WAVE VECTOR SELECTION RULES FOR SPACE GROUPS.

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Abstract.

A programme of work is in progress for the construction of tables of wave vector selection rules (WVSRs) for all the classical space groups. The general theory is briefly reviewed and some practical considerations which have arisen in the construction of these tables are also discussed. The use of induced compatibility tables (ICTs) is described and this is illustrated with an example taken from the space group $F\overline{4}3m$ (T_d^2).

1. Introduction.

For many years a considerable amount of energy was expended on the determination of the irreducible representations of the classical space groups. The principal motivation for studying the irreducible representations of the space groups is the fact that they are relevant to the quantum-mechanical treatment of particles or quasiparticles in Suppose that a certain particle or quasiparticle a crystalline solid. belongs to an irreducible representation Γ_i of a space group \underline{G} . Then the transformation properties of the wave function Ψ_i of the particle, under the symmetry operations of G, will be those of one component of a basis $\langle \phi_i |$ of Γ_i , while the degeneracy of the corresponding energy eigenvalue, E, for the particle will be equal to the degeneracy of Γ_i . These facts have been widely exploited to simplify the calculation of energy eigenvalues, E,, for electrons, phonons, and magnons in crystalline solids. The labels \int_{1}^{1} form the basis of a convenient scheme for labelling the eigenvalues E,.

For our present purposes we shall assume that the irreducible representations of all the 230 classical space groups are readily available (for references see, for example, Bradley and Cracknell (1972)). We shall be concerned with the problem of the reduction of the Kronecker products of these representations, that is, with determining the coefficients $C_{pq,r}^{\underline{k}_1\underline{k}_j,\underline{k}_1}$ in the decomposition

$$(\Gamma_{p}^{\underline{k}_{i}}\uparrow_{\underline{G}})\boxtimes(\Gamma_{q}^{\underline{k}_{j}}\uparrow_{\underline{G}}) \equiv \sum_{r} \sum_{l} c_{pq,r}^{\underline{k}_{i}\underline{k}_{j},\underline{k}_{l}}(\Gamma_{r}^{\underline{k}_{l}}\uparrow_{\underline{G}}).$$
(1)

 $(\Gamma_p^{\underline{k}_i} \uparrow_{\underline{G}})$ is an irreducible representation of the space group \underline{G} induced from the irreducible representation $\Gamma_p^{\underline{k}_i}$ of the little group $\underline{G}^{\underline{k}_i}$. The reason for constructing these tables is that the reductions of these products enable one to determine selection rules for various physical processes involving scattering between quantum-mechanical states of particles or quasiparticles in crystalline solids. These processes include infra-red absorption, Raman scattering, magnon sidebands on optical spectral lines in magnetically-ordered crystals, solid-state phase transitions, electron scattering and neutron scattering (for further details see Birman and Berenson (1974) and section 7 of Cracknell (1975)). We do not have sufficient space to discuss these processes in detail here. The formal theory of the reduction of products of the form given in equation (1) is already available and it has been applied to the determination of complete tables of the reductions for a few special space groups (references are quoted

in section 7.1 of Cracknell (1975)). We have been turning our attention to the problem of producing complete tables of these reductions for all the space groups. We have found it convenient to divide our work into two stages. First, there is the determination of wave vector selection rules, that is identifying the (relatively few) values of \underline{k}_1 that arise for each given pair of \underline{k}_i and \underline{k}_j . Secondly, once this is done, it remains to find the actual coefficients $C_{pq,r}^{\underline{k}_1,\underline{k}_1}$.

2. Theory.

We shall give a very brief résumé of the necessary theory; further details may be found, for example, in section 4.7 of Bradley and Cracknell (1972).

