Group theory and the classification of elementary excitations in crystals

Dr. Thomas Strohm

August 1999 (extracted from PhD thesis, Nov 2004)

Abstract

This publication presents the most important elements of group theory as seen from a solid state physicist's perspective. Examples are taken mostly from crystallography. Classification of phonons in crystals is discussed and applied to Raman scattering.

Contents

1 Motivation. The "why?" of group theory

In solid state physics there are a lot of complicated measurable quantities (observables) which depend crucially on the symmetry of the crystal under investigation. The 3×3 *dielectric tensor* ε_{ij} provides examples of such quantities. It is a symmetrical tensor and therefore consists of 6 complex independent components. Symmetries of the crystal further reduce the number of independent quantities in the dielectric tensor. To figure out the exact number of independent components in case of crystals with complicated structure is by no means a simple task.

Another interesting quantity is the 4th rank tensor $c_{\mu\nu\rho\sigma}$ representing the *elastic constants*. In triclinic systems this tensor has 21 independent real components which are reduced to only 3 in cubic materials. Group theory[1] provides the means to investigate these questions systematically.

Group theory is also used to classify and characterize the various crystal structure and plays a very important role in the classification of electronic and vibrational states in crystals. In doing so it detects and explains symmetry-caused degeneracies of states. Last but not least, group theory is used to eludicate selections rules for light absorption and Raman scattering among other things.

2 Definition of a group. Basic properties

Groups. A *group* $\mathcal{G}$ is a set of elements $\mathcal{G} = \{G_1, \ldots, G_g\}$ together with a mapping $\circ\colon \mathcal{G} \times \mathcal{G} \to \mathcal{G}$ called *group multiplication*. The latter satisfies the following *group axioms*:

(A) *Associativity:* For all $A, B, C \in \mathcal{G}$:

$$A \circ (B \circ C) = (A \circ B) \circ C$$

(N) *Existence of a neutral element* (also *unit element* or *identity element*): There is an element $E \in \mathcal{G}$ such that for each $G \in \mathcal{G}$:

$$E \circ G = G \circ E = G$$

[1] Introductions to group theory are given in [1, 2, 3, 4, 5].

(I) *Existence of an inverse element*: For each $G \in \mathcal{G}$ there is an element $G^{-1} \in \mathcal{G}$ such that

$$G \circ G^{-1} = G^{-1} \circ G = E$$

If in addition to these three axioms[2] also the commutativity holds, then the group is called a *commutative* or *Abelian group*:

(C) *Commutativity:* For all $A, B \in \mathcal{G}$:

$$A \circ B = B \circ A$$

If a group has a finite number of elements it is called a *finite group*, otherwise it is an *infinite group*. The number of elements g of a finite group $\mathcal{G}$ is called the *order of the group*.

Example: $\boldsymbol{C_{3v}}$. A very instructive example of a group is the group of symmetry operations of an equilateral triangle (see Fig. 1). These symmetry operations are rotations by 0°, 120°, and 240° (denoted by E, C_3 and C_3^{-1}, latter is the inverse element of C_3) with rotation axis perpendicular to the triangle through its center C. The reflections at planes perpendicular to the triangle and passing through an edge and the center of the side opposite to it are also symmetry operations, we denote these by σ_1, σ_2, and σ_3 (see Fig. 1). These symmetry operations of the triangle form the group $\boldsymbol{C}_{3v} = \{E, C_3, C_3^{-1}, \sigma_1, \sigma_2, \sigma_3\}$, the multiplication is defined by means of successive application of the symmetry operations; it is tabulated in the *multiplication table* of the group $\boldsymbol{C}_{3v}$ in Tab. 1.

The multiplication table maps each pair of group elements to another group element and therefore represents the mapping $\circ\colon \mathcal{G} \times \mathcal{G} \to \mathcal{G}$. Associativity holds. The group element E is the unit element and the fact that E appears exactly once in every column and row of the multiplication table shows that every element of the group has one and only one inverse element. Furthermore note that $\sigma_1\sigma_2 = C_3$, but $\sigma_2\sigma_1 = C_3^{-1}$, that is, the group is not commutative (not Abelian).

Subgroups. By inspecting the multiplication table, it can be seen that the subset

$$\boldsymbol{C}_3 = \{E, C_3, C_3^{-1}\}$$

[2]Actually, in (N) only $E \circ G = G$ is an axiom. The property $G \circ E = G$ is a consequence of this is the other axioms. This is similar for (I). See [1].

$\boldsymbol{C}_{3v}$	E	C_3	C_3^{-1}	σ_1	σ_2	σ_3
E	E	C_3	C_3^{-1}	σ_1	σ_2	σ_3
C_3	C_3	C_3^{-1}	E	σ_3	σ_1	σ_2
C_3^{-1}	C_3^{-1}	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	C_3^{-1}
σ_2	σ_2	σ_3	σ_1	C_3^{-1}	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	C_3^{-1}	E

Table 1: Multiplication table of the group $\boldsymbol{C}_{3v}$. The table entries are $a \circ b$, where a is given in the first row, and b is given in the first column of the table.

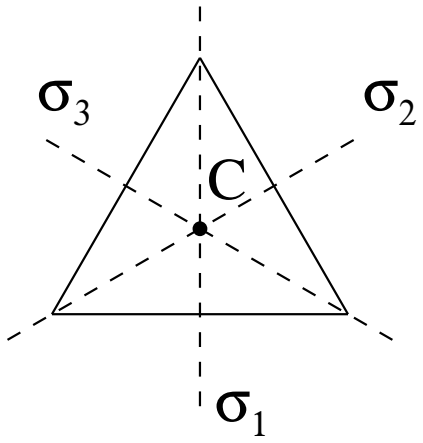

Figure 1: Mirror planes of an equilateral triangle.

of the group $\boldsymbol{C}_{3v}$ is a group of its own. (Note that the group itself and one of its elements both are denoted by the symbol C_3 in the literature. Usually it is clear from the context, whether the group or the symmetry operation is meant. To remove any ambiguity we denote the groups using boldface letters). A subset $\mathcal{H}$ of a group $\mathcal{G}$ which is also a group with respect to the multiplication in $\mathcal{G}$ is called a *subgroup* of $\mathcal{G}$. The subsets $\{E\}$ containing just the unit element of $\mathcal{G}$, and the "subset" $\mathcal{G}$ consisting of the full group $\mathcal{G}$ are the *trivial subgroups* of $\mathcal{G}$, all other subgroups are called *proper subgroups*. The group $\boldsymbol{C}_3$ has an interesting property. By applying C_3 repeatedly, all the group elements of $\boldsymbol{C}_3$ can be generated: $C_3 \circ C_3 = C_3^{-1}$ and $C_3 \circ C_3 \circ C_3 = E$ (Tab. 2, left panel). Therefore, $\boldsymbol{C}_3$ is called a *cyclic group* and the symmetry operation C_3 its *generating element*. Obviously, cyclic groups are always commutative (Abelian).

Isomorphism. Consider now the set $\mathbb{C}_3$ consisting of the three third roots of one, 1, $\alpha \equiv \exp(\frac{2\pi}{3}i)$, and $\alpha^2 \equiv \exp(\frac{4\pi}{3}i)$ with the complex multiplication as mapping (Tab. 2, right panel). This set forms a group. It is cyclic and of order 3 just as the group $\boldsymbol{C}_3$. Furthermore its multiplication table shows exactly the same structure as that of the $\boldsymbol{C}_3$ group (Table 2). The groups $\boldsymbol{C}_3$ and $\mathbb{C}_3$ are therefore called *isomorphic groups*. If a mapping $f\colon \mathcal{G} \to \mathcal{G}'$ exists between two groups $\mathcal{G}$ and $\mathcal{G}'$ that maps the elements $G \in \mathcal{G}$ to the elements $G' \in \mathcal{G}'$, that is, $G' = f(G)$, and has the property

$$f(G_i G_j) = f(G_i) f(G_j)$$

for arbitrary elements $G_i, G_j \in \mathcal{G}$, then the mapping f is called a *homomorphism* and the groups $\mathcal{G}$ and $\mathcal{G}'$ are called *homomorphic*, $\mathcal{G} \sim \mathcal{G}'$. The mapping $f\colon \boldsymbol{C}_3 \to \mathbb{C}_3$ given by $f(E) = 1$, $f(C_3) = \alpha$, and $f(C_3^{-1}) = \alpha^2$ has these properties but, in addition, the mapping is a one-to-one correspondence between the elements of the groups $\mathcal{G}$ and $\mathcal{G}'$. This is why such mapping is usually called an *isomorphism* and the groups are called *isomorphic*. Isomorphic groups can be considered equal, mathematically they have the same structure.

The definitions introduced so far are sufficient for an understanding of most of the theory of representations of *point groups*. In order to discuss the symmetry properties of *space groups* we need to introduce the following additional definitions and properties of groups.

Cosets. Let us come back to the $\boldsymbol{C}_{3v}$ group. The subset $\mathcal{H} = \{E, \sigma_1\}$ of $\boldsymbol{C}_{3v}$ is a subgroup of $\boldsymbol{C}_{3v}$, called $\boldsymbol{C}_s$. We can construct other subsets of

$\boldsymbol{C}_3$	E	C_3	C_3^{-1}
E	E	C_3	C_3^{-1}
C_3	C_3	C_3^{-1}	E
C_3^{-1}	C_3^{-1}	E	C_3

$\mathbb{C}_3$	1	α	α^2
1	1	α	α^2
α	α	α^2	1
α^2	α^2	1	α

Table 2: Multiplication tables of the groups $\boldsymbol{C}_3$ and $\mathbb{C}_3$.

$\boldsymbol{C}_{3v}$, the so-called *right cosets* by multiplying all elements of the subgroup $\mathcal{H}$ of $\mathcal{G}$ with a fixed element $G \in \mathcal{G}$ on the right,

$$\mathcal{H}G \equiv \{HG \mid H \in \mathcal{H}\} \ .$$

The element $G \in \mathcal{G}$ is called the *coset representative* of the coset $\mathcal{H}$.

