CONDENSED MATTER PHYSICS · GROUP THEORY

Group Theoretical Analysis of Vibrational Modes in Crystalline Silicon

From Crystal Symmetry to Phonon Selection Rules

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SPACE GROUP	POINT GROUP	T_2G RAMAN MODE
$Fd\bar{3}m$ · No. 227	O_h · Order 48	520 cm^{-1}

MOTIVATION

Why Group Theory for Phonons?

01 **Symmetry constrains** which vibrational modes are physically allowed.

02 Predicts **IR and Raman activity** without solving equations of motion.

03 Reduces the **3N×3N dynamical matrix** into block-diagonal form.

04 Labels modes at every **k-point in the Brillouin zone** via irreducible representations.

05 Essential for interpreting **experimental spectra** and comparing to DFT calculations.

CORE INSIGHT

*Group theory is a **bookkeeping tool** — it doesn't solve the physics, it tells us what the physics **must look like** given the symmetry.*

Conclusions are **exact**, not approximate — a rare guarantee in condensed matter physics.

Point Group Oh

Factor Group

Zone-Center Γ

Why Group Theory Matters in Materials Science

Crystal Symmetry

32 Point Groups

↓

230 Space Groups

Universal classification of crystal structures

Group theory provides the language used to describe crystal symmetry.

Vibrational Spectroscopy

Raman Spectroscopy

IR Spectroscopy

Predicting observable vibrational modes

Symmetry determines which phonons can be observed experimentally.

Electronic Structure

- **Band Structure**
- **Degeneracies**
- **Semiconductors**
- **Quantum Materials**

Symmetry governs electronic properties and modern functional materials.

GROUP THEORY AS A UNIVERSAL FRAMEWORK

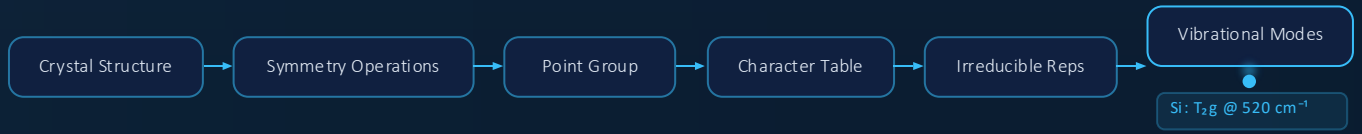
Crystal Structure → **Symmetry Operations** → **Representations** → **Physical Properties**

KEY TAKEAWAY

Group theory provides a universal framework for understanding crystal symmetry, vibrational spectroscopy, and electronic structure. The same mathematical tools can be applied across a wide range of materials and physical phenomena.

GROUP THEORY AS A UNIVERSAL FRAMEWORK

ANALYSIS PIPELINE



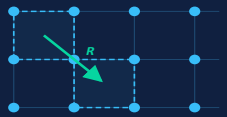
MATERIAL	CRYSTAL STRUCTURE	POINT GROUP	EXAMPLE USE
Silicon ★ CASE STUDY	Diamond cubic		Raman-active optical phonon — primary case study throughout
Graphene	Hexagonal honeycomb		In-plane & out-of-plane phonon modes classified by symmetry
Quartz	Trigonal		Symmetry-classified lattice vibrations across all branches
NaCl	Rock salt		Optical phonon modes — IR active, symmetry-forbidden in Raman

The method is universal — the material is the variable.

Why the Point Group O_h Is Sufficient at the Γ Point

LATTICE TRANSLATIONS

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

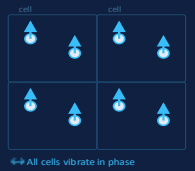


Translating by a lattice vector leaves the crystal unchanged.
Full space group for Silicone Crystal is

$Fd\bar{3}m$

Γ-POINT VIBRATIONS

$$k = 0$$



At the Γ point, every unit cell vibrates identically.
Lattice Vibrations can be written as
$u(r,t) = u_o \exp[i(k\cdot r - \omega t)]$

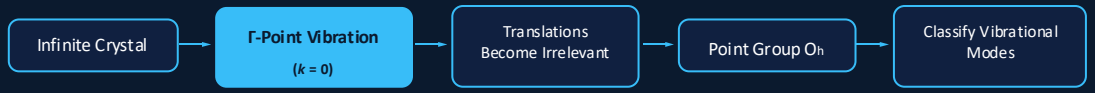
POINT-GROUP SYMMETRY

$$F = G / T \cong O_h$$

At Γ, translations do not change the vibrational pattern.