2.1 <u>Wave vector selection rules (WVSRs).</u>

The values of \underline{k}_1 which may appear on the right-hand side of equation (1) are restricted by the condition

$$R_{\boldsymbol{\beta}}\underline{k}_{i} + R_{\boldsymbol{\alpha}}\underline{k}_{j} \equiv \underline{k}_{l} \tag{2}$$

where $\{R_{\beta} \mid v_{\beta}\}$ and $\{R_{\lambda} \mid v_{\lambda}\}$ are elements of G. The values of R_{λ} and R_{β} are restricted so that $\{R_{\lambda} \mid v_{\lambda}\}$ and $\{R_{\beta} \mid v_{\beta}\}$ form quite a small subset of all the elements of the group G. The allowed values of R_{λ} and R_{β} have to be determined from a detailed examination of certain double-coset decompositions of G (see Bradley and Cracknell (1972)). Thus the allowed values of R_{λ} are found from writing

$$\underline{G} = \underbrace{\xi}_{a} \underline{G}^{\underline{k}_{1}} \{ \mathbb{R}_{a} | \underline{v}_{a} \} \underline{G}^{\underline{k}_{j}}$$
(3)

and, for each allowed R_{a} , the corresponding allowed values of R_{β} are found from the double-coset decomposition

$$\mathbf{G} = \sum_{\boldsymbol{\beta}} (\mathbf{G}^{\underline{k}_1} \cap \mathbf{G}^{\mathbf{R}_{\boldsymbol{\alpha}} \underline{k}_{\mathbf{j}}}) \{\mathbf{R}_{\boldsymbol{\beta}}\} \mathbf{G}^{\underline{k}_1}.$$
(4)

With the allowed values of R_{\star} and R_{β} the wave vector selection rules, that is the identification of the allowed \underline{k}_{1} for a given pair of \underline{k}_{i} and \underline{k}_{j} , can be determined by the use of equation (2). In practice the restrictions on R_{\star} and R_{β} are so severe that equation (2) frequently leads to only one value of \underline{k}_{1} for which the coefficients $C_{pq,r}^{\underline{k}_{1}\underline{k}_{j},\underline{k}_{1}}$ do not automatically vanish. $k_{i}\underline{k}_{i}.\underline{k}_{i}$

Assuming that the wave vector selection rule for a given \underline{k}_i and \underline{k}_j has been determined, the coefficient $C_{pq,r}^{\underline{k}_i \underline{k}_j, \underline{k}_l}$ can be obtained by

using the formula which is given, for example, on p. 211 of Bradley and Cracknell (1972)

$$C_{pq,r}^{\underline{k}_{\underline{i}}\underline{k}_{\underline{j}},\underline{k}_{\underline{l}}} = \underbrace{\xi}_{A} \underbrace{\xi}_{B} (|\underline{r}|/|N_{A}\beta|) \underbrace{\xi}_{R_{\delta}}|\underline{v}_{\delta}\xi \in \underbrace{N_{\delta}\beta}{}_{T} \chi_{p}^{\underline{k}_{\underline{i}}} (\{R_{\beta}|\underline{v}_{\beta}\}^{-1} \{R_{\delta}|\underline{v}_{\delta}\} \{R_{\beta}|\underline{v}_{\beta}\}) \times \chi_{q}^{\underline{k}_{\underline{i}}} (\{R_{\delta}|\underline{v}_{\delta}\}) \times (5)$$

Our task is to determine the WVSRs and the coefficients on the right-hand side of equation (1) for all possible sets of p, q, \underline{k}_i , and \underline{k}_j in the decomposition of the left-hand side of equation (1) for each of the 230 classical space groups. This involves a very large amount of tabulation and all that we can hope to do here is to describe some of the difficulties that we have encountered along the way and to indicate the form of the results for a few examples.

2.3 Symmetrized and antisymmetrized powers.

In addition to the reductions of the ordinary Kronecker products, there is also the special case when $\underline{k}_i = \underline{k}_j$ and p = q. The product $(\int_p^{\underline{k}_i} \uparrow \underline{G}) \otimes (\int_p^{\underline{k}_i} \uparrow \underline{G})$, or the square of $(\int_p^{\underline{k}_i} \uparrow \underline{G})$, can be separated into symmetrized and antisymmetrized parts and these symmetrized and antisymmetrized squares of space-group representations are of considerable importance in a number of applications. Symmetrized and antisymmetrized cubes, and higher powers, of space-group representations can also be considered by an adaptation of the theory already outlined (for details see Bradley and Davies (1970), Lewis (1973), Gard (1973a, 1973b)). We are also planning to tabulate the results of the reductions of symmetrized and antisymmetrized powers of the irreducible representations of all the 230 space groups; the extra tabulation involved in doing this is quite small since $\underline{k}_i = \underline{k}_j$ and p = q.