The right cosets of $\boldsymbol{C}_{3v}$ are $\mathcal{H}\sigma_2 = \{\sigma_2, C_3\}$ and $\mathcal{H}\sigma_3 = \{\sigma_3, C_3^{-1}\}$ (note that $\mathcal{H}C_3 = \{C_3\sigma_2\} = \mathcal{H}\sigma_2$ etc.). The conjunction of the elements of the three cosets $\mathcal{H}$, $\mathcal{H}\sigma_2$, and $\mathcal{H}\sigma_3$ together contains all the elements of the group $\boldsymbol{C}_{3v}$. The relation

$$\boldsymbol{C}_{3v} = \mathcal{H} + \mathcal{H}\sigma_2 + \mathcal{H}\sigma_3 \ , \quad \mathcal{H} = \{E, \sigma_1\}$$

is called the *decomposition of* $\boldsymbol{C}_{3v}$ *into right cosets* with respect to the subgroup $\mathcal{H}$. Another right coset decomposition of $\boldsymbol{C}_{3v}$ is the one with respect to the subgroup $\boldsymbol{C}_3$, given by

$$\boldsymbol{C}_{3v} = \boldsymbol{C}_3 + \boldsymbol{C}_3\sigma_1 \ , \quad \boldsymbol{C}_3 = \{E, C_3, C_3^{-1}\} \ .$$

The definition of *left cosets* and the *decomposition into left cosets* is analogous to the one given above for right cosets. Note that two cosets $\mathcal{H}A$ and $\mathcal{H}B$ for $A, B \in \mathcal{G}$ are either identical or do not contain any common elements (they are *disjunct sets*).

Let g and h denote the order of the group $\mathcal{G}$ and its subgroup $\mathcal{H}$, respectively, and l the number of cosets in the coset decomposition of $\mathcal{G}$ with respect to $\mathcal{H}$, called the *index* of $\mathcal{H}$ in $\mathcal{G}$. Then the relation $g = hl$ holds. An interesting consequence of this relationship is that a group with prime order does not have proper subgroups.

Conjugate classes. For the theory of representations of a group, the central part of this chapter, the notion of the *conjugate classes* is important. We define a relation on the group $\mathcal{G}$. Two elements A and B of $\mathcal{G}$ are called

conjugate, if there exists an element G of $\mathcal{G}$ such that $B = GAG^{-1}$. We represent conjugation of two elements as $A \sim B$, explicitly

$$A \sim B \quad \text{if and only if there is a } G \in \mathcal{G} \text{ such that } \quad A = GBG^{-1} \ . \qquad (1)$$

The properties of the conjugation are the *reflectivity (r)* which states that $A \sim A$, then the *symmetry (s)* implying $A \sim B$ if $B \sim A$, and the *transitivity (t)* which expresses the fact that if $A \sim B$ and $B \sim C$ ($C \in \mathcal{G}$), then $A \sim C$ holds. These are the axioms of a *relation*. Relations decompose sets into *disjunct subsets* called *classes*. The decomposition of sets into classes is called *classification* of the set with respect to the given relation. The group $\boldsymbol{C}_{3v}$ decomposes into the three classes

$$\mathcal{C}_1 = \{E\} \ , \quad \mathcal{C}_2 = \{C_3, C_3^{-1}\} \ , \quad \text{and} \quad \mathcal{C}_3 = \{\sigma_1, \sigma_2, \sigma_3\}$$

containing the unit element, the rotations, and the reflections, respectively.

The coset decomposition and the classification of groups are two methods to decompose groups into disjunct subsets the composition of which covers the whole group.

Now we construct the sets

$$G\mathcal{H}G^{-1} = \{GHG^{-1} \colon H \in \mathcal{H}\}$$

for a *fixed* element $G \in \mathcal{G}$. These sets turn out to be subgroups of $\mathcal{G}$, and are called *conjugate subgroups* of $\mathcal{H}$. The conjugate subgroups of the trivial subgroup $\{E\}$ as well as the proper subgroup $\boldsymbol{C}_s = \{E, \sigma_1\}$, and $\boldsymbol{C}_3 = \{E, C_3, C_3^{-1}\}$ of $\boldsymbol{C}_{3v}$ with respect to a element $G \in \mathcal{G}$ are given in Tab. 3. The conjugate subgroups of the trivial subgroup $\{E\}$ and $\boldsymbol{C}_3$ are the subgroups themself. This leads to the definition of the invariant subgroups.

Invariant subgroups. If all the conjugate elements to each element of the subgroup $\mathcal{H}$ of $\mathcal{G}$ are contained in $\mathcal{H}$, that is, if $G\mathcal{H}G^{-1} \in \mathcal{H}$ is fulfilled for *all* $G \in \mathcal{G}$, we call $\mathcal{H}$ an *invariant subgroup* of $\mathcal{G}$, also *normal divisor* ("Normalteiler" in German) or *normal subgroup*. In this case, $\mathcal{H}$ is composed out of classes of $\mathcal{G}$. The invariant subgroups of $\boldsymbol{C}_{3v}$ are the trivial ones, $\{E\}$ and $\mathcal{G}$, as well as the proper subgroup $\boldsymbol{C}_3 = \mathcal{C}_1 \cup \mathcal{C}_2$ (see Tab. 3). Note that $G\mathcal{H}G^{-1} \in \mathcal{H}$ implies $G\mathcal{H}G^{-1} = \mathcal{H}$ which also can be written in the form $G\mathcal{H} = \mathcal{H}G$ and expresses the fact that for invariant subgroups $\mathcal{H}$ left and right cosets are identical and therefore the left and right coset decompositions are equivalent.

$G\mathcal{H}G^{-1}$	$\mathcal{H}=\{E\}$	$\mathcal{H}=\{E,\sigma_1\}$	$\mathcal{H}=\{E,C_3,C_3^{-1}\}$
E	$\{E\}$	$\{E,\sigma_1\}$	$\{E,C_3,C_3^{-1}\}$
C_3	$\{E\}$	$\{E,\sigma_2\}$	$\{E,C_3,C_3^{-1}\}$
C_3^{-1}	$\{E\}$	$\{E,\sigma_3\}$	$\{E,C_3,C_3^{-1}\}$
σ_1	$\{E\}$	$\{E,\sigma_1\}$	$\{E,C_3,C_3^{-1}\}$
σ_2	$\{E\}$	$\{E,\sigma_3\}$	$\{E,C_3,C_3^{-1}\}$
σ_3	$\{E\}$	$\{E,\sigma_2\}$	$\{E,C_3,C_3^{-1}\}$

Table 3: Conjugate classes of some subgroups of $\boldsymbol{C}_{3v}$.

Using the notation of invariant subgroups, we can define new groups, the *factor groups*. Consider a group $\mathcal{G}$ of order g and an invariant subgroup $\mathcal{N}$ of $\mathcal{G}$ of order n. The coset decomposition is

$$\mathcal{G}=\mathcal{N}E+\mathcal{N}G_2+\cdots+\mathcal{N}G_l\ ,\quad G_i\in\mathcal{G}$$

with $l=g/n$. For two cosets $\mathcal{N}A$ and $\mathcal{N}B$ with $A,B\in\mathcal{G}$ a multiplication can be defined by[3]

$$\mathcal{N}A\cdot\mathcal{N}B\equiv\{NANB\colon M,N\in\mathcal{N}\}\ .$$

It can easily be seen that this set is the coset represented by AB, that is,

$$\mathcal{N}A\cdot\mathcal{N}B=\mathcal{N}(AB)$$

and, consequently, the product of two cosets is also a coset. The cosets of a coset decomposition with respect to an invariant subgroup form a group under the multiplication defined above. This group is called the *factor group* (or *quotient group*) of $\mathcal{G}$ with respect to the invariant subgroup $\mathcal{N}$, denoted by $\mathcal{G}/\mathcal{N}$. (This notation motivates the name *normal divisor* for an invariant subgroup).

As an example we mention the coset decomposition of the group $\boldsymbol{C}_{3v}$ with respect to its invariant subgroup $\boldsymbol{C}_3$,

$$\boldsymbol{C}_{3v}=\boldsymbol{C}_3+\boldsymbol{C}_3\sigma_1$$

[3]repeated elements in $\{NANB\colon M,N\in\mathcal{N}\}$ are considered to be removed.

$\boldsymbol{C}_{3v}/\boldsymbol{C}_3$	$\boldsymbol{C}_3$	$\boldsymbol{C}_3\sigma_1$
$\boldsymbol{C}_3$	$\boldsymbol{C}_3$	$\boldsymbol{C}_3\sigma_1$
$\boldsymbol{C}_3\sigma_1$	$\boldsymbol{C}_3\sigma_1$	$\boldsymbol{C}_3$

Table 4: Multiplication table of the factor group $\boldsymbol{C}_{3v}/\boldsymbol{C}_3$.

$\boldsymbol{D}_4$	E	C_4	C_2	C_4^{-1}	C_{2x}	C_{2y}	$C_{2x'}$	$C_{2y'}$
E	E	C_4	C_2	C_4^{-1}	C_{2x}	C_{2y}	$C_{2x'}$	$C_{2y'}$
C_4	C_4	C_2	C_4^{-1}	E	$C_{2x'}$	$C_{2y'}$	C_{2y}	C_{2x}
C_2	C_2	C_4^{-1}	E	C_4	C_{2y}	C_{2x}	$C_{2y'}$	$C_{2x'}$
C_4^{-1}	C_4^{-1}	E	C_4	C_2	$C_{2y'}$	$C_{2x'}$	C_{2x}	C_{2y}
C_{2x}	C_{2x}	$C_{2y'}$	C_{2y}	$C_{2x'}$	E	C_2	C_4^{-1}	C_4
C_{2y}	C_{2y}	$C_{2x'}$	C_{2x}	$C_{2y'}$	C_2	E	C_4	C_4^{-1}
$C_{2x'}$	$C_{2x'}$	C_{2x}	$C_{2y'}$	C_{2y}	C_4	C_4^{-1}	E	C_2
$C_{2y'}$	$C_{2y'}$	C_{2y}	$C_{2x'}$	C_{2x}	C_4^{-1}	C_4	C_2	E

Table 5: Multiplication table of the group $\boldsymbol{D}_4$.

which defines the factor group $\boldsymbol{C}_{3v}/\boldsymbol{C}_3$. This is a group of order 2 (and therefore cyclic, commutative and isomorphic to the group $\{1, -1\}$ with real number multiplication). The multiplication table is given in Tab. 4.

Direct product. We can do the other way around and construct "larger" groups by using the *direct product*. Given two groups $\mathcal{G} = \{G\}$ and $\mathcal{G}' = \{G'\}$ of order g and g' and a commutative multiplication $GG' = G'G$. Then the gg' pairs GG' form a group called the *direct product group* $\mathcal{G} \times \mathcal{G}'$.

3 An important example for HTCS's: The tetragonal $\boldsymbol{D}_{4h}$ group

We start by describing the tetragonal $\boldsymbol{D}_4$ group which turns out to be a subgroup of $\boldsymbol{D}_{4h}$, namely the group of all *proper* rotations of $\boldsymbol{D}_{4h}$. This group contains a four-fold rotation axis (E, C_4, C_2, C_4^{-1}) and perpendicular to it four two-fold axes $(C_{2x}, C_{2x'}, C_{2y}, C_{2y'})$ which are the symmetry operations of the object in Fig. 2, left panel and is of order 8. The multiplication table

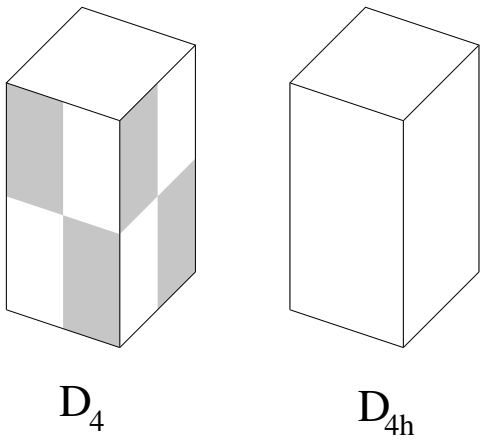

Figure 2: The tetragonal $\boldsymbol{D}_4$ and $\boldsymbol{D}_{4h}$ point groups.

is given in Tab. 5.

