

REPRESENTATION THEORY, SELECTION RULES, AND PHYSICAL
PROCESSES IN CRYSTALS*

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Abstract

This report has two purposes. We illustrate in a specific fashion how the Theory of Crystallographic Groups in Three Dimensions (Space Group Theory) works in practice. We introduce the idea of a state function, or eigenfunction, of a physical system. After a brief review of the structure of space group irreducible representations it is shown how states of physical (crystal) systems can be classified using the Lemma of Necessary Degeneracy. The derivation of space group selection rules is shown, based upon the decomposition of the tensor product - the Clebsch-Gordan series. Application of selection rules to the analyses of actual physical processes is illustrated on the Germanium crystal (diamond crystal structure space group $Fd3m:O_h^7$). Electronic and phonon types of processes are analyzed in practical cases. Then we introduce and discuss two different themes. Configurational instability of the entire crystal against spontaneous distortion of the high symmetry space group, which is the space group generalization of the Jahn-Teller Theorem. A conjecture is presented that accidental degeneracy in crystals may be a consequence of a higher (dynamical) but hidden symmetry. The higher symmetry is conjectured to be that of a crystallographic space group in higher (perhaps four) dimensions.

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1. Introduction

This report is intended as an introduction to applications of the group theory of crystallographic space groups in condensed matter physics. The emphasis here will be on group representation-related matters: rather than on the abstract structure of the crystallographic groups. We discuss: the structure of the irreducible representations of space groups and the classification of eigenstates of a physical crystal system by use of representation theory; the decomposition of the tensor or Kronecker product of two representations and use in obtaining selection rules; the application of selection rules to the analysis of physical processes - both electronic and lattice vibrational (phonon mediated); and certain specific illustrations in diamond structure with applications to processes and eigenstates in germanium crystal. We conclude with two less investigated topics: on the configurational instability of the entire crystal (space group Jahn-Teller Effect); and on a conjectured relationship between "accidental" degeneracy in three dimensions and higher symmetry - such as due to a four-dimensional crystal space group which "covers" the manifest three dimensional system.

Many of the topics treated here are discussed in greater detail in my book "Theory of Crystal Space Groups and Infra-Red and Raman Lattice Processes", published as Handbuch der Physik 25/2b, Springer-Verlag (1974); and revised as "Spatial Symmetry and Optical Properties of Solids" - Prosvanstvennaya Simmetriya i Opticheskie Svoistva Tverdoch Tel' - (Mir Publishers, Moscow 1978). Other relevant literature will be cited in the Reference section.

This article has been written to be accessible to an interdisciplinary audience such as participated in the ZIF Conference, including chemists, crystallographers, mathematicians, and physicists. I hope I have been able to give enough of the "flavor" and "charm" of applications of crystallographic group theory in condensed matter physics, as well as specific and detailed illustrations to encourage further work by scientists in these many disciplines. A complete survey of all applications is impractical so I have made a selection, but by following a chain of references the interested reader can gain access to the wider literature.

A general reference for this report is my Handbuch article referred to above. Owing to limitations of space certain topics could only be treated in an abbreviated form here - a more complete treatment is given in this reference. The reader may find it quite useful to liberally consult this work. Additional literature is given in Section 15.

2. The "State" of the System: Classification by Representation Theory

We propose at the outset to adopt a view of the state of a physical system (such as a crystal) which is quantum mechanical, in orientation. Thus we take the state of a system to be described by some "state function". In practice the state function employed here is a

- Schrodinger electronic eigenfunction $\psi(\vec{r})$, or a
- Classical normal mode eigenvector $[\vec{e}]$, or a
- Schrodinger vibration eigenfunction which depends on normal coordinate Q , of the vibrating ions.

Each of these objects is some function over the complex field of the coordinates \vec{r} of the entities comprising the crystal, such as electrons, ions, atoms.

The state function may also refer to many different types of elementary excitations of condensed matter (crystals) in addition to phonons; such as: excitons, polarons, polaritons, magnons. Symmetry can be applied in all these cases.

The state function will be taken as a basis (representation module) upon which a representation of the underlying crystallographic symmetry group is constructed. Representation theory permits the classification of states (or state functions), the assignment of a symmetry label to the state, and analysis of transition processes between states caused by applied perturbations: thus selection rules arise.

Some mathematical/physical objects of interest are:

a) The symmetry group of the physical system G_g , which is the set of isometries or symmetry transformations $\{g\}$ of the system. Each g produces a coordinate transformation in the physical space according to the rule

$$g \vec{r} = \vec{r}'$$

In a more usual notation with $g = (\phi|\vec{t})$

$$(\phi|\vec{t}) \cdot \vec{r} = \phi \vec{r} + \vec{t}$$

The homogeneous part ϕ is generally an orthogonal matrix (rotation or reflection) while the inhomogeneous part \vec{t} is a translation. Then G_g is one of the 230 Schoenflies-Federov groups if we ignore additional degrees of freedom, or a Shubnikov group or color group if we include magnetic or other degrees of freedom. We often call G_g the group G .

b) The unitary representation D over the complex field of G_g . We take D as already irreducible or as decomposable, by Maschke's Theorem.

Note we shall take $G_g \equiv G$ to be a finite group: i.e. by using 'periodic (Born-v Karman) boundary conditions we finitize the crystallographic space group. The elements of D are the unitary matrices denoted $D(g)$.

c) The state function, or eigenfunction, of the system denoted $\psi(\vec{r})$. In case of "degeneracy" there is more than one state function associated with a given eigenvalue. We denote the set $\{\psi(\vec{r})\}$ and label individual partner members $\psi_\mu(\vec{r})$, affixing other representation indices as needed.

d) The function transformation operators P_g associated with element g . The set of such operators forms the group G_{P_g} homomorphic to G . The action of P_g on $\psi(\vec{r})$ is

$$P_g \psi(\vec{r}) = \psi(g^{-1}\vec{r}).$$

e) For a set of "degenerate" eigenfunctions $\{\psi_\mu\}$ we have

$$\begin{aligned} P_g \psi_\mu(\vec{r}) &= \sum_\nu D_{\nu\mu}(g) \psi_\nu(\vec{r}) \\ &= \psi_\mu(g^{-1}\vec{r}) \end{aligned}$$

Consequently we assert that a set of degenerate eigenfunctions is a basis for representation D of G . This assertion is a consequence of the completeness of the subspace of degenerate eigenfunctions at some given energy E .

3. State Functions and Energies

Two examples of eigenfunctions are: first the solutions of a one-electron Schrodinger Equation for the motion of a single electron in a perfect crystal. This is

$$H\psi = (T + V) \psi = E\psi$$

where T is the electronic kinetic energy operator, V is the electronic potential energy operator, E is the eigenenergy and ψ the eigenfunction. The kinetic energy T for one electron is simply $-\nabla^2$, while $V(\vec{r})$ is a periodic function $V(\vec{r}) = V(\vec{r} + \vec{R}_L)$ where \vec{R}_L is some lattice vector. The ℓ_m degenerate solutions of this equation may be denoted

$$\psi_{\mu}^{\vec{k}j}(\vec{r}) \quad \mu = 1, \dots, \ell_m$$

with \vec{k} a member of the set $\{\vec{k}_v = \phi_v \vec{k}_1\}$ called the star of \vec{k} :

$$\vec{k} \in \star\vec{k} \equiv (\vec{k}_1, \vec{k}_2, \dots, \vec{k}_s)$$

where $\star\vec{k}$ is the star of \vec{k} , and each of the functions $\psi_{\mu}^{\vec{k}j}$ is a "Bloch Function". The energy is

$$E_j(\vec{k})$$

where \vec{k} is the wave vector ($\in \star\vec{k}$) and the index j is a band index which labels the "energy band", or allowable irreducible representation. The function $E_j(\vec{k})$ may be viewed as a "quasicontinuous" function of wave vector \vec{k} , since the \vec{k} are dense, and constant E_j defines an "energy surface" in the three dimensional \vec{k} space. The individual points on this surface labelled by individual \vec{k} are physically allowed energy states.

Thus allowing for degeneracy we can rewrite the one particle Schrodinger Equation as

$$H\psi_{\mu}^{\vec{k}j} = E_j(\vec{k}) \psi_{\mu}^{\vec{k}j}$$

where it is understood that \vec{k} is a member of the star $\star\vec{k}$. The index j refers to allowable irreducible representation. The eigenenergy $E_j(\vec{k})$ is independent of the index μ of the partner function.

