpha,\beta,\gamma\})_{-m',-m}$, which is given by

$$D^l(\{\alpha,\beta,\gamma\})_{-m',-m} = \mathrm{e}^{-\mathrm{i}m'\alpha}\, d^l(\beta)_{-m',-m}\, \mathrm{e}^{-\mathrm{i}m\gamma}. \tag{2.5}$$

However, (see Altmann and Bradley 1963*a*)

$$d^l(\beta)_{-m',-m} = (-1)^{m-m'}\, d^l(\beta)_{m'm}, \tag{2.6}$$

so that

$$\begin{aligned} D^l(\{\alpha,\beta,\gamma\})^*_{m',m} &= (-1)^{m-m'}\, D^l(\{\alpha,\beta,\gamma\})_{-m',-m} \\ &= (-1)^{m+m'}\, D^l(\{\alpha,\beta,\gamma\})_{-m',-m}, \end{aligned} \tag{2.7}$$

that is,

$$\bar{\boldsymbol{\Delta}}(\mathbf{u}) = \boldsymbol{\beta}^{-1}\boldsymbol{\Delta}(\mathbf{u})\,\boldsymbol{\beta}, \tag{2.8}$$

where $\boldsymbol{\beta}$ is the matrix whose m, n element is given by

$$\boldsymbol{\beta}_{mn} = (-1)^m \delta_{m,-n}, \tag{2.9}$$

so that $\boldsymbol{\beta}$ is real and $\boldsymbol{\beta}\boldsymbol{\beta}^*$ is equal to $\boldsymbol{\beta}^2$. Hence

$$\begin{aligned} (\boldsymbol{\beta}\boldsymbol{\beta}^*)_{mm'} &= (-1)^m \delta_{m,-n}\,(-1)^n \delta_{n,-m'} \\ &= (-1)^{m-m'}\,\delta_{mm'} \\ &= \delta_{mm'}, \end{aligned} \tag{2.10}$$

that is,

$$\boldsymbol{\beta}\boldsymbol{\beta}^* = +\mathbf{1}.$$

We have thus shown that, for $RO(3)$, $\bar{\boldsymbol{\Delta}}(\mathbf{u})$ and $\boldsymbol{\Delta}(\mathbf{u})$ are equivalent and $\boldsymbol{\beta}\boldsymbol{\beta}^* = +\mathbf{1}$. Therefore the coreps of this group will be of the first type for the case of integral spin (where $\boldsymbol{\Delta}(\mathbf{a}_0^2) = \boldsymbol{\Delta}(R^2) = +\mathbf{1}$) and of the second type for the case of half-integral spin (where $\boldsymbol{\Delta}(\mathbf{a}_0^2) = \boldsymbol{\Delta}(R^2) = -\mathbf{1}$). Thus, using equation (4.2) of APCI for the case of integral spin and equation (4.3) for the case of half-integral spin, it is possible to write down immediately the coreps of the group $RO(3)$.

III. Subduction of the Coreps of $RO(3)$

In ordinary crystal field theory when the rep $D^l(\{\alpha,\beta,\gamma\})$ is subduced onto a point group, the characters of $D^l(\{\alpha,\beta,\gamma\})$ for the point-group elements are evaluated and the point-group reps that arise from $D^l(\{\alpha,\beta,\gamma\})$ are usually identified by inspection of the character table of the point group. Alternatively, n_i, the number of times that the rep in which the element $\mathbf{g}$ has character $\chi_i(\mathbf{g})$ appears in the reducible representation in which that element has character $\chi(\mathbf{g})$, is given by the well-known formula

$$n_i = \frac{1}{N}\sum_{\mathbf{g}} \chi(\mathbf{g})\,\chi_i^*(\mathbf{g}), \tag{3.1}$$

where N is the order of the point group. We therefore consider the modification of this procedure necessary for dealing with $RO(3)$ and the magnetic point groups.