- Rotations
- Reflections
- Inversion

These 48 operations are sufficient to classify the vibrational modes.



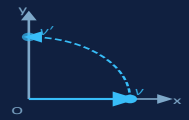
KEY IDEA

At the Γ point, every unit cell vibrates in phase. Translating the crystal does not change the motion, so only the point-group symmetry O_h is needed.

Representations and Characters: The Language of Group Theory

Symmetry Operation

$$Rz(90°) = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

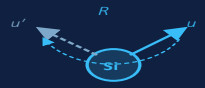


A symmetry operation can be represented by a matrix.

Action on Atomic Motion

$$u = (u_x, u_y, u_z)^T$$

$$u' = R\,u$$



Symmetry operations act on atomic displacements.

Character

$$\chi(R) = \mathrm{Tr}(R)$$

$$\chi(R_z) = 0 + 0 + 1 = 1$$

$$Rz(90°) = \begin{bmatrix} \mathbf{0} & -1 & 0 \\ 1 & \mathbf{0} & 0 \\ 0 & 0 & \mathbf{1} \end{bmatrix}$$

diagonal elements highlighted

The character is the **trace** of the representation matrix.

Characters are the entries used in character tables.

From symmetry to classification:

KEY TAKEAWAY

Group theory converts symmetry operations into matrices. The traces of these matrices — called **characters** — allow us to classify vibrational modes using character tables.

From Characters to Irreducible Representations

Representation

A representation describes how symmetry operations act on atomic motion.

represented by

Each operation maps to a transformation matrix.

Character Table

Irrep	E	C_3	C_4
A_1g	1	1	1
Eg	2	−1	0
T_2g	3	0	−1
T1u	3	0	1

The full O_h character table has 10 conjugacy classes and many irreps. This reduced table keeps the entries needed for this presentation.

Character tables organize the traces (characters) of symmetry operations.

Character Table → Classifi-cation → Irreducible Repre-sentations

Irreducible Representations

A_1g

Eg

T_2g

T_1u

Irreducible representations are the fundamental symmetry patterns.

Irreducible representations classify the symmetry of vibrational modes.

Different irreps correspond to different symmetry patterns of atomic

From symmetry to classification:

Representation → Characters → **Character Table** → **Irreducible Representations** → Physical Vibrational Modes

KEY TAKEAWAY

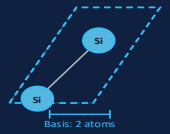
Character tables allow a complicated representation to be decomposed into simpler irreducible representations. These irreducible representations describe the fundamental symmetry patterns of atomic motion.

the full O_h character table because it has 10 conjugacy classes and many irreps. This reduced table keeps the entries needed for this presentation.

Next: counting and classifying silicon's vibrational degrees of freedom.

Counting Vibrational Degrees of Freedom in Silicon

Primitive Cell



N = 2 silicon atoms

The primitive cell of silicon contains two atoms.

Degrees of Freedom

Each atom can move in:

x y z

3N

3N = 3(2) = 6

Each atom contributes three independent displacement coordinates.

Mode Classification

6 Vibrational Modes

3 Acoustic Modes

Atoms move together.

3 Optical Modes

Atoms move opposite.

Acoustic: collective lattice motion. Optical: relative motion between atoms.

Building up to the group-theory classification:

Start Primitive Cell ▶ *Count* N = 2 Atoms ▶ *Multiply* 3N = 6 DOF ▶ ***Split*** **3 Acoustic + 3 Optical** ▶ *Next step* Classify w/ Group Theory

KEY TAKEAWAY

Before applying character tables and irreducible representations, we first count the available vibrational degrees of freedom. Silicon's two-atom primitive cell leads to **six vibrational modes**: three acoustic and three optical.

Next: which irreducible representations describe each mode?

Classifying Silicon's Vibrational Modes with Group Theory

6 Vibrational Modes → *Group-Theory Classification* → **Group-Theory Classification** → Irreducible Representations

ACOUSTIC MODES

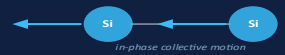
3 Acoustic Modes

↓

T_1u

Transforms as: x, y, z

Vector-like symmetry associated with translational motion.



Acoustic modes correspond to collective motion of the lattice.

OPTICAL MODES

3 Optical Modes

↓

T_2g

Transforms as: xy, xz, yz

Quadratic symmetry associated with Raman-active vibrations.

Optical modes correspond to relative motion between atoms.

