CRYSTALLINE SOLIDS IN 3D

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OVERVIEW

• First - are there any questions from the previous lecture?

• Today, we will answer the following questions:
  • Why should we care about crystal structure?
  • How many Bravais lattices are there in 3D?
  • How do we describe them mathematically?
  • What are some common examples of these structures?
  • What are some not-so common examples?
In 2D, we saw that there are 5 distinct Bravais lattices. Characterized by 2 lattice vectors (2 magnitudes + 1 angle between vectors).

- 1 = oblique
- 2 = rectangular
- 3 = centered rectangular
- 4 = triangular net/hexagonal
- 5 = square net

Recall that must assign a basis to the lattice to describe a real solid.
3D BRAVAIS LATTICES

• In 3D, lattices are characterized by **3 lattice vectors** (3 magnitudes, 3 angles)

• There are 2 common conventions for labeling lattice vectors:
  • Kittel (your book) uses:
    • Vectors: \((a_1, a_2, a_3)\)
    • Angles: \((\alpha_{12}, \alpha_{23}, \alpha_{31})\)
    • \(\alpha_{12}\) is the angle b/w \(a_1\) and \(a_2\)
  • Perhaps more common:
    • Vectors: \((a, b, c)\)
    • Angles: \((\alpha, \beta, \gamma)\)
    • \(\alpha\) is the angle b/w \(b\) and \(c\)

• We find that there are **14 distinct Bravais lattices**.
• These 14 can be divided further into **7 lattice classes**

Image source: Kittel
• **7 lattice classes, 14 distinct Bravais lattices**
  • You will also see ‘volume centered’ structures referred to as ‘body centered’

• There is an error in this table: trigonal refers to a crystal system, NOT a Bravais lattice. The Bravais lattice is actually called rhombohedral.

• For now, you will be most interested in the cubic lattice classes

• If you continue in condensed matter physics, you will probably encounter some of the more ‘exotic’ structures in your research

<table>
<thead>
<tr>
<th>Bravais lattice</th>
<th>Parameters</th>
<th>Simple (P)</th>
<th>Volume centered (I)</th>
<th>Base centered (C)</th>
<th>Face centered (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$a_1 \neq a_2 \neq a_3$</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a_1 \neq a_2 \neq a_3$</td>
<td><img src="image5.png" alt="Diagram" /></td>
<td><img src="image6.png" alt="Diagram" /></td>
<td><img src="image7.png" alt="Diagram" /></td>
<td><img src="image8.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a_1 \neq a_2 \neq a_3$</td>
<td><img src="image9.png" alt="Diagram" /></td>
<td><img src="image10.png" alt="Diagram" /></td>
<td><img src="image11.png" alt="Diagram" /></td>
<td><img src="image12.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a_1 = a_2 \neq a_3$</td>
<td><img src="image13.png" alt="Diagram" /></td>
<td><img src="image14.png" alt="Diagram" /></td>
<td><img src="image15.png" alt="Diagram" /></td>
<td><img src="image16.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Trigonal</td>
<td>$a_1 = a_2 = a_3$</td>
<td><img src="image17.png" alt="Diagram" /></td>
<td><img src="image18.png" alt="Diagram" /></td>
<td><img src="image19.png" alt="Diagram" /></td>
<td><img src="image20.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Cubic</td>
<td>$a_1 = a_2 = a_3$</td>
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<td><img src="image22.png" alt="Diagram" /></td>
<td><img src="image23.png" alt="Diagram" /></td>
<td><img src="image24.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a_1 = a_2 \neq a_3$</td>
<td><img src="image25.png" alt="Diagram" /></td>
<td><img src="image26.png" alt="Diagram" /></td>
<td><img src="image27.png" alt="Diagram" /></td>
<td><img src="image28.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

Table 1.1: Bravais lattices in three-dimensions.
CUBIC BRAVAIS LATTICES

Left to right: simple, body/volume centered, face centered

• You will often see the abbreviations sc, bcc, and fcc for these lattices.
• Assigning lattice vectors is, as in 2D, non-unique, but not all choices are equally useful.
• Let's consider a bcc example.
BODY CENTERED CUBIC EXAMPLE

- We can conceptualize the bcc structure as 2 interpenetrating sc structures.