A second example of an eigenfunction arises in small amplitude lattice dynamics of crystals. Call the instantaneous position of the atom at position $(\ell\kappa)$ in the crystal - cell ℓ basis atom κ :

$$\vec{r}(\ell\kappa) = \vec{r}(\ell\kappa) + \vec{u}(\ell\kappa)$$

where $\vec{r}(\ell\kappa)$ is the equilibrium position vector and $\vec{u}(\ell\kappa)$ a time dependent displacement.

In the harmonic (Hooke's Law) approximation the classical potential energy of the lattice is bilinear in the components of the cartesian displacements

$$V = 1/2 \sum_{\substack{\alpha\ell\kappa \\ \beta\ell'\kappa'}} u_{\alpha}(\ell\kappa) \phi_{\alpha\beta}(\ell\ell';\kappa\kappa') u_{\beta}(\ell'\kappa')$$

The kinetic energy is

$$T = 1/2 \sum_{\alpha\ell\kappa} M_{\kappa} \dot{u}_{\alpha}(\ell\kappa)^2$$

It is important at this point to transform variables from the independent set of cartesian displacements $u_{\alpha}(\ell\kappa)$ to normal coordinates $Q(\vec{k}j_{\nu})$:

$$u_{\alpha}(\ell\kappa) = (M_{\kappa}N)^{-1/2} \sum_{\vec{k}, j, \nu} e^{i\vec{k} \cdot \vec{R}_{L}} e_{\alpha}(\kappa|\vec{k}j_{\nu}) Q(\vec{k}j_{\nu})$$

The quantities $e_{\alpha}(\kappa|\vec{k}j_{\nu})$ are the eigenvectors of the dynamical matrix $D_{\alpha\beta}(\vec{k}; \kappa\kappa')$, which is defined as the Fourier transformed force constant matrix:

$$D_{\alpha\beta}(\vec{k}; \kappa\kappa') = \sum_{\ell\ell'} \phi_{\alpha\beta}(\ell\ell'; \kappa\kappa') e^{-i\vec{k} \cdot (\vec{R}_{L} - \vec{R}_{L'})} (M_{\kappa} M_{\kappa'})^{-1}$$

In these expressions $\phi_{\alpha\beta}(\ell\ell'; \kappa\kappa')$ are the elementary force constants (derivatives of the potential energy) M_{κ} are ion masses. The dynamical equation for the eigenvectors can be written

$$[D(\vec{k})] [e(\vec{k}j_{\nu})] = \omega^2(\vec{k}j) [e(\vec{k}j_{\nu})]$$

We have compressed the notation in writing this equation. To recover the full matrix expression take matrix elements and use an obvious convention on the indices. In this equation

$$\omega^2(\vec{k}j)$$

is the squared eigenfrequency (which corresponds to the energy of the Schroedinger problem),

$$[e(\vec{k}j_{\nu})]$$

is the eigenvector whose components are $e_{\alpha}(\kappa|\vec{k}j_{\nu})$. Evidently $[e(\vec{k}j_{\nu})]$

corresponds to the Schroedinger eigenfunction $\psi_{\vec{k}j}$. The eigenvector has $3r$ components at fixed wave vector \vec{k} , where r is the number of ions in the primitive unit cell. The index v refers to degeneracy. In phonon problems the index j or j_v refers to the "branch" index. The frequency surface in wave-vector or \vec{k} space is given by $\omega(\vec{k}j) = \text{constant}$. If $v > 1$ there is degeneracy which implies a touching or coincidence of two branches at that \vec{k} .

In a quantum mechanical treatment $Q(\vec{k}j_v)$ is considered as a generalized coordinate. The Schroedinger eigenfunction of the lattice is a function of the $Q(\vec{k}j_v)$. The classically determined symmetry properties of the normal coordinates $Q(\vec{k}j_v)$ are taken over to the quantum theory. The quantum lattice eigenfunction is a generalized "many harmonic oscillator" function consisting of a product of a Hermite polynomial in the $Q(\vec{k}j_v)$: times a "Gaussian" factor in the Q . This increases the complexity of calculation, but can be straightforwardly incorporated in the analysis.

4. Symmetry and Degeneracy

Consider the electronic energy band problem: motion of an electron in a crystal governed by a Schroedinger Equation in which the potential energy V has the full symmetry of the crystal. That is

$$P_g V(\vec{r}) = V(g^{-1}\vec{r}) = V(\vec{r})$$

Here g is an element in G . The rotational part ϕ of g is an orthonogal transformation and \vec{t} is a constant translation, clearly the kinetic energy T also has full symmetry

$$P_g T(\vec{r}) = T(g^{-1}\vec{r}) = T(\vec{r})$$

But $H = T+V$ is considered as an operator in the space of eigenfunctions ψ , so it is usual to write

$$H\psi(\vec{r}) = E\psi(\vec{r})$$

and then consider symmetry transformations on the operators

$$P_g H P_g^{-1} P_g \psi = E P_g \psi$$

But

$$P_g H P_g^{-1} = H(g^{-1}\vec{r}) = H$$

by symmetry. Then

$$H P_g \psi(\vec{r}) = E P_g \psi(\vec{r})$$

Consequently if ψ is an eigenfunction, $P_g \psi$ is an eigenfunction at the same energy E . It follows that the set

$$\{\psi, \psi_g \equiv P_g \psi, \psi_{g^2} \equiv P_{g^2} \psi, \dots\}$$

are eigenfunctions at the same energy E . If among the members of this set several are distinct, then degeneracy exists: distinct linearly independent eigenfunctions at the same energy E .

We gather the linearly independent degenerate eigenfunctions together into the linear vector space

$$\sum \equiv \langle \psi | \equiv \langle \psi_{g_1}, \psi_{g_2}, \dots, \psi_{g_m} | \equiv \langle \psi_m |$$

It is useful to take $g_1 \equiv e$ the identity of G . It is clear that \sum is a linear vector representation space for G . Apply P_g to \sum , treating \sum as a column vector, then:

$$P_g \sum = D(g) \sum$$

where $D(g)$ is a ℓ_m dimensional matrix, labelled by elements $g_1 \dots g_m$. Evidently, if $gg_a = g_b$

$$D(g)_{ba} = \delta_{g_a, g^{-1}g_b}$$

It is easy to verify that $D(g)$ forms a unitary representation of G . Since G is a finite group, $D(g)$ is equivalent to an irreducible representation or a decomposable representation. For simplicity we assume that we have taken correct linear combinations, (i.e. a similarity transformation has been made) and \sum is irreducible under G or G_p .

A similar result obtains in the case g of lattice dynamics. The basic force constant matrix $[\Phi]$ whose elements are $\Phi_{\alpha\beta}(\ell\ell';\kappa\kappa')$ is invariant under a symmetry transformation P_g . This can be expressed as the matrix equation.

$$P_g [\Phi] P_g^{-1} = [\Phi].$$

Passing to the dynamical matrix which is the Fourier transform of $[\Phi]$ we find

$$P_g [D(\vec{k})] P_g^{-1} = [D(\phi\vec{k})] = [D(\vec{k}_\phi)]$$

where $\phi\vec{k} \equiv \vec{k}_\phi$ is the wave vector, \vec{k} rotated by the rotational part of g . Evidently there are two cases to consider: \vec{k}_ϕ equivalent to \vec{k} (modulo a reciprocal lattice vector) or \vec{k}_ϕ inequivalent to \vec{k} . These can be denoted as

$$\vec{k}_\phi \equiv \vec{k} \text{ and } \vec{k}_\phi \not\equiv \vec{k} \text{ respectively.}$$

Consider the first case and the set of all g with property that their associated ϕ parts produce the stated equivalence. Call these g_1, \dots, g_2, \dots . Clearly the set of these is a group denoted $G(\vec{k})$. Then if g_α is one of the set $g_\alpha \in G$:

$$P_{g_\alpha} [D(\vec{k})] P_{g_\alpha}^{-1} = [D(\vec{k})]$$

so that

$$P_{g_\alpha} [D(\vec{k})] P_{g_\alpha}^{-1} P_{g_\alpha} [e(\vec{k}j_v)] = \omega^2(\vec{k}j) P_{g_\alpha} [e(\vec{k}j_v)]$$

It follows that $P_{g_\alpha} [e(\vec{k}j_v)]$ is an eigenvector with the same squared eigenfrequency $\omega^2(\vec{k}j)$. We gather the degenerate eigenvectors into a linear space:

$$\Sigma \equiv \langle [e(\vec{k}j_v)], \dots, [e_{g_\alpha}(\vec{k}j_v)] \dots \rangle$$

The space Σ is a basis for a representation of the group $G(\vec{k})$. Choosing the correct linear combinations we may assume this space is irreducible under $G(\vec{k})$.