PHYSICAL MEANING OF THE IRREPS

T_1u *Transforms as: x, y, z* Translation-like symmetry

T_2g *Transforms as: xy, xz, yz* Raman-active optical symmetry

Different irreducible representations correspond to different symmetry behaviors under the operations of O_h.

Group theory replaces complicated atomic motions with symmetry labels that describe how those motions transform under the crystal symmetry operations.

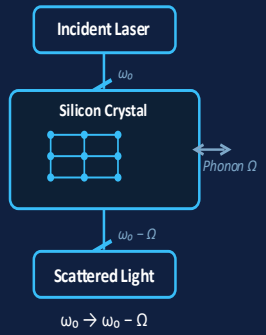
KEY TAKEAWAY

Group theory classifies vibrational modes using irreducible representations. The T_{1u} modes transform like the coordinates x, y, and z and naturally describes motion along the three Cartesian directions. While the $T_2{}^g$ mode transforms like xy, xz, and yz. These symmetry properties determine how the vibrations interact with experimental probes such as Raman spectroscopy.

Next: connecting these symmetry labels to observable Raman and IR activity.

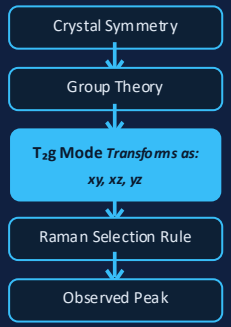
Raman Activity in Silicon: Where Group Theory Meets Experiment

Raman Scattering



Energy transferred to a lattice vibration (phonon).

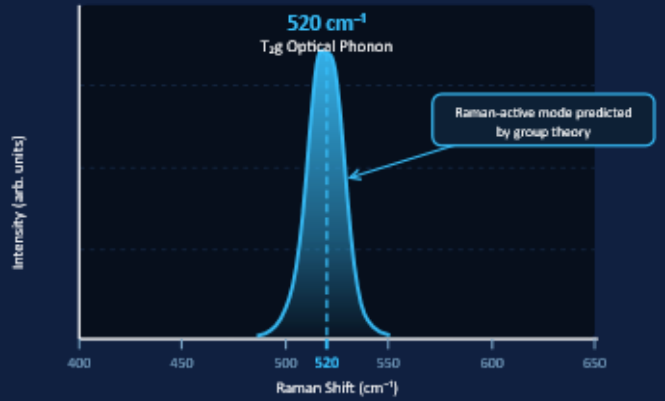
Symmetry Prediction



T_2g symmetry matches the Raman selection rules, allowing this vibration to interact with light.

Only vibrational modes with the proper symmetry appear in Raman scattering.

Experimental Signature



Why this matters:

Group Theory
Predicts Symmetry

→

Raman Spectroscopy
Measures Vibrations

→

Materials Science
Crystal Quality, Strain & Defects

Symmetry predictions become experimentally measurable quantities.

KEY TAKEAWAY

Group theory predicts which vibrational modes are Raman active. In silicon, the Raman-active T_2g optical phonon transforms as xy, xz, and yz and produces the characteristic Raman peak near 520 cm^{-1}. This provides a direct connection between crystal symmetry and experiment.

Selection Rules: Raman vs. Infrared Activity

O h symmetry

Centrosymmetric

Infrared Activity

Electric dipole transition

T_1u

Transforms as: x, y, z

Atomic Displacement

↓

Oscillating Dipole Moment

↓

Infrared Absorption

Infrared light couples to oscillating electric dipoles.

T_1u → IR active

IR-active modes transform like the coordinates x, y, and z.

VS

Raman Activity

Inelastic photon scattering

T_2g

Transforms as: xy, xz, yz

Atomic Vibration

↓

Changes Polarizability

↓

Raman Scattering

Raman light couples to changes in the polarizability tensor.

T_2g → Raman active

520 cm^{-1} silicon peak

Raman-active modes transform like quadratic functions.

MUTUAL EXCLUSION RULE

Centrosymmetric Crystal (Silicon)

u modes
ungerade (odd)
→ Infrared Active

g modes
gerade (even)
→ Raman Active

In centrosymmetric crystals, a vibrational mode cannot be both Raman active and infrared active.

KEY TAKEAWAY

Symmetry determines how vibrational modes interact with light. T_1u modes transform like x, y, and z and are infrared active, while the T_2g mode transforms like xy, xz, and yz and is Raman active. This explains why the silicon optical phonon is observed in Raman spectroscopy.