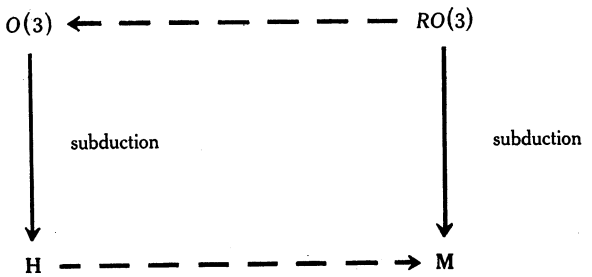
The process of the reduction of a representation is well known, but the problem of the reduction of a corepresentation hinges on the definition of equivalent corepresentations. Two corepresentations $\overline{\mathbf{D}}$ and $\mathbf{D}$ are said to be equivalent if there is some transformation matrix $\boldsymbol{\alpha}$ such that (Wigner 1959)

$$\overline{\mathbf{D}}(\mathbf{u}) = \boldsymbol{\alpha}^{-1}\,\mathbf{D}(\mathbf{u})\,\boldsymbol{\alpha} \tag{3.2}$$

for the unitary elements $\mathbf{u}$ and

$$\overline{\mathbf{D}}(\mathbf{a}) = \boldsymbol{\alpha}^{-1}\,\mathbf{D}(\mathbf{a})\,\boldsymbol{\alpha}^{*} \tag{3.3}$$

for the anti-unitary elements $\mathbf{a}$. Though the character of a matrix is invariant under a transformation according to equation (3.2), it is not invariant under a transformation according to equation (3.3) and therefore it is not possible to take the coreps of $RO(3)$ and perform a direct subduction onto the coreps of a magnetic point group $\mathbf{M}$ by using equation (3.1) or by direct inspection of the character table of the magnetic point group in question. This is an unfortunate restriction and an alternative procedure must be adopted, which can be illustrated as follows:



The direct transition from $RO(3)$ to $\mathbf{M}$ can be regarded as "first-order forbidden". We proceed therefore by the indirect route, from $RO(3)$ to $O(3)$, from $O(3)$ to $\mathbf{H}$, and from $\mathbf{H}$ to $\mathbf{M}$. The well-known steps are the subduction used in conventional crystal field theory from $O(3)$ to $\mathbf{H}$, an ordinary point group, and the deduction of the coreps of a magnetic group, i.e. from $\mathbf{H}$ to $\mathbf{M}$ and from $O(3)$ to $RO(3)$; it is then just a matter of reversing the step $O(3)$ to $RO(3)$ and combining all three steps to obtain the desired result.

IV. An Example, $4'mm'$ and $4m'm'$

Here we are not concerned with systems that are invariant under the operation of time inversion, that is, we are not concerned with the grey groups, for which it is quite unnecessary to use the theory of corepresentations at all, but only with those magnetic point groups, which, in APCII, were classed as type III groups, namely, magnetic groups from which R, the operation of time inversion, is absent. As an example, we study the energy levels in fields possessing the symmetry (and the antisymmetry) of the magnetic point groups $4'mm'$ and $4m'm'$, which are derived from the group of the square $4mm$ (C_{4v}). The magnetic point group of the antiferromagnetic layers in K_2NiF_4 is the direct product of $4'mm'$ with $(E+I)$, where I is the inversion (see Legrand and Verschueren 1964); it is harder to find a real example of $4m'm'$.

The first step in studying the splitting of the energy levels in these magnetic point groups is to identify **H**, the halving subgroup of unitary elements, for each group. These are (from Table V of APCII)

$$4'mm' \qquad E,\ C_{2z},\ \sigma_x,\ \sigma_y,$$
$$4m'm' \qquad E,\ C_{4z}^{+},\ C_{2z},\ C_{4z}^{-}.$$

Therefore we can quote the results for the splitting of the atomic energy levels on subduction of $D^l(\{\alpha,\beta,\gamma\})$ onto these two groups **H** from any of the usual crystal

TABLE 1

CHARACTER TABLE OF **H** FOR $4'mm'$

	E	C_{2z}	σ_y	σ_x	Type of Corep	
$D^l(\{\alpha,\beta,\gamma\})$	$2l+1$	$(-1)^l$	$(-1)^{2l}$	$(-1)^{2l}$	Integral Spin	Half-integral Spin
A_1	1	1	1	1	1	2
A_2	1	1	−1	−1	1	2
B_1	1	−1	1	−1	3	3
B_2	1	−1	−1	1	3	3