Next the classes are determined. The symmetry operation E forms its own class as the operation C_2 does. The C_4 and C_4^{-1} operations form the class called $2C_4$. The C_{2x} and C_{2y} operations constitute the class $2C_2'$ and the $C_{2x'}$ and $C_{2y'}$ operations constitute the class $2C_2''$. Therefore the $\boldsymbol{D}_4$ group has a total number of $n_c = 5$ classes.

Each of the 5 two-fold rotations forms together with the identity E a subgroup of order 2 of the $\boldsymbol{D}_4$ group. All these 5 subgroups are isomorphic to the group $\boldsymbol{C}_2 = \{E, C_2\}$. Furthermore, there are three subgroups of order 4. These are the groups $\boldsymbol{D}_2 = \{E, C_2, C_{2x}, C_{2y}\}$, the group $\{E, C_2, C_{2x'}, C_{2y'}\}$ which is isomorphic to $\boldsymbol{D}_2$, and the cyclic group $\boldsymbol{C}_4 = \{E, C_4, C_2, C_4^{-1}\}$. The five subgroups of order 2 and the latter 3 subgroups of order 4 exhaust the number of proper subgroups of $\boldsymbol{D}_4$. Invariant subgroups are subgroups which consist of classes. The subgroups $\boldsymbol{C}_2$, $\boldsymbol{C}_4$ and $\boldsymbol{D}_2$ are the invariant (proper) subgroups of $\boldsymbol{D}_4$, their decomposition in classes is given by

$$\begin{aligned}
\boldsymbol{C}_2 &= E \cup 2C_2 \\
\boldsymbol{C}_4 &= E \cup 2C_4 \cup C_2 \\
\boldsymbol{D}_2 &= E \cup C_2 \cup 2C_2' \ .
\end{aligned}$$

Using these 3 classes to perform a coset decomposition of $\boldsymbol{D}_4$, we get

$$\begin{aligned}\boldsymbol{D}_4 &= \boldsymbol{C}_4 + \boldsymbol{C}_4 C_{2x} \\ \boldsymbol{D}_4 &= \boldsymbol{D}_2 + \boldsymbol{D}_2 C_4 \\ \boldsymbol{D}_4 &= \boldsymbol{C}_2 + \boldsymbol{C}_2 C_4 + \boldsymbol{C}_2 C_{2x} + \boldsymbol{C}_2 C_{2x'}\end{aligned}$$

and the factor groups $\boldsymbol{D}_4/\boldsymbol{C}_4$, $\boldsymbol{D}_4/\boldsymbol{D}_2$, and $\boldsymbol{D}_4/\boldsymbol{C}_2$. The first two are isomorphic to the group $\boldsymbol{C}_2$, the last one is isomorphic to the group $\boldsymbol{C}_4$.

4 Representations of a group

With respect to applications, especially calculations with a computer, it is very handy to have a one-to-one correspondence between an abstract group under consideration, and a group of matrices, consisting of real or complex numbers, which "shares some properties" with the former group. These correspondences are investigated in the theory of group representations.

Representations. Let $\mathcal{G}$ be a finite group of order g and $\mathcal{M}$ the set of non-singular complex $n \times n$ square matrices, which, taking the matrix multiplication as the group multiplication, constitute a group called the *complex general linear group of order* n, denoted $GL(n, \mathbb{C})$. Furthermore let $D\colon \mathcal{G} \to \mathcal{M}$ be a mapping with the property of being *homomorphic*, that is,

$$AB = C \quad \Rightarrow \quad \hat{D}(A)\hat{D}(B) = \hat{D}(C) \tag{2}$$

for $A, B, C \in \mathcal{G}$. Then, the set $\mathcal{M} = \{\hat{D}(G)\colon G \in \mathcal{G}\}$ of matrices is called a *representation* of the group $\mathcal{G}$. The *dimension* d_α of a representation α is the size n of the matrices.

Putting $A = E$ or $C = E$, respectively, in the former equation, we immediately see that $\hat{D}(E) = \hat{1}$, the unit element of $\mathcal{G}$ is represented by the unit matrix. Moreover, $\hat{D}(A^{-1}) = \hat{D}(A)^{-1}$, that is, the matrix representing the inverse of a group element is the inverse of the matrix representing the group element itself.

If the mapping $\hat{D}$ is *isomorphic*, that is, homomorphic but one-to-one in both directions, then the representation is called *faithful*. Each group has a trivial representation, the *identity representation* given by the "1×1 matrix" $\hat{D}(G) = 1$ for all $G \in \mathcal{G}$. If the order of $\mathcal{G}$ is larger than 1, then this representation is obviously a homomorphism, not an isomorphism.

Example. To clarify the definitions and properties given, the point group $\boldsymbol{C}_4$ consisting of a single 4-fold rotation axis will serve. This is a cyclic group (and therefore Abelian) of order 4 with the elements E, C_4, C_2, and C_4^{-1} and is a subgroup of $\boldsymbol{D}_4$ (see Tab. 5). It is easy to see, that the 2×2 rotation matrices with rotations by 0, $\pi/2$, π, and $3\pi/2$ constitute a representation of the group $\boldsymbol{C}_4$:

$$\begin{aligned} \hat{D}(E) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , \qquad \hat{D}(C_4) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} , \\ \hat{D}(C_2) &= \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} , \qquad \hat{D}(C_4^{-1}) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} . \end{aligned} \tag{3}$$

This representation is faithful and also a *unitary representation*, because all constituent matrices are unitary. Instead of doing calculations using the elements G of the group $\mathcal{G}$, we can use, for many purposes, the representation matrices $\hat{D}(G)$.

Equivalent representations. Given a representation D_1, we can easily construct others. One method is to take the matrices $\hat{D}_2(G) = \hat{M}^{-1}\hat{D}_1(G)\hat{M}$ for all G in $\mathcal{G}$ and for a given non-singular matrix $\hat{M}$. It is easy to show that this set $\{\hat{D}_2(G) \colon G \in \mathcal{G}\}$ is also a representation of the group $\mathcal{G}$ isomorphic to D_1. As a consequence, a group has an infinite number of representations, most of them generated in a trivial way from others. To get rid of the seeming redundancy, we define an *equivalence relation* which relates representations which can be generated from each other in a trivial way. This relation decomposes the set of all representations into equivalence classes. Afterwards, we only consider these equivalence classes.

Two representation $\hat{D}_1$ and $\hat{D}_2$ are called *equivalent*, if there is a non-singular matrix $\hat{M}$ such that

$$\hat{D}_1(G) = \hat{M}^{-1}\hat{D}_2(G)\hat{M} , \qquad \text{for all } G \in \mathcal{G}. \tag{4}$$

Two representations which are not equivalent are called *inequivalent*.

Direct sum. Another method to construct new representation from existing ones is to form the set of diagonal matrices $\hat{D}(G) = \mathrm{diag}(\hat{D}_1(G), \hat{D}_2(G))$ from two representations D_1 and D_2 which also is a representation and called the *direct sum* $D = D_1 + D_2$ of the representation D_1 and D_2. For a representation to be used in a calculation, is should be as simple as possible, so we will investigate whether it is possible to decompose a given representation

into the direct sum of two or more representations. This is the central aim of the theory of group representations.

A representation which has the property that all of its representation matrices $\hat{D}$ can be written in the block form

$$\hat{D} = \begin{pmatrix} \hat{A} & \hat{0} & \hat{0} & \cdots \\ \hat{0} & \hat{B} & \hat{0} & \cdots \\ \hat{0} & \hat{0} & \hat{C} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

with blocks of the same size for all matrices of the representation is called a *reducible representation*. The reduction of a given reducible representation into irreducible representations is assisted by a number of important theorems stated in the next section.

5 Theorems about representations

If a crystal possesses a certain point group symmetry $\mathcal{G}$, then the Hamiltonian of the crystal (in absence of external fields and strong spin-orbit coupling) is invariant with respect to this group. Two electronic wave functions (with quasimomentum $\boldsymbol{k} = 0$) which are related by the transformation given by a group element therefore have the same energy eigenvalue, they are degenerate. The same is true for $\boldsymbol{k} = 0$ vibrational patterns. If there is no accidental degeneracy, the wave functions (or vibrational patterns) which belong to a given energy eigenvalues can be classified according to irreducible representations of the point group $\mathcal{G}$. Irreducible representations on the other hand are classified using their characters. This classification is contained in character tables, which are constructed by applying the theorems to be presented in this section. Proofs in general will be omitted, in this case references will be given.

Unitarization of a representation: Every representation of a finite group is equivalent to a unitary representation.

This is a very important theorem, with many consequences. As an example consider a 1-dimensional representation. The latter theorem implies that the 1×1 matrices of the representation can all be taken to have absolute value 1, that is, can be written in the form $\exp(i\varphi)$. In addition, this theorem allows us to consider only unitary representations. From now on, we only

consider *unitary, inequivalent, and irreducible representations (IRs).*[4]

Characters. The *character* $\chi^{(D)}(G)$ of a group element $G \in \mathcal{G}$ with respect to an IR D is given by the trace of the representation matrix $\hat{D}(G)$,

$$\chi(G) = \mathrm{Tr}\,\hat{D}(G) = \sum_{i=1}^{d_D} D_{ii}(G) \ ,$$

where d_D is the dimension of the representation D. Because of the property $\chi(\hat{M}\hat{D}\hat{M}^{-1}) = \chi(\hat{D})$, the character of a group element G is the same for all equivalent representations. The set of characters $\{\chi^{(D)}(G)\colon G \in \mathcal{G}\}$ is called the *character of the representation* D (and all equivalent ones).

The characters of the representation (3) of $\boldsymbol{C}_4$ are

$$\chi(E) = 2 \ , \quad \chi(C_4) = 0 \ , \quad \chi(C_4^2) = -2 \ , \quad \chi(C_4^{-1}) = 0 \ .$$

Note that the character of the unit element E with respect to an IR D is the dimension d_D of the IR. It gives the essential degeneracy of states belonging to D.