For both the electronic and the lattice dynamic problems then, the existence of a symmetry group implies degeneracy: the eigenfunctions or eigenvectors are bases for irreducible representations.

5. Irreducible Representations

A brief review of the structure of space group irreducible representations will be useful and will permit a connection with the physical results just given, and also with the review given by Prof. Cracknell in these Proceedings. Let T be the normal subgroup of pure lattice translations of G . The factor group $G/T = P$ is the "crystal class" or the "point group of the space group".

We reduce T by finding a complete set of Bloch functions $\psi_{\vec{k}}$. Let

elements in T be denoted $t_1 = e, t_2, \dots, t_L \dots$ where another notation for t_L is \vec{R}_L (a lattice vector in crystal space). The corresponding function operator P_t has the action

$$P_t \psi(\vec{r}) = \psi(\vec{r} - \vec{t}).$$

Then for the Bloch function $\psi^{\vec{k}}$:

$$\begin{aligned} P_t \psi^{\vec{k}}(\vec{r}) &= \psi^{\vec{k}}(\vec{r} - \vec{t}) = e^{i\vec{k} \cdot \vec{t}} \psi^{\vec{k}}(\vec{r}) \\ &= D^{\vec{k}}(t) \psi^{\vec{k}}(\vec{r}). \end{aligned}$$

Here $D^{\vec{k}}$ represents the translation irreducibly. The set of all \vec{k} which produce inequivalent irreducible representations span the First, or Reduced Brillouin Zone. Hence \vec{k} is defined mod 2π times a lattice vector in the reciprocal or dual lattice ($2\pi\vec{B}_H$). The wave vectors \vec{k} may be regarded as quasicontinuous.

The group G can be decomposed into cosets with respect to T as

$$G = T + g_2 T + \dots + g_p T + \dots + g_h T$$

Coset representatives g_p are in general of the form

$$g_p = (\phi_p | \vec{t}_p)$$

where \vec{t}_p can be a fractional translation for a non-symmorphic group, and ϕ_p is the rotational part of g_p .

To complete the reduction, select a \vec{k} in the zone and determine the orbit of \vec{k} , or the star: $^*\vec{k}$, by applying to \vec{k} all the rotational parts of coset representatives g_1, \dots, g_h . The set of inequivalent (mod $2\pi\vec{B}_H$) wave vectors \vec{k} are $^*\vec{k}$. Then define the group of the wave vector \vec{k} denoted $G(\vec{k})$. It is the stabilizer of \vec{k} , and is also a space group. Determine the complete set of r allowable irreducible representations of $G(\vec{k})$. These are denoted

$$\begin{aligned} D^{\vec{k}m} \quad m = 1, \dots, r \\ |D^{\vec{k}m}| = \ell_m \end{aligned}$$

Then $D^{\vec{k}m}$ are allowable because when this representation of $G(\vec{k})$ is restricted to T it subduces correctly:

$$D^{\vec{k}m} \text{ of } G(\vec{k}) + D^{\vec{k}} \text{ of } T (\ell_m \text{ times}).$$

Recall that $D^{\vec{k}}$ of T associates $e^{i\vec{k} \cdot \vec{t}}$ to each \vec{t} . In practice $D^{\vec{k}m}$ may be found by determining the projective representations of $G(\vec{k})/T \cong P(\vec{k})$ with the correct factor system, e.g. $r \equiv e^{i\vec{k} \cdot \vec{t}}$. A little group method may also be used. These matters are more completely discussed in Prof. Cracknell's lecture, my Handbuch article, and other references.

It is very useful to define a "dotted" matrix

$$\begin{aligned} \dot{D}^{\vec{k}m}(g) &= D^{\vec{k}m}(g) \quad \text{if } g \in G(\vec{k}) \\ &= 0 \quad \text{if } g \notin G(\vec{k}) \end{aligned}$$

Here 0 is the null matrix.

Using dotted matrices we induce the full irreducible representation of G from that of $G(\vec{k})$. Let the full irreducible representation be denoted $D^{*\vec{k}m}$. Label the bloc row and column matrices in $D^{*\vec{k}m}$

$$D^{*\vec{k}m}(g)_{\sigma\tau}$$

where bloc subscripts σ and τ refer to wave vectors in $^{*}\vec{k}$:

$$\vec{k}_{\sigma} \equiv \phi_{\sigma} \vec{k}, \quad \vec{k}_{\tau} \equiv \phi_{\tau} \vec{k}.$$

Then the standard induction procedure of Clifford gives for the bloc matrices

$$D^{*\vec{k}m}(g_p)_{\sigma\tau} = \dot{D}^{\vec{k}m}(g_{\sigma}^{-1} g_p g_{\tau})$$

Each of the elements g_{σ} , g_p , g_{τ} is the relevant coset representative in G decomposed with respect to T . In summary, the full irreducible representation $D^{*\vec{k}m}$ has form

$$D^{*\vec{k}m}(g) = \begin{pmatrix} \begin{array}{c|c|c|c} D_{11}^{\vec{k}m} & 0 & & \\ \hline 0 & 0 & & D_{22}^{\vec{k}m} \\ \hline \vdots & \vdots & & \\ \hline & & D & \end{array} \end{pmatrix}$$

where each bloc is either the m dimensional null matrix or the m dimensional $D^{\vec{k}m}$. The dimensionality of $D^{*\vec{k}m}$ is $(s\ell_m) = \text{star degeneracy} \times \text{local degeneracy}$.

It is obvious but nevertheless important that pure translation is

represented by a diagonal matrix

$$D^{*\vec{k}m}(\vec{t}) = \left(\begin{array}{c|c|c} e^{i\vec{k} \cdot \vec{t}_{I_m}} & 0 & 0 \\ \hline 0 & e^{i\vec{k} \cdot \vec{t}_{I_m}} & 0 \\ \hline 0 & 0 & \ddots \end{array} \right)$$

where I_m is the m dimensional unit matrix.

Later we discuss the Kronecker (Direct) product of two such representations and the decomposition of such a product.

6. Necessary Degeneracy and Irreducible Representation

Returning to the eigenfunctions previously discussed we now remark that the electronic eigenfunctions will be a basis for the irreducible representation of G . This assertion partially follows from the decomposability of the representation $D(g)$ introduced in section 3. However, an additional and essential Ansatz is needed which we denote as the Lemma of Necessary Degeneracy: each eigenstate corresponds to an irreducible representation of G .

Call the eigenfunctions

$$\{\psi_{\nu}^{\vec{k}_\tau j}\}$$

where $\vec{k}_\tau = \phi_\tau \vec{k}$ is contained in $^*\vec{k}$, j labels the allowable irreducible representation and ν refers to the partner function in the ℓ_j dimensional irreducible representation $D^{\vec{k}_\tau j}$ of the group $G(\vec{k}_\tau)$. Then the effect of a symmetry transformation by operator P_g is

$$P_g \psi_{\nu}^{\vec{k}_\tau j} = \sum_{\sigma\mu} D^{*\vec{k}j}(g)_{(\sigma\mu)(\tau\nu)} \psi_{\mu}^{\vec{k}_\sigma j}$$

This expresses the fact that the set of degenerate eigenfunctions generates $D^{*\vec{k}j}$. Corresponding to these eigenfunctions are the electronic band energies:

$$E_j(\vec{k}) = E_j(\vec{k}_\nu) = \dots = E_j(\vec{k}_s)$$

$$\vec{k}_\nu = \phi_\nu \vec{k}; \dots; \vec{k}_s = \phi_s \vec{k}$$

Note that, at given $\vec{k} \in ^*\vec{k}$, each band energy is repeated ℓ_j times to take account of the ℓ_j fold degeneracy at that \vec{k} resulting from the fact that $\dim D^{\vec{k}j} = \ell_j$.

Likewise, the eigenvectors of the lattice dynamic problem may be transformed as

$$P_g [e(\vec{k}_i j_v)] = \sum_{\sigma \mu} D^{* \vec{k} j} (g)_{(\sigma \mu) (\tau v)} [e(\vec{k}_\sigma j_\mu)]$$

Necessary degeneracy in this case means that the set $\{[e(\vec{k} j_v)]\}$ are a basis for irreducible representation of G. Lattice waves have characteristic symmetries according to irreducible representations $D^{* \vec{k} j}$ of G.