The 520 cm^{-1} Raman Fingerprint of Silicon

T_2g Raman-Active Optical Phonon

↓ Observed at 520 cm^{-1}

PEAK POSITION

520 cm^{-1}

Characteristic Raman peak of crystalline silicon.

LINEWIDTH

~3 cm^{-1} FWHM

Narrow peak indicates high crystal quality.

TEMPERATURE DEPENDENCE

Heating softens the phonon, shifting the peak to lower frequency.

STRAIN / PRESSURE DEPENDENCE

- Tensile strain shifts the peak lower.
- Compressive strain shifts the peak higher.

CRYSTAL QUALITY ASSESSMENT

Perfect Crystal

- Sharp Raman peak
- Narrow linewidth (~3 cm^{-1})

Defective Crystal

- Broad Raman peak
- Larger linewidth (>20 cm^{-1})

Defects, disorder, and amorphization broaden the Raman peak.

ISOTOPE EFFECT

^{28}Si	^{29}Si	^{30}Si
520.0 cm^{-1}	~511 cm^{-1}	~502 cm^{-1}
92.23% natural	4.67% natural	3.10% natural

$$\omega \propto 1/\sqrt{m}$$

Simple Harmonic Oscillator

Heavier isotopes vibrate more slowly, producing lower phonon frequencies.

KEY TAKEAWAY

Notice that everything on this slide is describing the same T_2g mode we identified using group theory. The symmetry classification tells us which vibration exists, and Raman spectroscopy tells us how that vibration changes with defects, strain, and temperature.

Symmetry → Vibrational Mode → Raman Signature → Materials Characterization

EXPERIMENTAL VERIFICATION OF SILICON PHONON SYMMETRY

Crystal Symmetry → Group Theory → T_2g Raman-Active Mode → Experimental Measurement → ✓ Agreement

Prediction from Group Theory

- Point Group : **O_h**
- Acoustic Modes → **T_1u**
- Raman-Active Optical Mode → **T_2g**
- Raman Peak → **520 cm^{-1}**

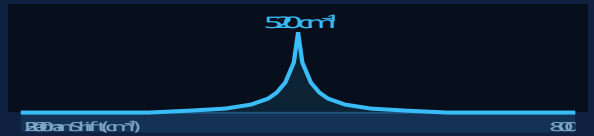
Crystal Structure
↓
Point Group O_h
↓
Irreducible Representations
↓
T_1u and T_2g

Symmetry analysis predicts the vibrational classification of silicon.

Experimental Measurements

Raman Spectroscopy

- Measures Raman-active phonons
- Observes the 520 cm^{-1} peak



Inelastic Neutron Scattering

- Measures phonon frequencies throughout the Brillouin zone
- Maps acoustic and optical branches

Experimental techniques directly probe lattice vibrations.

Agreement: Theory vs. Experiment

THEORY	EXPERIMENT
T_2g Raman-active optical phonon	Observed Raman peak
520 cm^{-1}	**520 cm^{-1}**

Confirmed

Symmetry predictions confirmed experimentally.

Agreement between theory and experiment is a landmark success of group theory in condensed matter physics.

KEY TAKEAWAY

Group theory predicts the symmetry, degeneracies, and selection rules of silicon's vibrational modes. Raman spectroscopy and neutron scattering confirm these predictions experimentally.

Group Theory
Predicts Symmetry
→
Experiment
Measures Vibrations
→
Agreement
Validates the Physical Model

Key Takeaways

1

Group Theory as a Universal Framework

Crystal Structure
↓
Point Group
↓
Character Table
↓
Irreducible Representations
↓
Vibrational Modes

Group theory provides a universal framework for understanding crystal vibrations.

2

Silicon Case Study

Point Group O_h
↓
6 Vibrational Modes
↓
3 Acoustic + 3 Optical
↓
$T_1u \oplus T_2g$

Silicon demonstrates how crystal symmetry classifies vibrational motion.

3

Selection Rules

T_1u
↓
IR Active
Transforms as x, y, z

T_2g
↓
Raman Active
Transforms as xy, xz, yz

Symmetry determines how vibrational modes interact with light.

4

Experimental Impact

T_2g Symmetry
↓
520 cm^{-1} Raman Peak
↓
Crystal Quality | Strain Measurement | Materials Characterization

Symmetry analysis leads directly to measurable and technologically useful material properties.

Group theory transforms crystal symmetry into experimentally testable predictions.

Symmetry → Vibrational Modes → Raman Signature → **Materials Characterization**

KEY TAKEAWAY: SYMMETRY → GROUP THEORY → PREDICTION → MEASUREMENT

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