3. Identification of space-group representations.

For our purposes it is necessary to have available a set of tables of the space-group representations themselves, such tables being complete, correct, and in a notation that is unambiguously defined. In a paper which is being submitted elsewhere (Davies and Cracknell 1975) we have examined the problem of establishing such a definitive set of tables. This has involved some synthesis, and also some extension, of the work of Miller and Love (1967) and of Bradley and Cracknell (1972). To construct unambiguous tables of WVSRs we have found it necessary to include all the special planes of symmetry; these were not included in any of the published sets of tables of space-group representations.

4. Determination of wave vector selection rules.

If both k_i and k_j are wave vectors corresponding to points of symmetry, the determination of WVSRs is quite easy and the results for any given space group can be presented quite concisely. On the other hand, if either k_i or k_j is a wave vector corresponding to a line or plane of symmetry then the allowed vectors k_1 in equation (2) will be linearly dependent on one or more parameters. If now the parameters of either k_i or k_j take on special values or are related to each other, then the symmetry of k_1 may be increased from a lower to a higher member of the sequence:

general <u>k</u>, plane of symmetry, line of symmetry, point of symmetry. Thus for completeness we need to identify the special values of \underline{k}_1 that arise from the use of special values of the parameters. For these special values of \underline{k}_1 it will be necessary to re-label the representations of <u>G</u> associated with \underline{k}_1 in terms of this higher symmetry. We illustrate what is involved by considering an example.

We consider $F\overline{4}3m$ (T_d^2) , which is the space group of the zinc blende structure, since this is a space group for which a lot of previous relevant work already exists (Birman 1962, 1963, Bradley and Davies 1970). We shall follow the notation used by Miller and Love (1967) in labelling the space-group representations, although we shall follow the notation of Bradley and Davies (1970) in labelling the symmetry operations. Suppose we consider the reduction of Kronecker products of representations belonging to two different DT (Δ) wave vectors so that

$$k_{i} = (0, d, 0); k_{i} = (0, d', 0).$$
 (6)

In general we can assume no special relationship between the values of \checkmark and \checkmark' . By performing the appropriate analysis (see equations (3) and (4)) it is straightforward to show that the allowed vectors \underline{k}_1 may be chosen to be

(i) (0, d+d', 0) where $R_d = E = R_\beta$, and \underline{k}_1 is a DT wave vector which is different from both \underline{k}_i and \underline{k}_j ;

(ii) (0, -d+d', 0) where $R_d = E$, $R_\beta = C_{2x}$, and k_1 is a DT wave vector which is different from both k_1 and k_j ;

(iii) (a, a', 0) where $R_a = E$, $R_\beta = \overline{C_{31}}$, and $\underline{k_1}$ is an A wave vector, which corresponds to a plane of symmetry.

The symmetry labels DT and A apply when no restriction is placed on the values of \checkmark and \checkmark' . However, it is also necessary to consider the possibility of a special relationship between \checkmark and \checkmark' or that \checkmark and \checkmark' may take special values. The possibilities are indicated in table 1 in which the appropriate symmetry labels for the corresponding wave vectors k_1 are also given. One of these special cases, namely $\checkmark' = \checkmark$, was included in the tables given by Bradley and Davies (1970).