It is also useful as mentioned above to introduce the notion of a phonon, which is the quantum elementary excitation corresponding to the normal coordinate $Q(\vec{k} j_v)$. We preserve the transformation properties under P_g :

$$P_g Q(\vec{k}_\tau j_\mu) = \sum_{\sigma \mu} D^{* \vec{k} j} (g)_{(\sigma \mu) (\tau v)} Q(\vec{k}_\sigma j_\mu)$$

The individual normal coordinates transform as partners under $D^{* \vec{k} j}$. Polynomial functions like $H_n(Q)$ of the $Q(\vec{k} j_v)$ transform as appropriate tensor products $D_n^{* \vec{k} j}$.

The essential point is that using the existence of symmetry elements and the symmetry group G the eigenstates of the electronic and normal mode lattice vibration problem can be strictly classified according to irreducible representation and partner function.

7. Examples of Classification of Eigenstates

In order to clarify and illustrate the points just made we present several figures which exemplify the kind of analysis we have been discussing.

In Fig.1 we exhibit the diamond structure unit cell. The space group is $Fd\bar{3}m = O_h^7$. The tetrahedral configuration is shown.

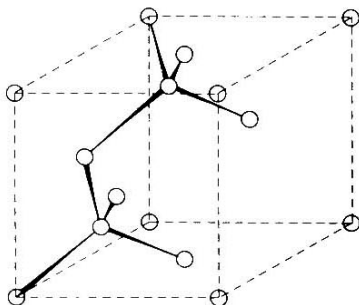


Fig. 1

In Fig. 2 the Reduced Brillouin Zone for the face centered cubic group is shown. Points of high symmetry are indicated; for such points the little group $G(\vec{k})/T$ is non-trivial. This cell is the "Fundamental-bereich" or Voronoi cell in the reciprocal (or dual) lattice.

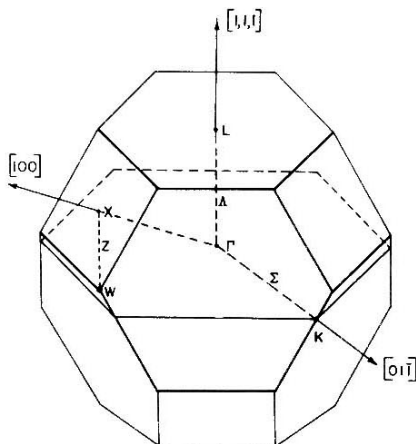


Fig. 2

In Fig. 3a we have exhibited the orbit, or star of one wave vector of high symmetry: this is \vec{W} . (See Fig.2). Note the 6 arms of the star.
 Fig.3a Fig.3b

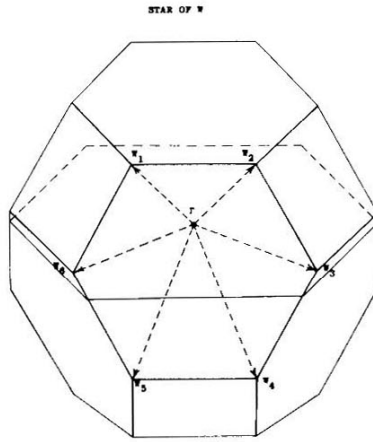


Fig. 3a

$$\vec{W}_1 = (2\pi, 0, \pi) (1/a)$$

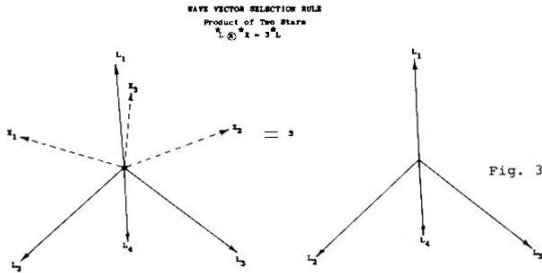


Fig. 3 b

In Fig.4 we exhibit a section in the reciprocal space showing the trace of the energy surfaces for various energy bands in germanium - a diamond structure crystal. We plot $E_j(\vec{k})$ for different bands j .

The energy bands shown are near the band 'gap' and each band carries the relevant symmetry label - the label applies to the high symmetry points. It should be recalled that a symmetry index j changes significance when \vec{k} and $G(\vec{k})$ change by, for example, passing from some general point on a line to a "special" point such as the end point of the line, since j refers to the allowable irreducible representation of that $G(\vec{k})$. However, compatibility conditions exist restricting the connectivity of representations - connecting $D^{\vec{k}j}$ and $D^{\vec{k}'j'}$ if $G(\vec{k}') \subset G(\vec{k})$. Such relations permit one to define all the states of one band in a consistent fashion, satisfying the compatibility conditions and permitting $E_j(\vec{k})$ to be an essentially continuous function of \vec{k} .

ELECTRONIC BANDS IN GERMANIUM AND PROCESSES

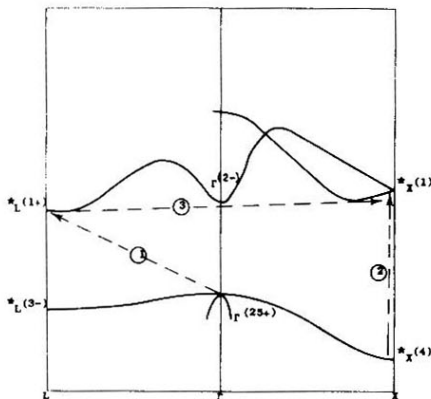


Fig. 4

1. Indirect gap process (photon + phonon).
2. Direct gap process (photon).
3. Intervalley scattering (phonon).

In Fig. 5 the phonon dispersion spectrum of a typical diamond structure crystal is given. The sections of $\omega_j(\vec{k})$ are similar to the $E_j(\vec{k})$ of electronic band theory, and in a similar manner one branch can be defined irrespective of the changed significance of index j when \vec{k} moves to a high symmetry point.

PHONON SPECTRUM O_h^7

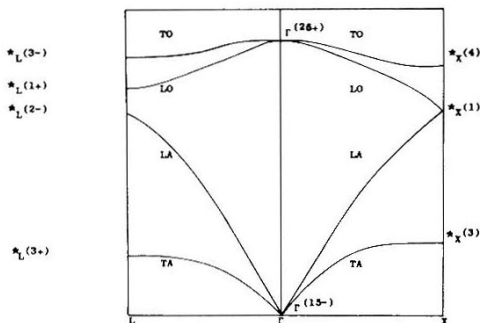


Fig. 5

It should now be apparent that the eigenstates of crystals can be and are strictly classified according to irreducible representations D^{*k_j} . The astute observer will note that at certain points (see the upper two branches in Fig. 4 along line Γ -X) bands cross at some point which is not higher symmetry than adjacent point. The crossing produces, at that point, a higher degeneracy than required by the allowable irreducible D^{*k_j} . In that case "accidental" degeneracy is said to occur. We return to the possible symmetry-related significance of such "accidents" below. But here we stress the point that the Lemma of Necessary Degeneracy applies "almost everywhere" in the Brillouin Zone; exceptions being generally isolated points.

A final observation worth recording is an illustration of the atom displacements in a particular normal mode. We choose the optic, Raman active, mode of symmetry Γ_{25+} in diamond. The displacements illustrated below in Figure 6 indicate \pm [111] direction motion of each of the two inequivalent atoms (at 0 and at $\frac{1}{4}$) in the unit cell.

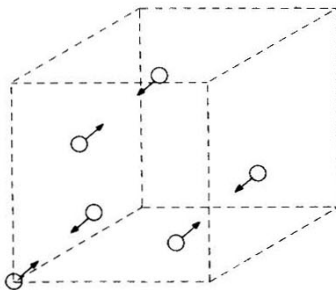


Fig. 6

3. Transition Processes in Crystals

Using standard first order quantum-mechanical perturbation theory (Rayleigh-Schroedinger) it is easily established that the rate of transition from an initial state $\psi(i)$ to a final state $\psi(f)$ caused by a perturbation operator which we denote \hat{O} represents in general the perturbing energy caused by taking into consideration some external force (electronic, magnetic, strain) or some additional interaction not previously included in the original Hamiltonian H . \hat{H} gives rise to the system eigenstates $\psi(i)$, $\psi(f)$, and the perturbation \hat{O} may be viewed as causing transitions between such states.