TABLE 2

CHARACTER TABLE OF **H** FOR $4m'm'$

Note that $n = \frac{1}{2}l$, l even; $n = \frac{1}{2}(l-1)$, l odd

	E	C_{4z}^{+}	C_{2z}	C_{4z}^{-}	Type of Corep	
$D^l(\{\alpha,\beta,\gamma\})$	$2l+1$	$(-1)^n$	$(-1)^l$	$(-1)^n$	Integral Spin	Half-integral Spin
A	1	1	1	1	1	2
B	1	−1	1	−1	1	2
^1E	1	i	−1	−i	1	2
^2E	1	−i	−1	i	1	2

field theory treatments, e.g. Bethe (1929). In the $(2l+1)$-dimensional rep $D^l(\{\alpha,\beta,\gamma\})$, the characters of these elements in **H** are given in the first row of Tables 1 and 2 for $4'mm'$ and $4m'm'$ respectively, and the last two columns of each table give the types of the coreps of the magnetic group **M** for integral and half-integral spin in each case. The rep $D^l(\{\alpha,\beta,\gamma\})$ leads to coreps of $RO(3)$ that are of the first type for the case of integral spin and of the second type for the case of half-integral spin.

If we consider the $4'mm'$ case first and take, for example, $l = 1$, we have from Table 1

	E	C_{2z}	σ_y	σ_x
$D^l(\{\alpha,\beta,\gamma\})$	3	−1	1	1

so that the triply degenerate p level in an atom is split into three levels with the

symmetry of A_1, B_1, and B_2 when the atom is in the environment with the symmetry of **H** of $4'mm'$, that is, of $2mm$ (C_{2v}); this can be seen from inspection of Table 1. In the commonly accepted notation we write

$$D^1 = A_1+B_1+B_2. \tag{4.1}$$

This is shown in Table 3.

TABLE 3

$D^1(\{\alpha, \beta, \gamma\})$ AND **H** OF $4'mm'$

	E	C_{2z}	σ_y	σ_x
A_1	1	1	1	1
B_1	1	−1	1	−1
B_2	1	−1	−1	1
$D^1(\{\alpha, \beta, \gamma\})$	3	−1	1	1

For the cases both of integral spin and of half-integral spin the coreps of $4'mm'$ derived from B_1 and B_2 are of the third type, i.e. there is an extra degeneracy and the two levels B_1 and B_2 "stick together". For integral spin the corep derived from A_1 is of the first type and for half-integral spin it is of the second type; in either case, since $\mathbf{\Delta}(\mathbf{u})$ and $\mathbf{\Delta}(\mathbf{u})$ are equivalent, there will be no sticking together of the levels. The splitting of the energy levels derived from the atomic p level is shown in Figure 1.

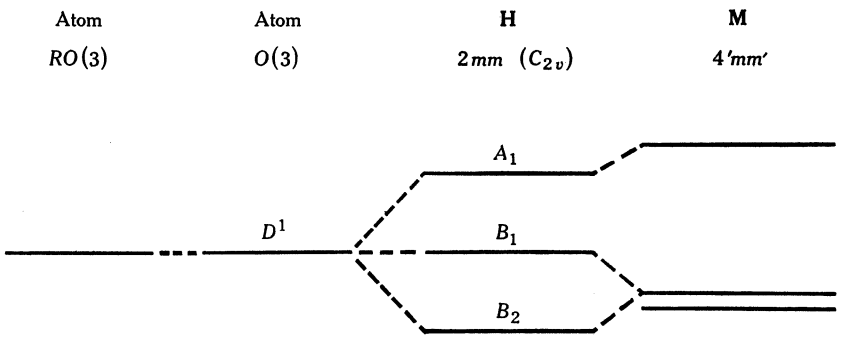


Fig. 1.—Energy levels in $4'mm'$ derived from an atomic p level.

The pattern of the splitting is the same whether the particles in question have integral or half-integral spin. The only difference is in the degeneracy of the coreps of $RO(3)$ and of the corep derived from the rep A_1 of **H**; for the half-integral spin case, where this corep is of the second type, the degeneracy will be twice that for the integral spin case, where the corep is of the first type.

The case of $4m'm'$ is very much easier to consider because no corep of this magnetic group is of the third type, so that there is never any sticking together of the energy levels at all, with the result that the pattern of the splitting of the energy levels in the magnetic group $4m'm'$ is exactly the same as in **H**, its halving subgroup, which is the point group 4 (C_4). The splitting of an atomic p level is shown in Figure 2.

These examples illustrate what always happens, namely that the addition to **H** of the anti-unitary elements never causes any extra splitting of the energy levels but may cause some levels to stick together, as might have been expected.