1

d,d' values	Stars of possible k					
ム, ペ unrelated	(0, d+d' ,0)	(0,- d + d' ,0)	(a , d', 0)			
and unrestricted	DT	D T	A			
d'=d	(0,2 2, 0)	(0,0,0)	(d,d, 0)			
	DT	GM	SM			
a' = - a	(0,0,0)	(0,-2 d ,0)	(ፈ,-ፈ, 0)			
	GM	DT	SM			
d'= d = t	(0, 1 ,0)	(0,0,0)	(1 ,1,0)			
	X	GM	Sm			
$\alpha' = -\alpha = \frac{1}{4}$	(0,0,0)	(0, <u>1</u> ,0)	(- 1 ,1,0)			
	GM	X	SM			

Table '	1	•
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By using the formula in equation (5) one can determine the reduction of DTI 🖾 DTJ where I and J may each take any value from 1 to 5. Let us consider DT1 🖾 DT1 for example; we obtain

DT1 🔼 DT1	=	DT1	+	D T 1	+	A1	(7)
(6) (6)		(6)		(6)		(24)	
(0, 4, 0) $(0, 4', 0)$	(0, x + d' ,0)		(0,- d+d',0))	(d,d',0)

where the appropriate wave vector is given below each representation and no special assumption is made about the values of \checkmark and \checkmark' . The numbers in brackets indicate the degeneracies of the induced representations $(\Gamma_p^{\underline{k}_1} \uparrow \underline{G}), (\Gamma_q^{\underline{k}_j} \uparrow \underline{G}), \text{ and } (\Gamma_r^{\underline{k}_1} \uparrow \underline{G})$. The corresponding reductions for the special values of \checkmark and \checkmark' can also be determined by using equation (5) directly:

DT1 DA DT1	=	DT 1	+	GM1	+	GM3	+	GM4	+	SM1	+	SM2	(8)
(6) (6)		(6)		(1)		(2)		(3)		(12)		(12)	
(0, d, 0) $(0, d, 0)$	((0,22	,0)		(0	,0,0)				(d,	ż,	0)	

5. Induced compatibility tables.

If one is to construct complete tables of the reductions of all the Kronecker products for a space group, one needs to include all the equations like equations (8) to (11) giving the reductions for all the special $\boldsymbol{\triangleleft}, \boldsymbol{\triangleleft}'$ values as well as equations like equation (7) for The question which we then had to consider was to the general case. see whether it is necessary to tabulate explicitly the reduction of DT1 \square DT1 for all the special cases of \prec and \prec' or whether these reductions could be deduced in a simple manner from equation (7). It happens in fact that it is not necessary to tabulate separately the reductions for all the special cases of \checkmark and \checkmark' because they can be obtained quite easily from equation (7) using what we may describe as "induced compatibility tables", which we call ICTs for short. These are not identical with the compatibility tables which one normally encounters. However, Raghavacharyulu and Shrestha (1966) demonstrated a very useful result. Suppose that $G^{\underline{k}}$ is a subgroup of G , that

$$\Gamma_{\lambda}^{\underline{k}} \circ \downarrow_{\underline{G}}^{\underline{k}} = \underbrace{\xi}_{\mu} \circ_{\lambda \mu} \Gamma_{\mu}^{\underline{k}}$$
(12)

and that

$$(\Gamma^{\underline{k}}_{\mathcal{M}} \uparrow \underline{G}) = \underbrace{\xi}_{\mathcal{N}} (\Gamma^{\underline{k}}_{\mathcal{N}} \uparrow \underline{G}).$$
(13)

The Frobenius reciprocity theorem then enables one to show that

$$C_{\mu\nu} = C_{\mu\nu}$$
 (14)

The question of degeneracies may be a little puzzling at first sight in the understanding of the construction of ICTs using equation (14). Suppose that k_0 and k differ by a small vector K, so that