Selection rules arise by investigation of these matrix elements.

We use the term selection rule to denote:

Necessary vanishing of $\langle f | \hat{O} | i \rangle$ caused by symmetry:

$$\langle f | \hat{O} | i \rangle = 0$$

Equality of apparently distinct matrix elements caused by symmetry:

$$\langle f' | \hat{O}' | i' \rangle = \langle f | \hat{O} | i \rangle.$$

Generally selection rules arise because ψ_{μ}^i is a set of degenerate eigenfunctions and the set is a basis for irreducible representation D^i :

$$\{\psi_{\mu}^i\} \rightarrow D^i \text{ of } G$$

and likewise for ψ_{ν}^f :

$$\{\psi_{\nu}^f\} \rightarrow D^f \text{ of } G$$

The operator \hat{O} itself is generally a quantity which transforms under the symmetry operations of G as some representation D^{OP} ; denoting the components of \hat{O} as \hat{O}_{λ} we write

$$\{\hat{O}_{\lambda}\} \rightarrow D^{OP} \text{ of } G$$

Then the matrix elements governing transitions from one of the degenerate manifold of initial states $\{\psi_{\mu}^i\}$, to one of the degenerate manifold of final states $\{\psi_{\nu}^f\}$ are the set

$$\langle f\nu | \hat{O}_{\lambda} | i\mu \rangle.$$

9. Generic Wigner - Eckart Theorem

The generic Wigner-Eckart Theorem concerns the matrix element

$$\langle m\alpha | n\beta \rangle \equiv \int \psi_{\alpha}^{m*} \psi_{\beta}^n d\tau$$

where

$$\{\psi_{\alpha}^m\} \rightarrow D^m \text{ of } G$$

$$\{\psi_{\beta}^n\} \rightarrow D^n \text{ of } G$$

We assume D^m and D^n are irreducible.

It is easily shown that the value of this integral is:

$$\langle m\alpha | n\beta \rangle = c_m \delta_{mn} \delta_{\alpha\beta}$$

Here

$$\delta_{mn} = 0 \text{ unless } D^m \text{ is equivalent to } D^n$$

$$(\text{i.e. unless } UD^m U^{-1} = D^n)$$

$$\delta_{\alpha\beta} = 0 \text{ unless } \alpha = \beta$$

c_m is a "reduced" matrix element,
independent of α and β , but depending
only on the representation index m .

A completely equivalent way of stating this result since G is a finite group, is that the matrix element $\langle m\alpha | n\beta \rangle = 0$ unless

$D^m \otimes D^n$ contains D^{1+} the trivial
(identity) representation of G .

The tensor (Kronecker) product is denoted \otimes .

It then follows that

$$\langle f\nu | \hat{O}_{\lambda} | i\mu \rangle = 0$$

unless the decomposable representation
 $D^{f*} \otimes D^i$ contains D^{0P} .

That is if the tensor product $D^{f*} \otimes D^i$ representation, when reduced, contains a representation in common with D^{0P} some of the matrix elements of the set $\langle f\nu | \hat{O}_{\lambda} | i\mu \rangle$ are different from zero.

All the ingredients needed to carry out this analysis for crystals are now in hand: initial and final eigenstates are of the type ψ_{μ}^{kj} , spanning irreducible representations D^{*kj} ; the operators \hat{O}_{λ} can be analyzed using the standard procedure to determine to which irreducible representation they belong.

10. Reduction of the Tensor Product

The set of initial eigenstate basis functions can be denoted

$$|i\mu\rangle: \{\psi_{\mu}^{\vec{k}m}\} \rightarrow D^{\vec{k}m}$$

the set of final eigenstates basis functions can be denoted

$$|fv\rangle: \{\psi_{\mu}^{\vec{k}'m'}\} \rightarrow D^{\vec{k}'m'}$$

The basis for the tensor product

$$D^{\vec{k}m} \otimes D^{\vec{k}'m'}$$

is the product space consisting of the set of all bilinears

$$\{\psi_1^{\vec{k}m} \psi_1^{\vec{k}'m'}, \dots, \psi_{\mu}^{\vec{k}m} \psi_{\mu}^{\vec{k}'m'}, \dots, \psi_{\ell}^{\vec{k}m} \psi_{\ell}^{\vec{k}'m'}\}$$

There are $(s_m^{\vec{k}})(s_m^{\vec{k}'})$ such bilinears. To avoid notational confusion we do not put in the conjugate complex for $D^{\vec{k}'m'}$ although it is easily inserted as needed.

In order to completely decompose the tensor product into irreducible components we first determine which representations appear by finding "reduction" coefficients. These are the positive integer (or zero) coefficients in the Clebsch-Gordan Series. We adopt notation

$$D^{\vec{k}'m'} \otimes D^{\vec{k}m} = \oplus (D^{\vec{k}''m''} | \vec{k}'m' \vec{k}m) D^{\vec{k}''m''}$$

and the reduction coefficients

$$(\vec{k}'m' \vec{k}m | \vec{k}''m'')$$

give the needed information on the appearance of $D^{\vec{k}''m''}$.

Let us now suppose we know which $D^{\vec{k}''m''}$ do appear in the reduction. To complete the work we need to take the next step and determine the correct linear combination. That is if $D^{\vec{k}''m''}$ appears at least once then, from the bilinear products we can construct the basis of $D^{\vec{k}''m''}$. Write the correct linear combinations as

$$\psi_{\mu}^{\vec{k}''m''} = \sum_{(\sigma\sigma')} \sum_{(\mu\mu')} (\vec{k}\sigma\mu\vec{k}'\sigma'\mu' | \vec{k}''\mu'') \times \psi_{\mu}^{\vec{k}\sigma m} \psi_{\mu'}^{\vec{k}'\sigma' m'}$$

where the coefficients

$$(\vec{k}\sigma\mu\vec{k}'\sigma'\mu' | \vec{k}''\mu'')$$

are Clebsch Gordan Coefficients. Remark that if the elements $(\vec{k}\sigma\mu\vec{k}'\sigma'\mu' | \vec{k}''\mu'')$ are suitably assembled into a matrix U, then U similarity transforms the direct product into fully reduced form:

$$U^{-1} (D^{\vec{k}m} \otimes D^{\vec{k}'m'}) U = \hat{A}$$

Here \bar{A} is fully reduced

$$\bar{A} = \left(\begin{array}{ccc|ccc} \cdot & & & 0 & & 0 \\ & \cdot & & & & \\ 0 & & \cdot & & 0 & \\ \hline 0 & 0 & 0 & 0 & \cdot & 0 \\ 0 & 0 & 0 & 0 & 0 & \cdot \end{array} \right)$$

with the null matrix outside the main diagonal. The case of multiplicity (some of $D^{*k''m''}$ occur more than once) requires some technical care, but is in principle solvable and in practical cases where the CGC have been evaluated, multiplicity has been accounted for.

Let us now give some concrete steps which are useful, and have been used, for the reduction of Kronecker products. We need to consider ordinary Kronecker products such as:

$$D^{*k'j'} \otimes D^{*k''j''} = \oplus D^{*k''j''},$$

symmetrized Kronecker products such as the symmetrized cube

$$D^{*k'j'}_{\{3\}} = \oplus D^{*k''j''},$$

and antisymmetrized products, such as the antisymmetrized square

$$D^{*k'j'}_{[2]} = \oplus D^{*k''j''}.$$

It may appear that the reduction is impractical since one must search through all possible resultant $D^{*k''j''}$, i.e. all irreducible representations of the space group G. But wave vector selection rules save the day! That is, in all cases the first step is to multiply the stars (orbits) and then decompose the tensor product into complete stars:

$$*k \otimes *k' = \oplus *k''$$

Another way of writing this is in terms of the wave vector reduction coefficients

$$*k \otimes *k' = \sum_{*k''} \{ *k *k' | *k'' \} *k''$$

The direct product of two orbits is defined as the set

$$*k \otimes *k' = \{ \vec{k}_\alpha + \vec{k}'_\alpha, \vec{k}_\alpha \in *k, \vec{k}'_\alpha \in *k' \}$$

We thus determine which orbits, or stars, appear in the reduction. Remark that this first step is really the reduction of the diagonal matrices representing pure translations: the form of these diagonal matrices was given above. It is a simple exercise to verify that the wave vector selection rules express this reduction. For symmetrized or antisymmetrized products of representations we again begin with the relevant wave vector rules which are the natural generalization.