We have seen that two elements $A, B \in \mathcal{G}$ are conjugated if an element $G \in \mathcal{G}$ exists, such that $A = GBG^{-1}$. For the IR D then $\hat{D}(A) = \hat{D}(G)\hat{D}(B)\hat{D}(G^{-1})$ is valid and because of $\hat{D}(G^{-1}) = \hat{D}(G)^{-1}$ and the property $\mathrm{Tr}(ABC) = \mathrm{Tr}(CAB)$ of the trace of matrices, the character of A is equal to that of B. Consequently the character of all group elements belonging to the same class is the same.

The character of an IR is its characteristic feature and can be used to identify the (inequivalent) IRs of a group. To determine the characters of the IRs of a group, some theorems are useful.

Dimensions of the IRs: The dimensions d_D of the IRs of a group $\mathcal{G}$ of order g obey the relation

$$\sum_D d_D^2 = g \ . \tag{5}$$

This is a very useful theorem; for groups with small g the dimensions d_D of all IRs can often be determined already by inspection of (5). The $\boldsymbol{C}_4$ group is of order $g = 4$. One IR is the trivial one of dimension $d = 1$. Only $1^2 + 1^2 + 1^2 + 1^2 = 4$ satisfies (5) and, consequently, the $\boldsymbol{C}_4$ group has 4 IRs of dimension 1 each. The representation given in (3) is therefore reducible.

[4] In the literature, unitary, inequivalent, and irreducible representations are usually abbreviated by "REP." We use the abbreviation "IR" to stress the property of *irreducibility.*

First Orthogonality of Characters: The characters of an irreducible representation of a finite group satisfy the orthogonality relation

$$\sum_{i=1}^{n_c} h_i \chi^{(\alpha)}(\mathcal{C}_i)^* \chi^{(\beta)}(\mathcal{C}_i) = g\delta_{\alpha\beta} \ , \tag{6}$$

the summation runs over all n_c classes $\mathcal{C}_i$ of group elements, $\chi^{(\alpha)}(\mathcal{C})$ denotes the character of a group element G of class $\mathcal{C}$ in the representation $D^{(a)}$.

Second Orthogonality of Characters: The characters of an irreducible representation of a finite group satisfy the orthogonality relation

$$\sum_{\alpha=1}^{n_r} \chi^{(\alpha)}(\mathcal{C}_i)^* \chi^{(\beta)}(\mathcal{C}_j) = \frac{g}{h_i}\delta_{ij} \ , \tag{7}$$

the summation runs over all n_r IRs of the group and h_i is the number of group elements contained in the same class as G_i.

Characters $\chi^{(\alpha)}(\mathcal{C})$ of irreducible representations are functions of the representations $D^{(\alpha)}$, $\alpha = 1 \ldots n_r$ and the class $\mathcal{C}_i$ of elements of the group, $i = 1 \ldots n_c$.

Number of IRs: The number N_r of inequivalent irreducible representations of a finite group $\mathcal{G}$ is equal to the number of classes n_c of group elements.

The characters of the n_c classes of group elements with respect to the n_r IRs are usually arranged in the *character table* of the group $\mathcal{G}$.

If we regard $(h_i/g)\chi^{(\alpha)}(\mathcal{C}_i)$ as components of n_c-dimensional vectors $\boldsymbol{v}^{(\alpha)} = ((h_i/g)\chi^{(\alpha)}(\mathcal{C}_i))$ with $i = 1 \ldots n_c$ or $\boldsymbol{v}_i = ((h_i/g)\chi^{(\alpha)}(\mathcal{C}_i)$ with $\alpha = 1 \ldots n_r$, the orthogonality theorems state that $\boldsymbol{v}^{(\alpha)}\boldsymbol{v}^{(\beta)} = \delta_{\alpha\beta}$ and $\boldsymbol{v}_i\vec{v}_j = \delta_{ij}$, that is, considered as rows or columns, they are orthonormal.

6 Example: Character table of the C_{4v} group

To give an example for the construction of character tables using the rules stated in the last section, we focus on the $\boldsymbol{C}_{4v}$ group. This group is both, simple enough to be suitable as an example to illustrate the structure and construction of character tables, and important for this work, because $\boldsymbol{C}_{4v}$ is an invariant subgroup of the tetragonal group $\boldsymbol{D}_{4h}$ which is the symmetry group of many high-temperature superconductors.

The point group $\boldsymbol{C}_{4v}$ consists of 4 vertical mirror planes, denoted by σ_x, $\sigma_{x'}$, σ_y, and $\sigma_{y'}$ (see Fig. 3), and an additional 4-fold rotation axis C_4. The

other symmetry operations of the group are the identity E and the rotations C_4^2 and $C_4^3 \equiv C_4^{-1}$. This makes a total of 8 symmetry operations, the group is of order $g = 8$.

Because of $\sigma_x C_4 \sigma_{x'} = C_4^{-1}$, the symmetry operations C_4 and C_4^{-1} belong to the same class which we call $2C_4$. Furthermore, because of $C_4^{-1}\sigma_x C_4 = \sigma_y$, the reflections σ_x and σ_y constitute a class $2\sigma_v$. Similarly, $\sigma_{x'}$ and $\sigma_{y'}$ belong to a class $2\sigma_d$. Therefore, $\boldsymbol{C}_{4v}$ decomposes into the $n_c = 5$ classes E, $2C_4$, C_4^2, $2\sigma_v$, and $2\sigma_d$. The number of inequivalent irreducible representations (IRs) n_r of a group is equal to the number n_c of its classes, consequently, $n_r = 5$ for $\boldsymbol{C}_{4v}$.

Now we use the fact expressed by (5) that the sum of the squares of the dimensions of all IRs of a group is equal to its order g. The only possibility to fulfill this is $1^2 + 1^2 + 1^2 + 1^2 + 2^2 = 8$, that is, the group $\boldsymbol{C}_{4v}$ has four one-dimensional and one two-dimensional (inequivalent) irreducible representations.

We start constructing the character table of $\boldsymbol{C}_{4v}$. The character of the identity E for any representation is equal to the dimension of the representation. This gives us the first column of Tab. 6. The first row is also easy, because for the unit representation the character is 1 for every symmetry operation in the group.

According to the unitarity law (Sect. 5), all representation matrices can be chosen to be unitary. Therefore, for one-dimensional representations, the magnitude of all characters is 1. On the other hand, the second orthogonality law (7) with $i = j$ states that for every class of symmetry operations, the sum of the magnitudes of the characters of all the IRs is equal to the order g of the group divided by the number h of symmetry operations in the class, g/h. In the case of the classes $2C_4$, $2\sigma_v$, and $2\sigma_d$, this is $g/h = 4$. The sum of the absolute squares of the 4 one-dimensional representations is already 4, consequently the character of the latter three classes is zero in the two-dimensional representation.

Now we use the fact that for *1-dimensional* representations the relation $\chi(G^n) = \chi(G)^n$ for $G \in \mathcal{G}$ holds. Therefore the characters of all the classes in the 1-dimensional representations of the $\boldsymbol{C}_{4v}$ group are ± 1. Since the reflection at a mirror plane is its own inverse, the character of a reflection has the property $\chi(\sigma_v)^2 = 1$ (and analogous for σ_d), therefore, $\chi(\sigma_v) = \pm 1$. This is also true for the rotation C_4. From the fact that C_4 and C_4^{-1} are in the same class, it follows that $\chi(C_4) = \chi(C_4^3)$, and therefore $\chi(C_4) = \pm 1$.

Let us compare this to the situation in the point group $\boldsymbol{C}_4$ which is the

$\boldsymbol{C}_{4v}$	E	$2C_4$	C_4^2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0
$\Gamma(\boldsymbol{r})$	3	1	-1	1	1
$\Gamma(\boldsymbol{r}) \times \Gamma(\boldsymbol{r})$	9	1	1	1	1

Table 6: Character Table of $\boldsymbol{C}_{4v}$. The characters of the 5 irreducible representations, of the reducible representation of a vector and the representation of a 2nd rank tensor are given.

cyclic group generated by the 4-fold rotation C_4 and therefore of order 4. Each symmetry operations is a class of its own. Therefore, we only have $C_4^4 = E$ and $\chi(C_4)^4 = 1$ with the consequence that ± 1 and $\pm i$ are all possible values of $\chi(C_4)$. A look into a group theory book shows that indeed there are IRs of the $\boldsymbol{C}_4$ group with the character of the C_4 4-fold rotation assuming the values $\pm i$. The additional mirror planes in $\boldsymbol{C}_{4v}$ prevent the characters of the 4-fold rotation to become imaginary.

The second orthogonality theorem of characters states that for two different classes, the characters of the different IRs, considered as vectors, are orthogonal. Using this and the property proved in the last paragraph that all the characters of the 1-dimensional representations are ± 1 in the case of the $\boldsymbol{C}_{4v}$ groups, the characters of the classes $2C_4$, $2\sigma_v$, and $2\sigma_d$ for all the IRs are determined. Now only the characters of the class C_4^2 are left.

These characters—considered as vectors—also have to be orthogonal to the characters of the other classes. This leaves only two possibilities, the first is the one in the character table in Tab. 6, and the second which differs only in an overall sign from the first. This sign is determined by the character of the trivial representation, $\chi^{(A_1)}(C_4^2) = 1$.

7 Lattices and translational symmetry

Point groups. We already introduced a considerable number of point of groups, namely the groups $\boldsymbol{C}_3$, $\boldsymbol{C}_{3v}$, $\boldsymbol{D}_{4h}$, and $\boldsymbol{D}_4$. All these groups are

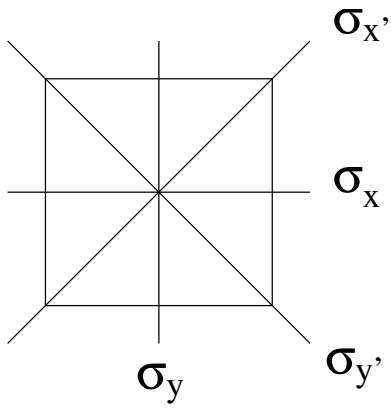

Figure 3: Mirror planes of $\boldsymbol{C}_{4v}$.

point groups, groups of transformations which leave a particular point fixed. Another one of these point groups is the cyclic group $\boldsymbol{C}_5$, consisting of the 5 rotations by $n \cdot 72°$, $n = 0, \ldots, 4$ which leave the pentagon invariant.

Bravais lattice. The characteristic symmetry of a crystal is the translational symmetry which is described by 3 vectors $\boldsymbol{a}_i$ called the *primitive vectors*. Such three vectors $\boldsymbol{a}_i$ generate a set of points $\boldsymbol{t}_n = \sum n_i \boldsymbol{a}_i$ called *lattice vectors* or *lattice points* (and sometimes *lattice sites*), $\boldsymbol{n} = (n_i)$ with integer numbers n_i. The set $\{\boldsymbol{t}_n\}$ is called a *Bravais lattice*[5]

In this section, we determine the possible point group symmetries which are compatible with the translational symmetry of a Bravais lattice given by three primitive vectors $\boldsymbol{a}_i$. But before doing this, we introduce some terms and constructions which are in use when discussing properties of crystal lattices.