- Vertices of a cube in one lattice lie at the center of the other.

- Consider 2 choices of lattice vectors:
  - Origin at an A atom:
    - 2 vectors to other A atoms, 1 to a B atom
    - All 3 vectors to B atoms

- Let’s codify this mathematically.
BODY CENTERED CUBIC EXAMPLE (CONT).

\[ a_1 = a \hat{x} \]
\[ a_2 = a \hat{y} \]
\[ a_3 = a/2 (\hat{x} + \hat{y} + \hat{z}) \]

\[ a_1 = a/2 (\hat{y} + \hat{z} - \hat{x}) \]
\[ a_2 = a/2 (\hat{z} + \hat{x} - \hat{y}) \]
\[ a_3 = a/2 (\hat{x} + \hat{y} - \hat{z}) \]
PRIMITIVE CELLS

• The **unit cell** is a volume that can fill all of space, without gaps, when translated by lattice vectors.
• The choice of unit cell is also non-unique, so it is convenient to have a standard for assigning them.
• This is called the **Wigner-Seitz cell**, it is an example of a **primitive cell**.

• A **primitive cell** is the minimum volume of space that can be used to characterize a Bravais lattice that contains **exactly 1 lattice point**.

• This is, of course, also non-unique:

• Notice that many of the choices have symmetries that differ from the underlying lattice...
PRIMITIVE CELLS (CONT.)

• Things can look even weirder in 3D...

• The unshaded area is the **conventional** fcc unit cell.

• The shaded area is one choice of the primitive cell

• This may seem counter-intuitive: parallelepiped has 8 vertices, each of which ‘contains’ 1/8 of a lattice point - \(8 \times \frac{1}{8} = 1\) point per cell

• Parallelepiped **does NOT** have the cubic symmetry of the original Bravais lattice...
We want a convenient standard for constructing **primitive cells that preserve the symmetry of the original Bravais lattice**.

Along came these 2 gentlemen...

Eugene Wigner
- Hungarian theoretical physicist
- Nobel laureate (1963)
- Fun fact: Paul Dirac’s brother-in-law

Frederick Seitz
- Wigner’s student
- Started big lab at UIUC
- Fun facts:
  - Global warming skeptic (before it was cool)
For a given lattice point, the Wigner-Seitz cell is the volume of space that is closer to that point than any other in the lattice.

**Algorithm for construction**
- Choose a lattice point
- Find its nearest neighbors
- Draw a line from the point to its neighbors
- Bisect this line with a plane
- Planes bound the Wigner-Seitz cell

We will find this same construction useful when we learn about Brillouin Zones.

If you ever wind up working in applied math/computer science/topology, a generalization of this concept is frequently found (Voronoi polyhedra) that actually goes all the way back to Descartes!
UNIT CELL VOLUME

• The volume of the unit cell, when occupied by a basis of atoms, will have some bearing upon the physical properties of the crystal.

• The volume of a conventional, cubic unit cell is simply $|\mathbf{a}_1|^3 = |\mathbf{a}_2|^3 = |\mathbf{a}_3|^3$.

• More generally, you can use the lattice vectors to calculate the volume of the unit cell:
  $$|\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)| = |\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)| = |\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)|$$

• So far we have only considered the conventional unit cell...
• What about the primitive unit cell?
  • Conventional unit cell for fcc and bcc have 4 and 2 atoms per cell, respectively.
  • What is the volume of the primitive cells for fcc and bcc structures?
EXEMPLARY CRYSTAL STRUCTURES

• Remember, to create an actual crystal, we need to assign a basis of atoms to the Bravais lattice.
• What are some of the more common crystal structures that arise in solid state physics?

• CsCl: simple cubic with a basis of 2 atoms
• NaCl (halite, rock salt): fcc lattice with a basis of 2 atoms
• Diamond: fcc lattice with a basis of 2 atoms of the same species
• ZnS (zincblende): fcc lattice with a basis of 2 atoms of different species
• Hexagonal close packed (HCP): simple hexagonal lattice with a two atom basis

• Let’s look at these individually, in more detail...
CESIUM CHLORIDE

• Simple cubic lattice with a basis of 2 atoms:
  • Green sites are Chlorine
  • Blue sites are Cesium
• Simple choice of basis: (0,0,0) and (a/2,a/2,a/2)
• Each site has 8 nearest neighbors of the opposite species.