Let $\dim D^{k'j'} = i_j$. Then for $D^{*k'j'}$ the symmetrized cube wave vector selection rule becomes:

$$(\chi_j^* \vec{k})_{(3)} = \frac{1}{6} [\frac{3}{j} (\chi_j^* \vec{k})_3 + 3 \chi_j^2 (\chi_j^* \vec{k})_0 - (\chi_j^* \vec{k})_3 + 2 \chi_j (3 \chi_j^* \vec{k})]$$

$$\begin{aligned} \text{where } \chi_j^* \vec{k} \chi_j^* \vec{k} &= (\chi_j^* \vec{k})_j \\ &= \{ \vec{k}_\alpha + \vec{k}_\alpha, \vec{k}_\alpha, \vec{k}_{\alpha''}, \vec{k}_{\alpha'} \chi_j^* \vec{k}, \vec{k}_\alpha, \chi_j^* \vec{k}, \chi_j^* \vec{k}_{\alpha''} \chi_j^* \vec{k} \} \end{aligned}$$

The corresponding symmetrized wave vector reduction coefficient is

$$(\chi_j^* \vec{k})_{(3)} = \sum (\chi_j^* \vec{k})_0 (\chi_j^* \vec{k})_j$$

We remark here that in all the star-product reductions, complete stars occur in the fully reduced form. This is evident since only complete irreducible representations occur when a decomposition is carried out.

After the first step of the reduction has been carried out, the reduction can now be completed. If it is known that some star (e.g. $\chi_j^* \vec{k}$) occurs then attention may be restricted to determining which of the allowable j occur. This is a much more restricted and thus solvable problem.

Now we outline the methods we developed for completion of the reduction. The method of Linear Algebraic Equations always works to determine the reduction coefficients. Denote the characters of the irreducible representations

$$\chi^* \vec{k}_j(g) = \text{Tr } D^* \vec{k}_j(g)$$

Then the characters satisfy the equations

$$\chi^* \vec{k}_j(g) \chi^* \vec{k}'_{j'}(g) = \sum (\chi^* \vec{k}_j \chi^* \vec{k}'_{j'} | \chi^* \vec{k}''_{j''}) \chi^* \vec{k}''_{j''}(g)$$

The left hand side of this equation is known since all matrices and therefore characters are known for each of the participating irreducible representations. Assuming the dimensions of the factors are: $\dim D^* \vec{k}_j = s^*_{j,j}$; $\dim D^* \vec{k}'_{j'} = s'^*_{j',j'}$; etc then the total dimensionality of all representations which will occur in the reduction is $(ss')(\chi^* \vec{k}_j \chi^* \vec{k}'_{j'})$. Viewed as linear algebraic equations for the coefficients

$$(\chi^* \vec{k}_j \chi^* \vec{k}'_{j'} | \chi^* \vec{k}''_{j''}),$$

we obtain at most $(ss')(\chi^* \vec{k}_j \chi^* \vec{k}'_{j'})$ equations by selecting this number of elements $g \in G$, which give rise to distinct equations. In most cases

Then augment the factor groups according to

$$G/N_Y \rightarrow N_Y/N_{Y''} \rightarrow G/N_{Y''}$$

$$G/N_{Y'} \rightarrow N_{Y'}/N_{Y''} \rightarrow G/N_{Y''}$$

Call the Reduction Group

$$R \equiv G/N_{Y''}$$

It is the cosets in G/T augmented by pure translations. The set of matrices

$$D^{\vec{k}j}(g), D^{\vec{k}'j'}(g), D^{\vec{k}''j''}(g) : g \in R$$

is closed. The reduction group works because the expression derived from character orthonormality is now quite manageable. In practice the order of R is a simple multiple of the order of $P = G/T$:

$$|R| = n_{Y''} |G/T|.$$

In a purely formal sense the reduction group method has certain similarities to the Enlarged Unit Cell procedure introduced by Prof. Koptsik to deal with imperfect crystals.

A final practical method we used to carry out the reduction is based on the construction of a Projection Operator (member of the group algebra). If we know that \vec{k}'' is present, from the wave vector selection rule, we may test the bilinear products by attempting to project out different allowable j'' . That is we construct the projector $P^{\vec{k}''j''}$

$$P^{\vec{k}''j''} (\psi_{\alpha}^{\vec{k}j} \psi_{\alpha'}^{\vec{k}'j'}) =$$

$$|G/N_{Y''}|^{-1} \sum_g \chi^{\vec{k}''j''}(g)^* P_g (\psi_{\alpha}^{\vec{k}j} \psi_{\alpha'}^{\vec{k}'j'})$$

As j'' varies through the allowed ones, for fixed $\alpha\alpha'$ if one obtains a non-zero result the j'' will occur. Permitting $\alpha\alpha'$ to range throughout all possible values will then determine all multiplicities and all j'' which can arise.

11. Selection Rules and Physical Processes

Recapitulating, we have now obtained the complete set of reduction coefficients for the reduction of the tensor products of any two space group irreducible representations; so we know which $D^{*\vec{k}''j''}$ arise. How is this used for analysis of physical processes?

Recall that the amplitude for the rate of a physical transition process is governed by a matrix element of type

$$\langle f | \hat{O}_\lambda | i \rangle$$

We have reduced the product

$$D^f \otimes D^i \sim D^{*\vec{k}'j'} \otimes D^{*\vec{k}''j''}$$

into components

$$D^{*\vec{k}''j''}$$

A necessary condition for the matrix element to be non-zero is if the perturbing potential energy operator denoted \hat{O}_λ has symmetry of one of the components which occur in the reduction:

$$\hat{O}_\lambda \sim D^{*\vec{k}''j''}$$

To illustrate, see list (Table I) of certain generic types of physical transition processes and the operators pertaining to them. This part of the work has been discussed in some detail elsewhere in the theoretical physics literature and we must simply take over needed results in an ad hoc fashion. Specific illustrations will be taken from the Germanium crystal whose space group is the diamond O_h^7 type. Recall Figures 4 and 5 in which electronic band and phonon dispersion curves were given respectively.

In Table I, $|*\vec{k}j\rangle$ refers to the electronic state with symmetry $D^{*\vec{k}j}$; $Q(*\vec{k}''j'')$ refers to a phonon (quantum) eigenstate of symmetry $D^{*\vec{k}''j''}$; symmetrized products are so indicated. The operator \hat{O} is also indicated. Now, referring to O_h^7 space group we determine the symmetry of each operator. We use a conventional notation for the irreducible representations j of the $G(\vec{k})$. Then

$$\vec{\gamma}: \Gamma_{15} \quad (G(\Gamma)/T = O_h)$$

$$[\alpha]: \Gamma_{1+} \oplus \Gamma_{12+} \oplus \Gamma_{25} \oplus \quad (G(\Gamma)/T = O_h)$$

Table I (a)	
Process	Matrix Element
<u>A. Electronic</u>	
Interband Optical Absorption	$\langle \vec{k}' j' \vec{v} \vec{k} j \rangle$
Interband Scattering (1 phonon)	$\langle \vec{k}'_{\sigma}, j' Q(\vec{k}'' j'') \vec{k}_{\sigma} j \rangle$ $\vec{k}'_{\sigma}, \vec{k}_{\sigma} \neq \vec{k}$
Intraband Scattering (1 phonon)	$\langle \vec{k}_{\sigma} j Q(\vec{k}'' j'') \vec{k}_{\tau} j \rangle$ $\vec{k}_{\sigma}, \vec{k}_{\tau} \in \vec{k}$
<u>B. Vibrational</u>	
Optical Absorption (1 phonon)	$\langle Q(\vec{k} j) \vec{v} 0 \rangle$
Optical Absorption (2 phonon combination)	$\langle Q(\vec{k}' j') Q(\vec{k} j) \vec{v} 0 \rangle$
Optical Absorption (overtone)	$\langle Q(\vec{k} j)_{(2)} \vec{v} 0 \rangle$
Raman Scattering	Replace $\hat{O} \sim \vec{v}$ by $\hat{O} \sim \vec{k} a$ in above 3 lines
<u>C. Configurational Instability</u>	
Phonon mediated	Set: $\{ \langle \vec{k}_{\sigma} j Q(\vec{k}'' j'') \vec{k}_{\tau} j \rangle, $ or $\langle \vec{k} j \rangle_{(2)} Q(\vec{k}'' j'') \rangle$

(a) See my Handbuch article and references for more complete details.