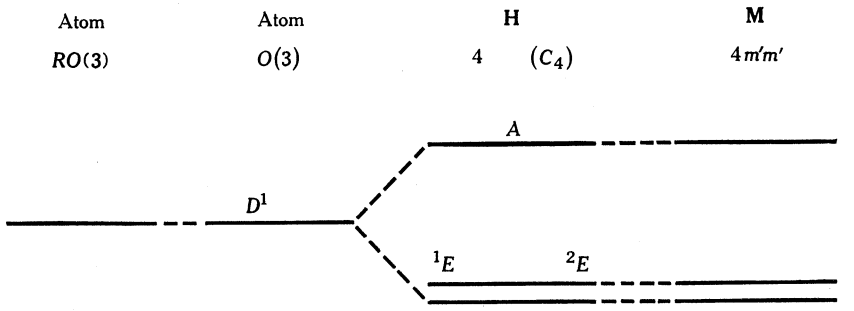


Fig. 2.—Energy levels in $4m'm'$ derived from an atomic p level.

Just for comparison, we show in Figure 3 the splitting of an atomic p level in the non-magnetic group $4mm$ to which these two magnetic groups are related. In this case the level is well known to split as

$$D^1 = A_1 + E\,, \tag{4.2}$$

where A_1 is non-degenerate and E is doubly degenerate.

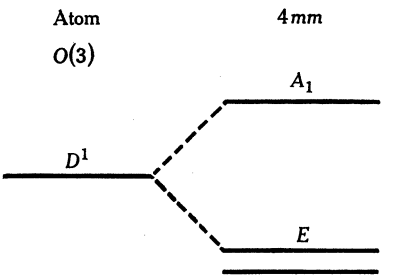


Fig. 3.—Energy levels in $4mm$ (non-magnetic) derived from an atomic p level.

V. Symmetry-adapted Functions for Magnetic Point Groups

The discussion of the previous sections shows how, if the reps of the halving subgroup **H** and their matrix representatives are known, the coreps of a magnetic point group **M** may be found. This means that, in addition to studying the splitting of the levels, we can also study the symmetry properties of the wave functions and can set about trying to produce functions that are symmetry adapted to the various coreps of **M**. One might try to proceed *ab initio* using the methods of projection operators, similar to Altmann (1957) for example. However, this is hardly necessary because **H** is a point group for which symmetry-adapted functions are already available, e.g. Altmann and Bradley (1963*b*). It is therefore a fairly simple matter to obtain the functions that are symmetry adapted to the coreps of **M** from the functions that are symmetry adapted to the reps of **H**. The results are implied in Wigner (1959).

If ψ_k $(k = 1, 2, \ldots l)$ is a basis of the rep $\mathbf{\Delta}(\mathbf{u})$, of dimension l, of $\mathbf{H}$, then $\psi'_k = \mathbf{a}_0\psi_k$ $(k = 1, 2, \ldots l)$ is a basis of the rep $\bar{\mathbf{\Delta}}(\mathbf{u}) = \mathbf{\Delta}(\mathbf{a}_0^{-1}\mathbf{u}\,\mathbf{a}_0)^*$, and it is almost trivial to show that for the three types of corep, whose matrices are given in equations (4.2)–(4.4) of APCI, the basis functions are

First type (dimension of corep $= l$)

$$\psi_k \qquad (k = 1, 2, \ldots l) \tag{5.1}$$

Second type (dimension of corep $= 2l$)

$$(\psi_k, -\psi'_k\,\boldsymbol{\beta}^{-1}) \qquad (k = 1, 2, \ldots l) \tag{5.2}$$

Third type (dimension of corep $= 2l$)

$$(\psi_k, \psi'_k) \qquad (k = 1, 2, \ldots l)\,. \tag{5.3}$$

As an example of this, we consider again the two magnetic groups $4'mm'$ and $4m'm'$. We need to know $\mathbf{H}$, the basis functions of the reps of $\mathbf{H}$, the element $\mathbf{a}_0$ used in the derivation of the magnetic group $\mathbf{M}$, and also the method of finding the coreps of a magnetic point group $\mathbf{M}$ from the reps of $\mathbf{H}$ (the required method is given in Tables VI and VII of APCII).