Primitive cell. A region of space which contains exactly one *lattice point* $\boldsymbol{t}_n$ and which fills (without overlapping) the whole space if translating it through the lattice vectors, is called a *primitive cell*. One obvious choice for the primitive cell is the parallelepiped spanned by the three primitive vectors $\boldsymbol{a}_i$ (see Fig. 4(a)). Usually this choice has the disadvantage of not having the full symmetry of the Bravais lattice. Two ways to circumvent this problem are common.

Conventional cell and Wigner-Seitz-cell. The first is the *conventional (or crystallographic) unit cell* which is chosen to be larger than the

[5]note that for a given Bravais lattice the choice of primitive vectors is not unique.

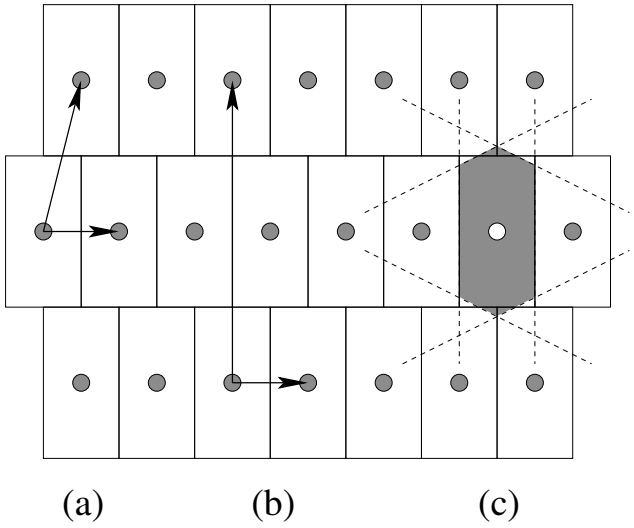

Figure 4: (a) Two different primitive vectors and the primitive cell they span, (b) non-primitive translations vectors spanning a conventional unit cell, and (c) the Wigner-Seitz cell of $YBa_2Cu_4O_8$ (Y-124).

primitive cell in order to have the full point group symmetry (see Fig. 4(b)). The second choice is the *Wigner-Seitz cell* which is a primitive cell. Given a lattice point, the Wigner-Seitz cell contains all points which are closer to the lattice point under consideration than to any other equivalent (upon translations) point of the crystal (see Fig. 4(c)). This cell by construction has the full symmetry of the lattice.

Figure 4 shows the $b-c$ plane of the lattice of $YBa_2Cu_4O_8$ (Y-124), the points show the position of a particular atom, for instance the Y atom, in the lattice. On the left side (a) a certain choice for the primitive vectors is shown. The perpendicular vectors in (b) are the basis vectors of a suitable choice of a conventional unit cell. On the right side (c) of the figure the construction of the Wigner-Seitz cell (grey area) is illustrated.

Let us return to the question of the compatibility of translational and point group symmetries and the classification of Bravais lattices. We look for the rotations which are compatible with the translational symmetry of a Bravais lattice. The origin of the rotation is considered to be a lattice point. Due to the discrete nature of the lattice, n successive rotations have to be equal to the identity operation, that is, we consider n-fold rotation

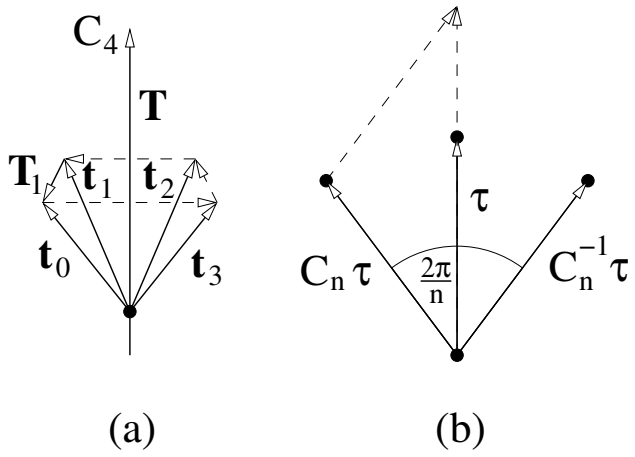

Figure 5: The proof (see text) that only the rotations C_2, C_3, C_4, and C_6 are compatible with translational symmetry.

axes ($n \neq \infty$). First we show that the rotation axis of a rotation compatible with the translational symmetry necessarily is parallel to a lattice vector. Take a lattice vector $\boldsymbol{t}_0$ and generate the vectors $\boldsymbol{t}_i = (C_n)^i \boldsymbol{t}_0$ for $i = 1, \ldots, n$. The lattice vector $\boldsymbol{T} \equiv \sum_{i=0}^{n-1} \boldsymbol{t}_i$ (see Fig. 5(a)) is invariant with respect to the rotation C_n, and therefore parallel to the rotation axis (if it vanishes accidentally, we choose another lattice vector $\boldsymbol{t}_0$). The lattice vectors $\boldsymbol{T}_i = \boldsymbol{t}_i - \boldsymbol{t}_{i-1}$ (Fig. 5(a)) are perpendicular to $\boldsymbol{T}$ because $\boldsymbol{T}_i \boldsymbol{T}$ is invariant upon rotation and $\sum_i \boldsymbol{T}_i \boldsymbol{T} = 0$. We have thus proved that if C_n is a rotation leaving the Bravais lattice invariant, there are lattice vectors perpendicular to the rotation axis of C_n. The problem now is reduced to a two-dimensional one. For the shortest $\vec{\tau}$ of the lattice vectors perpendicular to the rotation axis, then $C_n\vec{\tau} + C_n^{-1}\vec{\tau} = 2\cos(2\pi/n)\vec{\tau}$ must be a primitive vector (Fig. 5(b)). This is only possible for $n = 1$, 2, 3, 4, and 6 (the case $n = 1$ is trivial). Therefore, only rotations by π, $2\pi/3$, $\pi/2$, and $\pi/3$ are possible candidates for point group symmetry operations leaving a given Bravais lattice invariant. Other rotations can be excluded.

Taking these rotations and also the inversion, 32 different groups can be constructed. They are called the *32 crystallographic point groups*. All these groups are possible point symmetry groups of a given Bravais lattice. Two of the 32 point groups are the tetragonal $\boldsymbol{D}_{4h}$ and $\boldsymbol{D}_4$ groups. Only the former of these groups is important when classifying the Bravais lattices, because if

a Bravais lattice has $\boldsymbol{D}_4$ symmetry, it automatically also has $\boldsymbol{D}_{4h}$ symmetry. This observation decomposes the set of 32 point groups into 7 subsets. The 7 symmetry groups with maximum symmetry in each of these 7 subsets are the *7 crystal systems* which are cubic ($\boldsymbol{O}_h$), hexagonal ($\boldsymbol{D}_{6h}$), tetragonal ($\boldsymbol{D}_{4h}$), trigonal ($\boldsymbol{D}_{3d}$), orthorhombic ($\boldsymbol{D}_{2h}$), monoclinic ($\boldsymbol{C}_{2h}$), and triclinic ($\boldsymbol{S}_2$).

Lattice with a basis. More complex crystals, as for instance crystals consisting of different kinds of atoms, do not have the property that all the atoms are located on a site of a Bravais lattice. This is also the case for some apparently simple structures as for instance the honeycomb net, which cannot be described by using just three primitive vectors $\boldsymbol{a}_i$. In such crystals, however, it is possible to group together few atoms and describe the position of these groups by means of a Bravais lattice. This construction is called a *lattice with a basis*. A simple example for the first case is sodium chloride (NaCl) which is cubic, with Cl atoms as nearest neighbors of the Na atoms and vice versa. This lattice is described by a face centered cubic lattice with a basis consisting of a sodium and a chloride atom. In the system $YBa_2Cu_4O_8$, for instance, each primitive cell of the Bravais lattice contains 15 atoms. Sometimes a lattice with a basis is used also to describe the body-centered cubic (bcc) and face-centered cubic (fcc) Bravais lattices to make more explicit their cubic symmetry.

The simple Bravais lattice can be considered as a Bravais lattice with a basis having the full symmetry of the simple Bravais lattice. A basis which does not have (at least) the full symmetry of the Bravais lattice breaks this symmetry. This symmetry breaking is possible in different ways which generate the 32 crystal systems. Consider a orthorhombic Bravais lattice which has $\boldsymbol{D}_{2h}$ symmetry. A basis can destroy this symmetry in two ways, either it destroys the horizontal mirror plane and the symmetry becomes $\boldsymbol{C}_{2v}$ or it destroys the vertical mirror planes and the symmetry becomes $\boldsymbol{D}_2$.

We summarize. Bravais lattices are the set of points generated in three dimensions by three non-collinear primitive vectors. Symmetry operations leaving a point invariant have to be compatible with the Bravais lattice. This is fulfilled just by the C_2, C_3, C_4, and C_6 operations out of all possible rotations. The point groups compatible with the Bravais lattice turn out to be 32, this is the number of different crystallographic point groups describing the different types of Bravais lattices with a basis. Selecting the groups with maximum symmetry, the Bravais lattices without a basis are found. These can be grouped into 7 types, corresponding to the number of crystal systems.

8 Vectors, tensors, and their transformation behavior

The derivation of selection rules for light absorption, Raman scattering, and other forms of spectroscopy, is intimately related to the decomposition of the representations that correspond to the transformation laws for the appropriate vectors and tensors, into irreducible representations of the point group of the crystal under consideration.

Vectors and representation matrices. When rotating by an angle of φ about an axis $\boldsymbol{n}$, a vector $\boldsymbol{v} = (v_i)$ transforms according to the law

$$\boldsymbol{v} \to R_{ij}(\boldsymbol{n}, \varphi)\, v_j$$

where $\hat{R}(\boldsymbol{n}, \varphi) = (R_{ij}(\boldsymbol{n}, \varphi))$ is a *rotation matrix*, which in the special case of $\boldsymbol{n} = \boldsymbol{e}_z$ has the form

$$\hat{R}(\boldsymbol{e}_z, \varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} . \tag{8}$$

Rotations about another axis $\boldsymbol{n}'$ can be written in the form

$$\hat{R}^{-1}\hat{R}(\boldsymbol{e}_z, \varphi)\hat{R}$$

with another rotation matrix $\hat{R}$, rotating first the axis $\boldsymbol{n}'$ to $\boldsymbol{e}_z$, then performing a rotation about the axis $\boldsymbol{e}_z$, and rotating back to $\boldsymbol{n}'$: All rotations by a given angle φ are equivalent. Particularly,

$$\mathrm{Sp}\, \hat{R}(\boldsymbol{n}', \varphi) = \mathrm{Sp}\, \hat{R}(\boldsymbol{e}_z, \varphi)$$

holds for any rotation axis $\boldsymbol{n}'$.