$|\mathbf{k}_j\rangle$: Symmetry of electronic band eigenstates as on Fig.4
 $Q(\mathbf{k}_j)$: Phonon symmetry $D^{\mathbf{k}_j}$ as shown on Fig.5
in principal directions.

In order to satisfy the necessary conditions for non-vanishing matrix element, the wave vector rule must be obeyed. Thus if an interband optic absorption mediated via \vec{v} will occur, $\mathbf{k} \otimes \mathbf{k}'$ must contain \vec{v} : these are vertical transitions. In Fig.4 such a transition is labelled (2) taking an electron from $\mathbf{k}_1 + \mathbf{k}_4$ in an interband transition mediated by a photon (operator \vec{v}).

An example of a wave vector selection rule is given in Fig.3b showing $\mathbf{L} \otimes \mathbf{X} = 3 \mathbf{L}$. Such rules lend themselves nicely to geometrization. Some other wave vector rules for O_h^7 are given below:

Wave Vector Selection Rules

Ordinary

$$\mathbf{X} \otimes \mathbf{X} = 3\Gamma \oplus 2 \mathbf{X}$$

(Note since ℓ_j are all = 2, this must be taken as $12\Gamma \oplus 8 \mathbf{X}$)

$$\mathbf{L} \otimes \mathbf{X} = 3 \mathbf{L}$$

(but all $\ell_j = 2$ for X; $\ell_j = 1, \text{ or } 2$ for L; modify accordingly) .

Symmetrized

$$(\ell_j = 2 \quad \text{all cases for } \mathbf{X})$$

$$\mathbf{X}_{(2)} = 9\Gamma \oplus 4 \mathbf{X}$$

$$\mathbf{L}_{(3)} = 30 \mathbf{L}$$

The remainder of the reduction of the tensor products is to find the j , which occur. This also has been carried out and results are tabulated. We can cite and use the relevant results. Again refer to the Figs for clarification. We shall now give physical selection rules appropriate to the generic types of processes illustrated on Fig. 4. Also we shall give selection rules for optical excitation (absorption or scattering) of one or more phonons. It is to be understood that each point on each branch of the phonon dispersion curve, Fig.5 is a possible lattice vibration eigenstate: the high symmetry points are labelled and lower symmetry regions are given a branch indexing: the full irreducible label is given also for these branches.

Table II^(a)

Selection Rules: Processes in Ge

<u>A. Electronic</u>		
Interband Absorption (direct gap: vertical)	$\Gamma_{25+} \rightarrow \Gamma_{2-}$ $*L_{3-} \rightarrow *L_{1+}$ $*X_4 \rightarrow *X_1$	Allowed " "
Interband Scattering (electron 1 phonon) (hole 1 phonon) (electron 1 phonon)	$\Gamma_{2-} \rightarrow *L_{1+}$ $\Gamma_{25+} \rightarrow *L_{3-}$ $*X(1) \rightarrow *L(1+)$	L2- (LA phonon) L2- (LA phonon) and L3- (TO phonon) Lj (all L phonons)
Intraband ("intravalley" electron 1 phonon)	$L_{1+} \rightarrow L'1+$	L1+ (LO) or L2- (LA). (Omit Γ modes).
<u>B. Vibrational</u>		
Optical Absorption (1 phonon)	Excite Γ_{25+}	Forbidden
Optical Absorption (2 phonon combination)	Excite $*L_{j+} \oplus *L_{j'}-$	Allowed Optical
Optical Absorption (overtone)	Excite (2) Γ_{25+} (2) $*X_j$	Forbidden "
Raman Scattering (1 phonon)	Excite Γ_{25+}	Allowed
Raman Scattering (overtone)	Excite (2) Γ_{25+} (2) $*X_j$	Allowed "

^(a) See my Handbuch article and references for more complete details.

Examination of Table II shows that many physical processes can be strictly identified by using these selection rules. In actual practice these rules were used in conjunction with other experimental and theoretical evidence in order to:

- locate energy states (bands or phonons);
- assign symmetry designation to these eigenstates.

Because this is a very elaborate program we refer the reader to literature for detailed working out of this program for specific materials. A detailed discussion is given in my Handbuch article.

Let us summarize this part of our report by simply stating that we have attempted to illustrate the theme

"Group Theory at Work in the Physical World".

12. Configurational Instability - Spontaneous Space Group Symmetry Breaking

One of the most interesting and curious manifestations of spontaneous symmetry-breaking arises in molecules when one considers electronic and lattice displacement degrees of freedom simultaneously. The idea for this phenomenon seems to have originated with L.D. Landau, who suggested configurational instability to Jahn-Teller. The existence of this effect in molecules has been amply supported experimentally. The first extension to crystals was given by me in 1962 in which I showed the configurational instability argument applied mutatis mutandis to crystal space groups. Only two of the 230 Schoenflies-Fedorov groups were examined: diamond O_h^7 -Fd3m and zincblende T_d^2 -F43m structures; the extension to all space groups was claimed. In this section we will discuss this phenomenon in a manner equally applicable to molecules or crystals.

We consider the physical system with non-trivial isometry group G. Assume that G refers to the situation where all the nuclei (atoms or ions) are in their (average) high symmetry positions. The electronic Schrodinger equation for motion of an electron in the self-consistent potential due to the other electrons and the stationary ions is:

$$H \psi_\alpha^j = E^j \psi_\alpha^j; \alpha = 1, \dots, |D^j|$$

where $H(r, R)$ is the Hamiltonian with ion positions R held fixed. The isometry group G has irreducible representation D^j . We take the ground state electronic eigenfunctions to be members of the degenerate set $\{\psi_\alpha^j\}$. As before, the necessary degeneracy of the eigenstates is assumed. So, symmetry produces the degeneracy. Now we may ask - is the system, with electrons in degenerate state, stable under small deviations of the ions from high symmetry positions?

Suppose ions are displaced from their high symmetry positions. Any arbitrary small amplitude displacement can be decomposed into normal modes. For each normal mode $Q(j'a')$ present there will be a change in the electronic Hamiltonian. Assume an expansion of the Hamiltonian in a power series in the normal modes:

$$H(rR) = H(rR^0) + \sum_{j'a'} (\partial H / \partial Q(j'a'))_0 Q(j'a') + \dots$$

We only show linear terms but all orders appear. The individual coefficients, such as $(\partial H / \partial Q(j'a'))_0$ are functions of the electron coordinates r , but not of the nuclear coordinates, or normal modes $(j'a')$.

Now transform the system by element $g \in G$. The set of degenerate normal modes transforms as representation $D^{j'}$. Then terms

$$\sum_{\alpha'} (\partial H / \partial Q(j'a'))_0 Q(j'a')$$

transform into

$$\sum_{\alpha'} \sum_{\beta'} (\partial H / \partial Q(j'a'))_0 D^{j'}(g)_{\beta'a'} Q(j'\beta').$$

But this can be considered as if the $Q(j'\beta')$ are fixed, while the coefficients (as function of electron coordinate) transform as the adjoint representation to $D^{j'}$. Taking all representations real, or "physically real" we may take the set $(\partial H / \partial Q(j'a'))_0$ to transform as $D^{j'}$.

Our problem can be examined as a form of linear stability analysis using perturbation theory. The initial set of electronic eigenstates is $\{\psi_{\alpha}^{j'}\}$. The total Hamiltonian is

$$H = H(rR^0) + H' \equiv H(rR^0) + \sum (\partial H / \partial Q(j'a'))_0 Q(j'a')$$

with perturbation H' . The perturbed problem we wish to solve is

$$H \Psi = E \Psi$$

and we assume the true eigenfunction is expanded in the set of unperturbed eigenfunctions:

$$\Psi = \sum_{\alpha} A_{\alpha} \psi_{\alpha}^{j'}$$

The new (perturbed) eigenenergy is given as the solution of a secular equation of the form

$$|| H_{\alpha\beta} - E \delta_{\alpha\beta} || = 0$$

where

$$H_{\alpha\beta} = \langle j\alpha | H' | j\beta \rangle + E^j \\ = \sum_{\alpha'} Q(j'\alpha') \langle j\alpha | @ H/3 j'\alpha' \rangle_0 | j\beta \rangle + E^j$$

If the perturbed energy is of form

$$E = E^j + E_1^j Q(j'\alpha') + E_2^j (Q(j'\alpha'))^2 + \dots$$

then the initial configuration is unstable. For, if a term linear in $Q(j'\alpha')$ is present a quasiforce

$$- \partial E / \partial Q(j'\alpha') = F_{j'\alpha'}$$

will exist tending to distort the crystal from group G to the group G' which is the image of D^j . This is the origin of the "configurational instability". The electron occupying a state ψ_α^j , which is one partner in the degenerate manifold $\{\psi_\alpha^j\}$ spanning irreducible representation D^j , experiences this quasiforce tending to distort the system from its initial high symmetry G to the group G' which is a subgroup of G. Remark that the distortion will proceed until restoring forces, due to the terms in E bilinear in the $Q(j'\alpha)$, produce a new equilibrium (whose symmetry is G').