TABLE 4

THE SPHERICAL HARMONICS FOR $2mm$ (C_{2v})

A_1	A_2	B_1	B_2
$Y_0^{0,c}$			
$Y_1^{0,c}$		$Y_1^{1,c}$	$Y_1^{1,s}$
$Y_2^{0,c}$		$Y_2^{1,c}$	$Y_2^{1,s}$
$Y_2^{2,c}$	$Y_2^{2,s}$		
$Y_3^{0,c}$		$Y_3^{1,c}$	$Y_3^{1,s}$
$Y_3^{2,c}$	$Y_3^{2,s}$	$Y_3^{3,c}$	$Y_3^{3,s}$
$Y_4^{0,c}$		$Y_4^{1,c}$	$Y_4^{1,s}$
$Y_4^{2,c}$	$Y_4^{2,s}$	$Y_4^{3,c}$	$Y_4^{3,s}$
$Y_4^{4,c}$	$Y_4^{4,s}$		
.	.	.	.
.	.	.	.
.	.	.	.

Considering $4'mm'$ first, the elements in $\mathbf{H}$ are, from Table 1,

$$E,\ C_{2z},\ \sigma_x,\ \sigma_y\,,$$

in $R(\mathbf{G}-\mathbf{H})$ they are (Table V of APCII)

$$RC_{4z}^{+},\ RC_{4z}^{-},\ R\sigma_{da},\ R\sigma_{db}\,,$$

and our choice of $\mathbf{a}_0$ is $R\sigma_{da}$. The coreps of $4'mm'$ have been identified in Table 1 and are either of the first type or of the third type. If they are of the first type, i.e. derived from A_1 or A_2, then the basis functions of the coreps of $\mathbf{M}$ are given by the expression (5.1), and are therefore immediately available, e.g. from Altmann (1957). If they are of the third type, i.e. derived from B_1 or B_2, then the basis functions of the coreps of $\mathbf{M}$ are given by the expression (5.3), when it becomes necessary to evaluate $\psi'_k = \mathbf{a}_0\psi_k$, where ψ_k will be either a single spherical harmonic or some linear combination of spherical harmonics. Wherever possible we choose RI as $\mathbf{a}_0$, but in many cases it is not possible to do so; $4'mm'$ is one such case and for this group we chose $\mathbf{a}_0$ to be $R\sigma_{da}$. Thus

$$\begin{aligned}\mathbf{a}_0\psi_k &= (R\sigma_{da})\psi_k \\ &= R(\sigma_{da}\psi_k) \\ &= RIC_{2a}\psi_k\,,\end{aligned} \tag{5.4}$$

and, since ψ_k is a spherical harmonic or some linear combination of spherical harmonics and C_{2a} is a member of the three-dimensional rotation group, we can find $C_{2a}\psi_k$ by

using the matrix elements of the rotation group. From Table 12 of Altmann (1957), we can see that the spherical harmonics are assigned to the reps of **H** ($= 2mm$ (C_{2v})) as in Table 4, where

$$Y_l^{m,c} = \tfrac{1}{2}(Y_l^m + Y_l^{-m}) \tag{5.5}$$

and

$$Y_l^{m,s} = -\tfrac{1}{2}\mathrm{i}(Y_l^m - Y_l^{-m}). \tag{5.6}$$

In Table V of APCII we have been able to choose $\mathbf{a}_0$ so that β, the second Euler angle of the rotational part of $\mathbf{a}_0$, is either 0 or π for each magnetic group and never takes any other value; the rotation coefficient $D^l(\{\alpha, \beta, \gamma\})_{m'm}$ therefore always has the particularly simple form (Altmann 1957) of

$$D^l(\{\alpha, 0, \gamma\})_{m'm} = \mathrm{e}^{\mathrm{i}m\alpha}\,\mathrm{e}^{\mathrm{i}m\gamma}\,\delta_{m'm} \tag{5.7}$$

or

$$D^l(\{\alpha, \pi, \gamma\})_{m'm} = (-1)^l\,\mathrm{e}^{\mathrm{i}m\alpha}\,\mathrm{e}^{-\mathrm{i}m\gamma}\,\delta_{m',-m}. \tag{5.8}$$

For $4'mm'$ the Euler angles for C_{2a}, the rotational part of $\mathbf{a}_0$, are $\{\alpha, \beta, \gamma\} = \{\tfrac{1}{2}\pi, \pi, \pi\}$ so that from equation (5.8)

$$\begin{aligned} C_{2a}\,Y_l^m &= \sum_{m'} Y_l^{m'}\,D^l(\{\tfrac{1}{2}\pi, \pi, \pi\})_{m'm} \\ &= \sum_{m'} Y_l^{m'}\,(-1)^l\,\mathrm{e}^{\frac{1}{2}\mathrm{i}m\pi}\,\mathrm{e}^{-\mathrm{i}m\pi}\,\delta_{m',-m}. \end{aligned} \tag{5.9}$$