Consider now a point group $\mathcal{G}$. The proper rotations of the point group correspond to rotation matrices $\hat{R}$ and yield a 3-dimensional representation of the point group $\mathcal{G}$. Vectors transform according to this representation, therefore it is called the *vector representation* $\Gamma(\boldsymbol{r})$. The character of the rotation C_n by an angle of $2\pi/n$ in the vector representation is given by the trace of $\hat{R}(\boldsymbol{n}, \varphi)$, that is,

$$\chi^{(\Gamma(r))}(C_n) = \mathrm{Sp}\, \hat{R}(\boldsymbol{n}, 2\pi/n) = 1 + 2\cos\frac{2\pi}{n}$$

n	1	2	3	4	6
$\chi^{(\Gamma(\boldsymbol{r}))}(C_n)$	3	-1	0	1	2

Table 7: Characters of the n-fold rotation in the vector representation.

and is tabulated in Tab. 7 for the rotations which are consistent with the translational symmetry of Bravais lattices. The character of rotatory inversions is the one of the corresponding proper rotation times -1 for the inversion. Mirror planes have the character $+1$.

Let us focus on the $\boldsymbol{C}_{4v}$ group (Tab. 6) and reduce $\Gamma(\boldsymbol{r})$ into irreducible representations. The characters of the vector representation $\Gamma(\boldsymbol{r})$ in the group $\boldsymbol{C}_{4v}$ are given by Tab. 6. From this, the decomposition

$$\Gamma(\boldsymbol{r}) = A_1 + E \qquad (\text{in } \boldsymbol{C}_{4v}) \tag{9}$$

follows easily.

As an illustration of the reduction of the representation associated with tensors of rank r, we treat the special case $r = 2$. Extension to the general case is straightforward. A tensor of rank 2 consists of $3 \times 3 = 9$ quantities T_{ij} which transform under rotation according to

$$(T_{ij}) \rightarrow R_{ik} R_{jl} T_{kl} \ ,$$

that is, like a product of two vectors. The multiplication of rotation matrices $\hat{R}$ is related to the *product of representations* that must be defined next.

Product representation. Given two representations A and B of a group $\mathcal{G}$ with the representation matrices $D^{(A)}(G)$ and $D^{(B)}(G)$ for $G \in \mathcal{G}$, respectively, we define the *product representation* $A \times B$ by the representation matrix

$$D^{(A\times B)}_{ij,kl}(G) \equiv D^{(A)}_{ik}(G) D^{(B)}_{jl}(G) \ . \tag{10}$$

The character $\chi^{(A\times B)}(G) = \sum_{ij} D^{(A\times B)}_{ij,ij}(G)$ of the product group is given by the relation

$$\chi^{(A\times B)}(G) = \chi^{(A)}(G) \cdot \chi^{(B)}(G) \ , \tag{11}$$

that is, by the product of the character of the representations A and B.

Using this, we see that a tensor of second rank gives raise to a IR corresponding to the product representation of two vector representations

$\Gamma(\boldsymbol{r}) \times \Gamma(\boldsymbol{r})$. The characters of these representations are also tabulated in Tab. 6.

In order to be specific, we once again consider the example of the $\boldsymbol{C}_{4v}$ group. After playing around a little bit with the character table, it turns out that

$$\Gamma(\boldsymbol{r}) \times \Gamma(\boldsymbol{r}) = 2A_1 + A_2 + B_1 + B_2 + 2E \tag{12}$$

is the decomposition we looked for.

Decomposition of a nth rank tensor. For tensors of rank $r > 2$ the decomposition works in a similar way, but it becomes difficult to carry it out just by inspection. Fortunately, there is a systematic way to perform the decomposition. We write the reducible representation D as a direct sum

$$D = \sum_{\alpha} q_\alpha D^{(\alpha)} \tag{13}$$

of irreducible representations $D^{(\alpha)}$, and look for a way to determine the coefficients in (13). Calculating the trace of the representation matrices which are related to (13) yields the equation

$$\chi^{(D)}(G) = \sum_{\alpha} q_\alpha \chi^{(\alpha)}(G) \qquad \text{for all } G \in \mathcal{G}, \tag{14}$$

which decomposes the characters of the representation D into those of the irreducible representations. Multiplying (14) by $\chi^{(\beta)\,*}(G)$, summing over all group elements, and applying the First Orthogonality of Characters, we find

$$q_\beta = \frac{1}{g} \sum_{G \in \mathcal{G}} \chi^{(\beta)\,*}(G) \chi^{(D)}(G) \tag{15}$$

where g is the order of $\mathcal{G}$.

This is a very important result which leads to the decompositions of a reducible representation into irreducible ones by using (13), provided the character table of the group $\mathcal{G}$ is known.

The decomposition of an nth rank tensor is now straightforward. Because of (10), the nth rank tensor transforms according to the representation

$$D^{[n]} \equiv \underbrace{D^{\Gamma(\boldsymbol{r})} \times D^{\Gamma(\boldsymbol{r})} \times \cdots \times D^{\Gamma(\boldsymbol{r})}}_{n \text{ factors}} \tag{16}$$

whose character is (see 11)

$$\chi^{[n]}(G) = \left(\chi^{\Gamma(\boldsymbol{r})}\right)^n \tag{17}$$

and the decomposition into irreducible representations is given by

$$D^{[n]} = \sum_\alpha q_\alpha D^{(\alpha)} \; ; \quad q_\alpha = \frac{1}{g} \sum_{G\in\mathcal{G}} \chi^{(\beta)\,*}(G) \left(\chi^{\Gamma(\boldsymbol{r})}(G)\right)^n \; . \tag{18}$$

We determined so far the irreducible representations which are contained in the representations of a nth rank tensor. But we did not yet decompose the tensor into parts which transform according to those irreducible representations. Such a decomposition is possible for all objects f for which the transformation behavior with respect to the operation of the point symmetry group $\mathcal{G}$ is defined. We write

$$f = \sum_\alpha f^{(\alpha)} \quad \text{with} \qquad G f^{(\alpha)} = D^{(\alpha)}(G) f^{(\alpha)} \quad \text{for all} \qquad G \in \mathcal{G} \; .$$

The quantity $D^{(\alpha)}(G)$ is the representation matrix of the group element G in the irreducible representation α.

The decomposition can be performed using *projection operators*. For each irreducible representation of a group $\mathcal{G}$, projection operator is given by

$$P^{(\alpha)} = \frac{d_\alpha}{g} \sum_{G\in\mathcal{G}} \chi^{(\alpha)\,*}(G)\, G \; , \tag{19}$$

where D_α is the dimension of the irreducible representation α, and g is the order of $\mathcal{G}$.

We apply this to the real 2nd rank tensor $\hat{T}$, choose the point group $\boldsymbol{C}_{4v}$ as symmetry group, and work in 2 dimensions. The 2×2 representation matrices of the vector representation have the form

$$\hat{D}(G) = \pm \begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix}$$

for $\varphi = n\pi/4$, and the application of the group elements of $\boldsymbol{C}_{4v}$ to the tensor is defined by

$$G\hat{T} = \hat{D}(G)\hat{T}\hat{D}^T(G) \; .$$

Therefore, the decomposition yields

$$\hat{T} = \sum_{\alpha} \hat{T}^{(\alpha)} \ , \quad \hat{T}^{(\alpha)} = \frac{1}{8} \sum_{G \in \boldsymbol{C}_{4v}} \chi^{(\alpha)}(G) \hat{D}(G) \hat{T} \hat{D}^T(G) \ ,$$

which evaluates to $\hat{T} = \hat{T}^{A_1} + \hat{T}^{A_2} + \hat{T}^{B_1} + \hat{T}^{B_2}$ with

$$\hat{T}^{A_1} = \begin{pmatrix} T_{xx}+T_{yy} & \\ & T_{xx}+T_{yy} \end{pmatrix} \ , \quad \hat{T}^{A_2} = \begin{pmatrix} & T_{xy}-T_{yx} \\ -(T_{xy}-T_{yx}) & \end{pmatrix} \ ,$$
$$\hat{T}^{B_1} = \begin{pmatrix} T_{xx}-T_{yy} & \\ & T_{xx}-T_{yy} \end{pmatrix} \ , \quad \hat{T}^{B_2} = \begin{pmatrix} & T_{xy}+T_{yx} \\ T_{xy}+T_{yx} & \end{pmatrix} \ .$$

The E_{1g} representation does not appear in the decomposition. A table which shows the results of the decomposition of the 2nd rank Raman tensor for different point groups can be found in [6].

Independent components of a tensor. One of the important topics of this chapter is to answer the question concerning the number of independent components of a tensor (see [2], Sect. 8.5) for a particular point group symmetry of a crystal under consideration.

The tensor components corresponding to the irreducible representations which are different from the identity representation are not invariant when applying the symmetry operations on the lattice, and therefore have to vanish. Only the components which transform according to the identity representation are non-vanishing. Consequently, we are interested in the number of times the identity representation occurs in the tensor representation. Putting $\gamma = 1$ into (18), we find the answer that

$$n_{\text{ind}} = \frac{1}{g} \sum_{G \in \mathcal{G}} \left(\chi^{\Gamma(\boldsymbol{r})}(G) \right)^n \tag{20}$$

for a nth rank tensor. For the $\boldsymbol{C}_{4v}$ group a (non-symmetric) tensor of 2nd rank therefore has

$$n_{\text{ind}} = \frac{1}{8}[9 + 2 \cdot 1 + 2 + 2 \cdot 1 + 2 \cdot 1] = 2$$

independent components. In the $\boldsymbol{D}_{4h}$ group, a 4th rank tensor has

$$n_{\text{ind}} = \frac{2}{16}[81 + 2 \cdot 1 + 1 + 2 \cdot 1 + 2 \cdot 1] = 11$$

independent components.

Tensors with additional symmetries. When calculating the Raman efficiency for electronic Raman scattering in superconductors, 4th rank tensors like

$$\mu_{ijkl} = \langle \mu_{ij}^{-1} \mu_{kl}^{-1} \rangle \tag{21}$$

have to be discussed. The 4th rank tensor $c_{\mu\nu\rho\sigma}$ of elastic constants is analogous to μ_{ijkl} with respect to the symmetries. These tensors clearly are symmetric when interchanging $(i \leftrightarrow j)$, or $(k \leftrightarrow l)$, or $((i,j) \leftrightarrow (k,l))$.[6] The question arises as to how many independent components a tensor with this permutation symmetry in a crystal of a given point group symmetry has.

This question can be answered using (18), but the quantity $(\chi^{\Gamma(\boldsymbol{r})}(G))^n$ has to be replaced by the character of the accordingly symmetrized tensor.