Schematically:

Symmetry Group G +
Necessary Degeneracy of Eigenstates
+ Virtual Perturbation +

Instability \rightarrow
 Symmetry Breaking to G' \rightarrow
 Restoration of Stability.

A sufficient condition for stability is if there is no term in E linear in $Q(j'a')$. But this requires that all off diagonal matrix elements $K'_{\alpha\beta} \equiv 0$ by symmetry, or

$$D_{(2)}^j \otimes D^{j'} \neq D^{1+}$$

That is the symmetrized square of D^j , the representation by which the degenerate electron states transforms, contains no representation in common with the phonon or lattice displacement representation $D^{j'}$.

Expressed in space group terminology we require of the reduction coefficients for $D_{(2)}^{*k_j} \otimes D^{*k'j'}$:

$$((^{*k_j})_{(2)} \otimes ^{*k'j'} | \Gamma 1+) = 0$$

The test for configurational instability in the electronic state ψ^{*k_j} requires evaluation of this coefficient. Using the various algorithms we gave above, the needed reduction coefficients can be found and configurational instability in each eigenstate of the system can be tested.

We found that in O_h^7 -Fd3m; T_d^2 -F43m:

"Almost all degenerate electronic states are configurationally unstable". "A consequent crystal distortion and splitting of the degeneracy are to be expected".

This result was established by examining by enumeration the reduction coefficients for irreducible representations with general orbit (general $*k$) as well as those with special orbit (high symmetry $*k$ lying on planes, or lines, or at points of special symmetry). Only a few of the points of high symmetry were found to be stable. Thus the use of the terminology "almost all" states are unstable.

The physical interpretation of this result is not as straightforward as in the molecular case. There, the electron in its degenerate electronic state may contribute an appreciable fraction of the total molecular binding energy so the destabilization due to configuration interaction may be very significant. For a crystal one electron, or even one single electron-like elementary excitation such as an exciton, may only contribute negligibly to the total binding. Our theorem however as well applies to the entire crystal eigenstate of the many - electrons should they be in a spatially degenerate state. These aspects require further elaboration.

It should be noted that a closely related situation has been investigated recently. It is the "cooperative Jahn-Teller effect", in which is interaction between localized degenerate orbital electronic states usually of rare earth ions, and the crystalline lattice symmetry is lost and electronic degeneracy is split. The relation between this effect and our theorem also needs elaboration.

13. A Conjecture: Accidental Degeneracy and Higher Dimensional Crystallographic Groups

It seems appropriate to close our survey at this conference on Crystallographic Groups with a conjecture about possible application of crystallographic groups in higher dimensions.

Recalling Fig. 4 we again remark that in actual calculations of eigenvalues such as electronic band $E_j(\vec{k})$ or phonon eigenfrequency $\omega(\vec{k}_j)$ it is often noted that surfaces of constant energy cross when not required to by symmetry. A crossing or touching produces a degeneracy: several eigenfunctions from different bands or branches have the same energy. Such a crossing is called "accidental degeneracy".

It was at first believed that such accidental degeneracy could be removed if the potential $V(\vec{r})$ in the electron Schrödinger equation were changed: $V(\vec{r}) \rightarrow V(\vec{r}) + \delta V(\vec{r})$, or if the force constants and thus the dynamical matrix $[D(\vec{k})]$ were perturbed: $[D(\vec{r})] \rightarrow [D(\vec{r})] + \delta [D(\vec{r})]$. Experience shows that it is not always possible to remove crossings by such numerical changes.

The investigation of the types of accidental degeneracy which could occur in a crystal: removable and non-removable, and possible relations to symmetry elements $g \in G(\vec{k})$, where \vec{k} is the wave vector at the point of accidental degeneracy, was first given by Herring in 1937, using a combination of perturbation theory and topological methods. He gave certain specific results on the structure of the surfaces of contact.

It is well known that in certain quantum mechanical problems such as the Kepler problem of a single electron moving in an inverse square (constant) force field, or the isotropic harmonic oscillator, accidental degeneracy occurs. For example, in the Kepler problem for Hydrogen atom with one electron in the coulomb field, the symmetry group is $O(3)$ - the orthogonal group in three dimensions. The irreducible representation of $O(3)$ are based on the surface spherical harmonics $Y_{\ell m}(\theta, \phi)$ and the dimension of irreducible representations is $(2\ell+1)$. But it is found by explicit solution of this Schrödinger Equation

$$(-\nabla^2 - e^2/r) \psi = E\psi$$

that the degeneracy of a given level is actually

$$n^2 = \sum_{l=0}^{n-1} (2l+1)$$

The explanation of this accidental degeneracy was first given by Fock and Bargmann and has been since discussed thoroughly. The above Schrödinger Equation can be Fourier transformed to "dual" space and then the resultant equation can be recognized as a four dimensional isotropic potential equation. The symmetry of this equation is $O(4)$ - the orthogonal group in four dimensions. The irreducible representations of $O(4)$ have indeed dimension n^2 , and the bases are the correct linear combination of the $Y_{lm}(\theta, \phi)$ for different l .

Motivated in part by these results, I conjectured that accidental degeneracy in energy bands or phonon dispersion in three dimensions was due to a "residue" of the hidden symmetry due to a covering four-dimensional crystallographic space group. Perhaps this is the residue of a three dimensional array of bare coulombian potentials, whose Fourier transformed problem is a four-dimensional crystal group. This direct approach of constructing such a model coulomb lattice and determining any hidden symmetry of the resultant Schrödinger Equation has not yet been implemented although I plan to return to it.

With Li -Ching Chen I examined a more indirect approach, which could be, and was, solved in a straightforward group theoretical fashion. Assuming the conjecture to be true we sought to examine consequences for three-dimensional groups embedded as subgroup in a suitable four-dimensional group assumed to be the hidden group of symmetry.

We considered the cubic crystal point group in four dimensions [45] of order 1152 which is a subgroup of the four-dimensional orthogonal group $O(4)$.

This group has a cubic subgroup denoted 47, of index 3 and in turn 47 has a subgroup of index 8 which is isomorphic to $O_h(3)$ the usual cubic point group in three dimensions. We determined all the projective inequivalent irreducible representations of 45: this includes the ordinary or vector representations of 45. We then consider the compatibility of representations by subduction

$$D^j \text{ of } 45 \rightarrow \oplus D^i \text{ of } O_h(3).$$

Recall that the allowable irreducible representation of $G(\vec{k})$ are projective irreducible representations of $G(\vec{k})/T$. Consequently we may

examine sticking of space group representations in $O_h(3)$ by studying subduction of the point group projective representations from 45 to $O_h(3)$.

We found that when a representation from 45 split, on going to $O_h(3)$, the components D^Y were of different parity. Conversely representations of different parity stick (touch) on going from $O_h(3)$ to 45. A second general feature is that when representations of 45 split, there was no multiplicity: a given D^Y only occurs once. The latter result implies, or is consistent with, the "no crossing" rule: two states of the same symmetry originating from a particular eigenvalue - eigenvector problem cannot cross as the potential is continuously varied in magnitude not changing its symmetry. These "no crossing rules" are well known in both molecular and solid state crystal eigenvalue problems with the original theoretical investigation dating back to Von Neumann and Wigner.

It appears that the one specific example which we studied - subduction in the chain of subgroups $45 + 47 + O_h(3)$ does not give a result in disagreement with the conjecture that accidental degeneracy or crossing of bands in three-dimensional crystal group theory may reflect a higher four-dimensional symmetry.

On this note of a possible application in three dimensional crystal physics for the growing knowledge of crystallographic groups in four-dimensional (or even higher dimensional) space I conclude this paper.

14. Acknowledgement

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15. References

Selected references will be given to a few texts, or original articles. The references are arranged to correspond to the numbered Sections in this article.

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