• Alkali halide, so bonding is similar to NaCl, but here the atoms have very different sizes...
SODIUM CHLORIDE

• Face centered cubic lattice with a basis of 2 atoms:
  • Green sites are Chlorine
  • Red sites are Sodium
• Same choice of basis: (0,0,0) and (a/2,a/2,a/2)
  • Centering is different here!
• Each site has 6 nearest neighbors of the opposite species.

• Again an alkali halide, so bonding will be similar, but the atoms have similar ‘sizes’, so the crystal structure is different.
DIAMOND

- Face centered cubic lattice with a basis of 2 atoms of the same species (Carbon for “diamond” diamond)

- New choice of basis: (0,0,0) and (a/4,a/4,a/4)
- Centering is different here!
- Each site has 4 nearest neighbors of the same species.

- Diamond structures typically arise in covalently bonded crystals
- Of great technological importance:
  - Silicon solidifies in the diamond crystal structure
ZINCBLENDE

• Face centered cubic lattice with a basis of 2 atoms of the different species (Zinc and Sulfur)
• Same choice of basis: (0,0,0) and (a/4,a/4,a/4)
• Each site has 4 nearest neighbors of the opposite species.

• Zincblende structures also arise in covalently bonded crystals
• Also of great technological importance:
  • Commonly arises in III-V semiconductors
  • GaAs is a good example
**HEXAGONAL CLOSE PACKED (HCP)**

- Simple hexagonal lattice with a basis of 2 atoms
- Think of this as stacking layers of 2D triangular nets
- Basis: \((0,0,0)\) and \((a/3,a/3,a/2)\)

- The name comes from packing hard spheres (bottom)

- 30 elemental solids crystallize in HCP
  - (Mg and Be are the most common)

- Many different types of close-packing arrangements
  - Think of it like close-packing 2D layers...
  - HCP is not Bravais lattice, but FCC close-packing is...
MODERN APPLICATIONS

• The topological insulating state is a topic of considerable contemporary interest.

• In a conventional band insulator, the electrons in a crystalline solid are immobile throughout the entire crystal (i.e., even at the surface).

• In a topological insulator, symmetries of the underlying crystal, along with spin-orbit coupling effects give rise to materials where the bulk insulates, but the surfaces have electronic states that can participate in conduction.

• These surface states are very ‘exotic’:
  • Electron spin is locked perpendicular to its (quasi)-momentum
  • Scattering channels are suppressed by symmetry, so the conduction is ballistic (free of scattering)
  • Anomalous magnetoelectric effect (non-Maxwellian electrodynamics)

• Some of the associated crystal structures are quite complex...
MODERN APPLICATIONS

• On the left is Bi$_2$Se$_3$, a confirmed topological insulator
  • Rhombohedral Bravais lattice

• On the right is Tl$_2$Hg$_3$Te$_4$, a potential topological insulator
  • Monoclinic Bravais lattice

• I am studying the latter, trying to figure out whether or not this state will arise in this particular material
CONCLUSIONS

• Take home points from today’s lecture:
  • There are **14 distinct Bravais lattices in 3D**.
  • Each lattice is **characterized by 3 lattice vectors** (3 magnitudes, 3 angles)
  • Primitive cell can be constructed using **Wigner-Seitz method**

• In Monday’s lecture, we will discuss:
  • What type of **experimental probes** exist for characterizing crystalline solids?
  • What is a **reciprocal lattice** and what is its relationship to the lattices we have already discussed?
  • What is a **Brillouin Zone**, and why is it theoretically useful?

• Any questions?

• Before leaving, take out a piece of paper - here is a 5 minute quiz.
• Consider the simple cubic, face centered cubic, and body centered cubic lattices.

• Assuming each lattice site is occupied by a basis consisting of a single sphere at (0,0,0), with a radius such that it is touching its nearest neighbor, what percentage of the conventional unit cell is filled by spheres?