The symmetry of a tensor is described by a subgroup of the group $\mathcal{P}_n$ of permutations of n objects (refer to [3], Chap. 15). A permutation of n objects is denoted by the symbol

$$p = \begin{pmatrix} 1 & 2 & \cdots & n \\ p_1 & p_2 & & p_n \end{pmatrix}$$

and describes the replacement of the object i by p_i. Permutations often produce cyclic replacements. For instance, in the permutation

$$p = \begin{pmatrix} 1\,2\,3\,4 \\ 3\,2\,4\,1 \end{pmatrix} ,$$

the object 1 is replaced by 3, 3 by 4, and 4 by 1. Object 2 is replaced by itself, which is also some kind of cyclic replacement. In the *cycle notation* the permutation p is denoted by $p = (1\,3\,4)(2)$, it is said to consist of two cycles of length $\nu_1 = 3$, and $\nu_2 = 1$. The equation $\sum_m \nu_m = n$ is always fulfilled.

But let us go back to the 4th rank tensor μ_{ijkl}. We denote the mth index of μ_{ijkl} by m. Then the permutations which are symmetry operations of μ_{ijkl}, are

$$\begin{aligned}
(i \leftrightarrow j) \quad &\rightarrow \quad p = (1\,2)(3)(4) \quad \text{with } \nu_1 = 2,\ \nu_2 = \nu_3 = 1 \\
(k \leftrightarrow l) \quad &\rightarrow \quad p = (1)(2)(3\,4) \quad \text{with } \nu_1 = 2,\ \nu_2 = \nu_3 = 1 \\
((i,j) \leftrightarrow (k,l)) \quad &\rightarrow \quad p = (1\,3)(2\,4) \quad \text{with } \nu_1 = \nu_2 = 2.
\end{aligned}$$

[6] Recall that $\hat{\mu}^{-1}$ is the inverse effective mass tensor which has the property $\mu_{ij}^{-1}(\boldsymbol{k}) = \mu_{ji}^{-1}(\boldsymbol{k})$.

Point group of crystal	independent components of μ_{ijkl}
$\{E\}$	21
$\boldsymbol{D}_{2h}$	9
$\boldsymbol{D}_{4h}$	6
$\boldsymbol{O}_h$	3

Table 8: Independent components of the tensor $\boldsymbol{k}$-independent tensor μ_{ijkl} defined in (21).

These three permutations generate a subgroup $\mathcal{P}$ of $\mathcal{P}_n$. This subgroup consists of 12 elements, all of which leave the tensor μ_{ijkl} invariant.

The character of a tensor which is invariant under the subgroup $\mathcal{P}$ is given by the sum

$$\chi_{\mathcal{P}}(a) = \frac{1}{\operatorname{ord}\mathcal{P}} \sum_{p\in\mathcal{P}} \{\chi(a)\}^{\nu_1}\{\chi(a^2)\}^{\nu_2}\cdots\{\chi(a^m)\}^{\nu_m} \ , \tag{22}$$

(see [2], Eq. (8.5.13)) where $\chi(a)$ is the character of $a \in \mathcal{G}$ in the vector representation and ν_i is the length of the cycles in the permutation p. The number of independent elements n_{ind} then is given by (18), that is,

$$n_{\text{ind}} = \frac{1}{\operatorname{ord}\mathcal{G}} \sum_{a\in\mathcal{G}} \chi_{\mathcal{P}}(a) \ ,$$

where $\operatorname{ord}\mathcal{G}$ denotes the order of the point group $\mathcal{G}$.

For a given group $\mathcal{G}$, we consider (22) for the special case of a symmetric second rank tensor. The permutation group is given by $\mathcal{P} = \{E, (1\,2)\}$ where $\nu_1 = 2$ for $p = E$ and $\nu_2 = 1$ for $p = (1\,2)$. This yields

$$\chi^{\text{sy}}(a) = \frac{1}{2}\left[\chi(a)^2 + \chi(a^2)\right]$$

which is the character of the symmetric product representation.

In Tab. 8 we have tabulated the number of independent elements of μ_{ijkl} for some given crystal point groups. If the crystal has no point symmetry at all (or is triclinic) then only the symmetry with respect to the permutation of the tensor indices reduces the number of independent components of the tensor, in our case from $3^4 = 81$ to 21. Additional point group symmetries further reduce the number of independent components of the tensor down to 3 for the cubic case.

9 Classification of Γ-point phonons according to point group symmetry

The irreducible representations of a point group of a crystal are an indispensable tool for the classification of the normal vibration modes of the crystal. For one-phonon (dipole) Raman scattering, only phonons with the full *translational symmetry* of the crystal, that is, $k = 0$ or Γ-point phonons are of importance, and will be under consideration exclusively in this section.

The restriction to $k = 0$ phonons, and its consequence that the vibrational displacement patterns have the same translational symmetry as the crystal, allows us to focus on just one unit cell. When performing the group-theoretical treatment of the phonons, we also have to identify atoms which are related by a translation of the Bravais lattice. In the case of a system of two CuO planes, there are 6 independent sites. In the upper plane, there is one Cu (Cu(2)) site and two O sites (O(2) and O(3)). In the lower plane, there are also three independent sites, one Cu site and two O sites. The point symmetry group is $\boldsymbol{D}_{4h}$ (see Fig. 6).

An important observation is the fact that *normal modes transform according to irreducible representations* of the point group $\mathcal{G}$ of the crystal. If we label the inequivalent atoms in the primitive unit cells with $k = 1, \ldots, N$, then the relation between the displacement $\boldsymbol{u}_k$ of a certain atom k, and the phonon normal coordinate Q_s of the phonon labeled by $s = 1, \ldots, 3N$ is given by

$$\boldsymbol{u}_k = \frac{1}{\sqrt{m}_k} \sum_s Q_s \boldsymbol{e}_k^{(s)} \ . \tag{23}$$

The mass of atom k is denoted by m_k, and $\boldsymbol{e}_k^{(s)}$ are the eigenvectors of the phonon s. The Hamiltonian is given by

$$E = \frac{1}{2} \sum_s \left[\dot{Q}_s^2 + \omega_s^2 Q_s^2 \right]$$

where ω_s denotes the frequency of the phonon s. From this equation it becomes clear that the normal coordinates which belong to a given energy ω, transform according to a certain representation of the point group $\mathcal{G}$. For cases of no accidental degeneracy, which are the only ones being considered here, this implies that the normal coordinates transform according to an

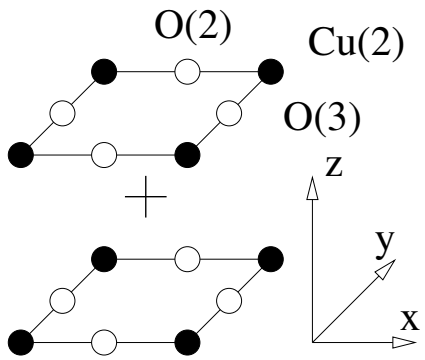

Figure 6: The two CuO planes in two-plane high-T_c superconductors.

irreducible representation of $\mathcal{G}$, and we write

$$GQ_s = \sum_{s'} Q_{s'} D_{s's}(G)$$

for all $G \in \mathcal{G}$. According to 23, the normal coordinates Q_s and the displacements $\boldsymbol{u}_k$ are related linearly. Therefore, we will perform a group-theoretical investigation of the displacements.

We consider the effect of symmetry operations on the equilibrium position $\boldsymbol{r}_k$ and displacement $\boldsymbol{u}_k$ of the atom k in the primitive unit cell. The vectors $\boldsymbol{r}_k$ transform according to the vector representation, that is,

$$G\boldsymbol{r}_k = \hat{R}(G)\boldsymbol{r}_k = \boldsymbol{r}_{k'} \ ,$$

the transformation takes the atom from the position k to position k'. For the case of the displacements, the transformation law is more difficult, because the displacements transform like vectors, but at the same time, the atoms to which they refer, change place. When the transformation takes an atom from site k to site k', then displacement vector of the atom at site k' becomes that one of the atom at site k rotated by a rotation matrix,

$$G\boldsymbol{u}_{k'} = \hat{R}(G)\boldsymbol{u}_{\hat{R}^{-1}(G)\boldsymbol{r}_{k'}} = \hat{R}(G)\boldsymbol{u}_k \ .$$

The N displacement vectors $\boldsymbol{U} = (\boldsymbol{u}_1, \ldots \boldsymbol{u}_N)^T$ transform according to a $3N$-dimensional representation $\hat{R}_{3N}$ like

$$G\,\boldsymbol{U} = \hat{R}_{3N}(G)\,\boldsymbol{U} \ .$$

	E	$2C_4$	C_4^2	$2C_2'$	$2C_2''$	I	$2IC_4$	σ_h	$2\sigma_v$	$2\sigma_d$
N_R	6	2	6	0	0	0	0	0	6	2
$\chi^{(\Gamma(\boldsymbol{r}))}$	3	1	-1	0	0	0	0	0	1	1
$\chi^{(3N)}$	18	2	-6	0	0	0	0	0	6	2

Table 9: For each class of the tetragonal point group $\boldsymbol{D}_{4h}$, the number N_R of invariant atoms of Fig. 6, the character of the class in the vector representation and in the representation $\hat{R}_{3N}$ is given.

The decomposition of the representation $\hat{R}_{3N}$ gives the different irreducible representations of the normal modes. For the decomposition we only need the character of the representation, that is, the trace of $\hat{R}_{3N}$. Only atoms that do *not move* in the transformation contribute non-vanishing *diagonal* elements to $\hat{R}_{3N}$. For an atom k that does not move, $G\boldsymbol{u}_k = \hat{R}\boldsymbol{u}_k$, where $\hat{R}$ is a 3×3 rotation matrix. The character of $\hat{R}$ was already calculated in Sect. 8 and tabulated in Tab. 7. As a consequence, the character of the representation $\hat{R}_{3N}$ is given by

$$\chi^{(3N)}(G) = N_R \chi^{(\Gamma(\boldsymbol{r}))}(G) \ ,$$

where N_R is the number of atoms which are not moved in the transformation represented by G.

The system shown in Fig. 6 is composed of 6 independent sites and possesses tetragonal $\boldsymbol{D}_{4h}$ symmetry. In Tab. 9, the number N_R of atoms which are not moved by the transformation represented by $G \in \mathcal{G}$, the character G in the vector representation, and its product, the character of the representation $\hat{R}_{3N}$ is given for each of the classes of $\boldsymbol{D}_{4h}$.

The decomposition of the representation $\hat{R}_{3N}$ by using (14) and (15) is easy now, and yields the result

$$2A_{1g} + B_{1g} + 3E_g + 2A_{1u} + B_{1u} + 3E_u \ .$$

The displacement patterns which belong to the particular normal modes are determined by applying the projection operators to the displacement vectors $\boldsymbol{U}$.