$$k = k_0 + \kappa_2 \tag{15}$$

where K may be arbitrarily small. The conventional compatibility

tables can be regarded as "subduced compatibility tables"; that is. they identify $C_{\lambda\mu}$ in equation (12) in the reduction of the subduced representation $(\prod_{k=1}^{k} \downarrow_{G_{k}}^{k})$. Since it is the small representations, i.e. representations of \underline{G}^{k} or \underline{G}^{k} , which are commonly used in the group-theoretical labelling of electronic band structures, and of phonon dispersion relations etc. it is the subduced compatibility tables that are used in this connection. But when we consider the reductions of Kronecker products of space-group representations it is really the product of the induced representations $(\prod_{n=1}^{K_1} \uparrow G)$ and $(\prod_{\alpha}^{k} \uparrow \mathbf{G})$ which we are considering (see equation (1)); that is, we require to know C_{k} in equation (13). Recalling that G^{k} is a subgroup of $\underline{g}^{\underline{k}_{0}}$, we see that the subduced representation $(\Gamma_{\lambda}^{\underline{k}_{0}} \downarrow \underline{g}^{\underline{k}})$ may be reducible. Also if $(\Gamma_{\mu}^{k} \uparrow_{G}^{G})$ is regarded as $((\Gamma_{\mu}^{k} \uparrow_{G}^{K} \uparrow_{G}^{K}) \uparrow_{G}^{G})$ then $(\Gamma_{\mu}^{k} \uparrow_{G}^{K} \uparrow_{G}^{K})$ may be a reducible representation of \underline{G}^{k0} . That is, a reduction in degeneracies of the irreducible (small) representations occurs for $\prod_{k=1}^{k} as$ one <u>decreases</u> the symmetry of k, but a reduction of degeneracies also occurs for $(\prod_{k=1}^{k} \uparrow G)$ as one <u>increases</u> the symmetry of k. Whereas the former is widely appreciated, the latter is much less widely appreciated.

One can illustrate the use of induced compatibility tables very easily by showing how they can be used in the case of DT1 \blacksquare DT1 for F43m. The conventional compatibility tables for this group are given, for example, on page 387 of Miller and Love (1967); we have used those tables to construct that part of the induced compatibility tables for this group that is relevant to equation (7), see table 2. The degeneracies of the induced representations have also been included in table 2 for reference. If $\measuredangle = \cancel{4}$ equation (7) becomes

DT1 🛛	9DT1 :	= DT1 +	- (DT1 ↑ GM)	+	(A1 1 SM)	(16)
(6)	(6)	(6)	(6)		(24)	
(0, 1, 0)	(0, d, 0)	(0,22,0)	(0,0,0)		(d,d,0)	

and by using table 2 we see that this leads immediately to equation (8). One can obtain equations (9), (10), and (11) very easily in a similar manner. The important point for our purpose is that although one needs to use equation (5) to determine equation (7), one does not then need to use equation (5) again to obtain equations (8) - (11). This simplifies our task of constructing tables of reductions of Kronecker products; it means that

(i) We only need to tabulate the reductions of $(\int_{D}^{\underline{k}_{i}} \uparrow_{\underline{G}}) \mathbf{a} (\int_{a}^{\underline{k}_{j}} \uparrow_{\underline{G}})$

for general values of d and d'. (ii) Reductions for special values of d and d' can be obtained by using ICTs. (iii) We do not need to tabulate the ICTs explicitly because they can be obtained in a trivial manner from the compatibility tables in Miller and Love (1967).

	Table_	2.	Part (of the	induc	ed	compatil	<u>pility</u>	table	es for	F43m.
	DT1	(6)	DT2	(6)	DT3	(6)	DT4	(6)	DT5	(12)	
GM	GM1	(1)	GM2	(1)	GM4	(3)	GM4	(3)	GM6	(2)	
	GM3	(2)	GM3	(2)	GM5	(3)	GM5	(3)	GM7	(2)	
	GM4	(3)	GM5	(3)					2GM	(8) (2((4))
X	- X1	(3)	X2	(3)	X5	(6)	X5	(6)	X6	(6)	
	X3	(3)	X4	(3)				,	X7	(6)	

	A1	(24)
SM	SM1 SM2	(12) (12)

The arguments illustrated above can be extended to products involving planes of symmetry. All we need to do is to make some additions to the compatibility tables of Miller and Love (1967) to cover the additional points, lines, and planes of symmetry that they did not include.

6. Conclusion.

We are now well advanced in determining WVSRs for the orthorhombic and cubic space groups and we hope to complete the work for the other space groups too within the next few months.

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