However, $\mathbf{a}_0$ is RIC_{2a}, so that for $4'mm'$

$$\begin{aligned} \mathbf{a}_0\,Y_l^m &= R(-1)^l \sum_{m'} Y_l^{m'}\,(-1)^l\,\mathrm{e}^{\frac{1}{2}\mathrm{i}m\pi}\,\mathrm{e}^{-\mathrm{i}m\pi}\,\delta_{m',-m} \\ &= R\sum_{m'} Y_l^{m'}\,\mathrm{e}^{-\frac{1}{2}\mathrm{i}m\pi}\,\delta_{m',-m} \\ &= R\sum_{m'} Y_l^{m'}\,(-\mathrm{i})^m\,\delta_{m',-m} \\ &= R\,Y_l^{-m}\,(-\mathrm{i})^m. \end{aligned} \tag{5.10}$$

Thus, if ψ_k is $Y_l^{m,c}$, then

$$\begin{aligned} \mathbf{a}_0\psi_k &= \tfrac{1}{2}\mathbf{a}_0(Y_l^m + Y_l^{-m}) \\ &= \tfrac{1}{2}R(Y_l^{-m}(-\mathrm{i})^m + Y_l^m(-\mathrm{i})^{-m}), \end{aligned} \tag{5.11}$$

which can be rearranged and expressed in terms of $Y_l^{m,c}$ or $Y_l^{m,s}$, depending on the actual value of m; if $m = 1$ then

$$\begin{aligned} \mathbf{a}_0\,Y_l^{1,c} &= \tfrac{1}{2}R(-\mathrm{i}\,Y_l^{-1} + \mathrm{i}\,Y_l^1) \\ &= -R\,Y_l^{1,s}. \end{aligned} \tag{5.12}$$

Similarly $\mathbf{a}_0 Y_l^{m,s}$ can be found. The functions ψ_k' for the first few l values for the coreps of $4'mm'$ derived from B_1 and B_2 are given in Table 5.

Thus we have completed the method for finding the basis functions of the coreps of $4'mm'$ for the case of integral spin. The case of half-integral spin is not essentially different, except that where we had coreps of the first type and used expression (5.1), we now have coreps of the second type, whose basis is given by expression (5.2). Although these coreps of the second type are of dimension $2l$, the functions ψ_k' are linear combinations of the ψ_k so that, since we are usually only concerned with using

complete sets of functions in an expansion, there is no real need to evaluate ψ'_k or $-\psi'_k \boldsymbol{\beta}^{-1}$ of expression (5.2). If we did wish to evaluate $-\psi'_k \boldsymbol{\beta}^{-1}$ for some reason, $\boldsymbol{\beta}$ is known from equation (2.9) and ψ'_k can be found in the way we have just considered.

TABLE 5

ψ'_k FOR 4′*mm*′

B_1		B_2	
ψ_k	ψ'_k	ψ_k	ψ'_k
$Y_1^{1,c}$	$-RY_1^{1,s}$	$Y_1^{1,s}$	$-RY_1^{1,c}$
$Y_2^{1,c}$	$-RY_2^{1,s}$	$Y_2^{1,s}$	$-RY_2^{1,c}$
$Y_3^{1,c}$	$-RY_3^{1,s}$	$Y_3^{1,s}$	$-RY_3^{1,c}$
$Y_3^{3,c}$	$RY_3^{3,s}$	$Y_3^{3,s}$	$RY_3^{3,c}$
$Y_4^{1,c}$	$-RY_4^{1,s}$	$Y_4^{1,s}$	$-RY_4^{1,c}$
$Y_4^{3,c}$	$RY_4^{3,s}$	$Y_4^{3,s}$	$RY_4^{3,c}$
.	.	.	.
.	.	.	.
.	.	.	.
$Y_l^{m,c}$	$(-1)^{\frac{1}{2}(m+1)}RY_l^{m,s}$	$Y_l^{m,s}$	$(-1)^{\frac{1}{2}(m+1)}RY_l^{m,c}$
	m odd		

VI. Conclusion

The above considerations show that, in studying a crystal with the symmetry of one of the magnetic point groups, the splitting of the energy levels and the symmetry properties of the wave functions are best studied via the halving subgroup **H** of unitary elements. The extension from **H** to **M** is then relatively straightforward.

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