The modes carrying an index "g" (gerade) are even with respect to the inversion operation. Therefore they carry no dipole momentum and are forbidden in absorption. The "u" (ungerade) modes are odd with respect to

inversion and are forbidden in Raman scattering (see next section). The even modes turn out to be Raman active. The odd modes are active in infrared absorption saved one exception: the A_{1u} and B_{1u} modes. The B_{1u} modes possesses an odd parity symmetry pattern, but due to the fact that $\chi^{(B_{1u})}(C_4) = -1$, the dipole momentum vanishes (O(2) and O(3) carry the same ionic charge) and so does the coupling. This can also be seen in a more formal way. The Raman vertex (in effective mass approximation, i.e. far from resonance) corresponds to a symmetric 2nd rank tensor and decomposes in $\boldsymbol{D}_{4h}$ into

$$\text{symmetric 2nd rank tensor} \rightarrow 2A_{1g} + B_{1g} + B_{2g} + E_g \ ,$$

and the vector decomposes into

$$\text{vector} \rightarrow A_{2u} + E_u \ .$$

Therefore, the A_{1u}, B_{1u}, and E_u phonons are Raman active and the E_u phonons are infrared active. The A_{1u} and B_{1u} phonon, however, are neither Raman- nor infrared-active. They are called *silent* modes.

10 Selection rules for Raman scattering by phonons

When talking about *selection rules* for Raman scattering, one usually refers to the fact that for different *polarization configurations* $(\boldsymbol{e}_L, \boldsymbol{e}_S)$ of the incoming and scattered light, different excitations can be detected using Raman spectroscopy.

The Raman efficiency S is related to a 2nd rank tensor, the *Raman tensor* $\hat{T}$ via the light polarization unit vectors $\boldsymbol{e}_S$ and $\boldsymbol{e}_L$ by the relation

$$S \sim \left| \boldsymbol{e}_S^* \cdot \hat{T} \cdot \boldsymbol{e}_L \right|^2 \ .$$

Certain excitations cause certain non-vanishing matrix elements of the Raman tensor $\hat{T}$ and allows for selecting them by an appropriate choice of the light polarization.

We focus on phonon Raman scattering (restricted to Stokes scattering) and discuss its microscopic mechanism. The basic process leading to phonon Raman scattering is shown in Fig. 7. The incoming photon is annihilated

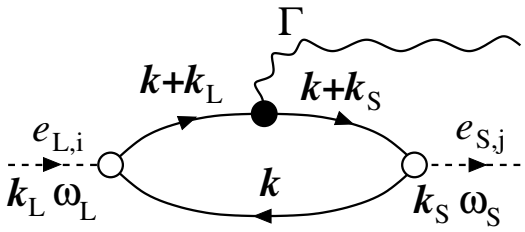

Figure 7: The photon-phonon vertex involving an electronic pair-excitation. Note that there is also another diagram contributing in which the phonon is created by scattering with the hole.

and creates an electron-hole pair. Then either the electron or the hole scatter and create a phonon. The electron-hole pair finally recombines and creates the scattered photon. Due to the fact that the velocity of light is much larger than the Fermi velocity, the transition leading to the electron-hole pair can be considered to be direct. The transition corresponding to the recombination of the electron-hole pair has to be direct as well, and therefore the created phonon is a Γ-point phonon.

The vertices related to the creation and the annihilation of the electron-hole pair are matrix elements of the operators $\boldsymbol{e}_L \cdot \boldsymbol{p}$ and $\boldsymbol{e}_S^* \cdot \boldsymbol{p}$, respectively. We use cartesian components and take the unit vectors out of the expression for the transition amplitude of the process described by the diagram in Fig. 7. Then the matrix elements are $\langle n_1 \boldsymbol{k}|p_i|n_i \boldsymbol{k}\rangle$ and $\langle n_i \boldsymbol{k}|p_j|n_2 \boldsymbol{k}\rangle$. They transform like vectors and thus their product like a 2nd rank tensor.

We assume now that it is possible to consider only one phonon in our discussion. This is given for instance when the other phonons are not very close in frequency to the phonon under discussion.[7] Then, the phonon will not mix with other phonons, and it is enough to take into account one electron-phonon vertex g. The creation of a phonon is accompanied by the scattering of an electron (hole) with quasimomentum $\boldsymbol{k}$ from band n_1 to n_2, and therefore the vertex g depends on $\boldsymbol{k}$, n_1, and n_2 only.

The expression corresponding to the diagram in Fig. 7, which gives the amplitude for the process of creating a phonon by inelastic scattering of light (involving an electron-hole pair), is given by a product of the vertices and

[7] Otherwise, a perturbation like anharmonic coupling may mix different modes which belong to the same IR, but have different energy eigenvalues.

three electronic Green's functions, and involves a summation $\langle\cdot\rangle$ over the Brillouin zone. We write

$$\langle p_i(n_i \to n_1, \boldsymbol{k}) \cdot g_{n_1 n_2;\boldsymbol{k}} \cdot p_j(n_2 \to n_i, \boldsymbol{k}) \cdot \Lambda_{n_i n_1 n_2;\boldsymbol{k}}(\omega)\rangle \ , \tag{24}$$

where the product of the Green's functions has been denoted by $\Lambda_{n_i n_1 n_2;\boldsymbol{k}}(\omega)$. This treatment also shows that the quantity defined in (24) is proportional to the Raman tensor $\hat{T}$.

The displacement pattern of a Γ-point phonons can be classified[8] according to the irreducible representations of the point group of the crystal. We denote the IR which represents the transformation properties of the displacement pattern of the phonon by μ. Then, the electron-phonon vertex belongs to the same IR, we write $g^{\mu}_{\boldsymbol{k}}$.

The matrix elements of the momentum operator in (24) transform according to the components of the vector representation. Hence, the product of both transforms like a 2nd rank tensor.

Green's functions transform only by virtue of their dependence on the dispersion relation of the excitations which they describe. The dispersion relation $\epsilon_{\boldsymbol{k}}$ of the electrons is fully symmetric. Therefore the quantity $\Lambda_{\boldsymbol{k}}(\omega)$ in (24) is a scalar.

The averaging of the second rank tensor formed by the two momentum matrix elements and the electron-phonon vertex projects the irreducible representation μ out of the 2nd rank tensor,[9] all other irreducible representations vanish. As a conclusion, the amplitude (24) (which is proportional to the Raman tensor) only yields a non-vanishing contribution to that component of a the Raman tensor which belongs to the IR μ.

We give an example using the point group $\boldsymbol{C}_{4v}$. This group describes the point symmetry of a square. Its group table is given in Tab. 6.

The representation to which the Raman tensor (as every second rank tensor) belongs is denoted by $\Gamma(\boldsymbol{r}) \times \Gamma(\boldsymbol{r})$ and is the product of two vector

[8] if there is no accidental degeneracy.

[9] This can be seen as follows. Denote the product of the momentum matrix elements by T_{ij}, and decompose it into irreducible representations $T_{ij} = \sum_{\alpha} T^{(\alpha)}_{ij}$. The product of the electron-phonon vertex $g_{\boldsymbol{k}}$ and the function $\Lambda_{\boldsymbol{k}}$ will be denoted by $h_{\boldsymbol{k}}$. If $g_{\boldsymbol{k}}$ transforms according to the irreducible representation μ, then $h_{\boldsymbol{k}}$ does so as well, hence we write $H^{(\mu)}_{\boldsymbol{k}}$. Then the average $\langle T^{(\alpha)}_{\boldsymbol{k};ij} h^{(\mu)}_{\boldsymbol{k}}\rangle$ vanishes if $\alpha \neq \mu$. This is the same is we replace the average $\langle\cdot\rangle$ by a sum $\sum_{\boldsymbol{k}\in \mathrm{star}\{\boldsymbol{k}_0\}} \cdot$ over the star of a particular, but arbitrary quasimomentum $\boldsymbol{k}_0$. The product $T^{(\alpha)}_{\boldsymbol{k};ij} h^{(\mu)}_{\boldsymbol{k}}$, however, does not vanish necessarily (saved cases when the star of $\boldsymbol{k}$ consists of just one element).

representations. Using the orthogonality relations for characters of representations, the decomposition

$$\Gamma(\boldsymbol{r}) \times \Gamma(\boldsymbol{r}) = 2 \cdot A_1 + A_2 + B_1 + B_2 + 2 \cdot E$$

can be given. The projection of the components of the Raman tensor to the different IRs is performed using projection operators and yields the result

$$\hat{T} = \hat{T}_1^{A_1} + \hat{T}_2^{A_1} + \hat{T}^{A_2} + \hat{T}^{B_1} + \hat{T}^{B_2} + \hat{T}_1^{E} + \hat{T}_2^{E} \ , \tag{25}$$

where the components $\hat{T}^{\mu}$ are given by

$$\begin{aligned}
\hat{T}_1^{A_1} &= \begin{pmatrix} a & & \\ & a & \\ & & \end{pmatrix} \ , \quad \hat{T}_2^{A_1} = \begin{pmatrix} & & \\ & & \\ & & b \end{pmatrix} \ , \quad \hat{T}^{A_2} = \begin{pmatrix} & & c \\ -c & & \\ & & \end{pmatrix} \\
\hat{T}^{B_1} &= \begin{pmatrix} d & & \\ & -d & \\ & & \end{pmatrix} \ , \quad \hat{T}^{B_2} = \begin{pmatrix} & e & \\ e & & \\ & & \end{pmatrix} \ , \quad \hat{T}_1^{E} = \begin{pmatrix} & & f \\ & & f \\ & & \end{pmatrix} \\
\hat{T}_2^{E} &= \begin{pmatrix} & & \\ & & \\ g & g & \end{pmatrix} \ .
\end{aligned} \tag{26}$$

From this result is becomes clear, that in parallel polarizations, only A_1- and B_1-phonons can be detected. Phonons belonging to other IRs will not appear in the Raman spectrum. On the other hand, A_1- and B_1-phonons will not be visible in crossed polarization configurations.

One important final note is in order. The selection rules only involve the polarization vectors, but not the direction of the wavevectors of the incoming and scattered light and, therefore, are not depending on whether a Raman experiment is performed in backscattering or forward scattering geometry.

References

[1] L. M. Falicov, *Group Theory and Its Physical Applications*, Chicago & London 1969.

[2] W. Ludwig and C. Falter, *Symmetries in Physics*, Springer Series in Solid-State Sciences 64.

[3] T. Inui, Y. Tanabe, and Y. Onodera, *Group Theory and Its Applications in Physics*, Springer Series in Solid-State Sciences 78.

[4] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors*, Springer 1996.

[5] E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*, New York and London 1959.

[6] M. Cardona, *Resonance Phenomena*, in: *Light Scattering in Solids II*, ed. M. Cardona and G. Güntherodt.