

## Lecture 5

### Nearly Free Electron Model

5.1 Nearly Free Electron Model

5.1.1 Brillouin Zone

5.1.2 Energy Gaps

5.2 Translational Symmetry – Bloch's Theorem

5.3 Kronig-Penney Model

5.4 Examples

References:

1. Marder, Chapters 7-8
2. Kittel, Chapter 7
3. Ashcroft and Mermin, Chapter 9
4. Kaxiras, Chapter 3
5. Ibach, Chapter 7

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## Sommerfeld's theory does not explain all...

Metal's conduction electrons form highly degenerate Fermi gas

Free electron model: works only for metals

- heat capacity, thermal and electrical conductivity, magnetic susceptibility, etc

Drawbacks:

predicted electron mean path is too long

increases with temperature

positive values for the Hall coefficient, magnetotransport

difference between a good conductor ( $10^{-10}$  Ohm-cm) and a good insulator ( $10^{22}$  Ohm-cm) –  $10^{32}$  !!!

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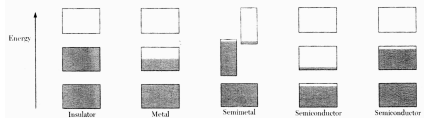
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## Electron Occupancy of Allowed Energy Bands



**Figure 1** Schematic electron occupancy of allowed energy bands for an insulator, metal, semimetal, and semiconductor. The vertical extent of the boxes indicates the allowed energy regions. The shaded areas indicate the regions filled with electrons. In a semimetal (such as bismuth) one band is almost filled and another band is nearly empty at absolute zero, but a pure semiconductor (such as silicon) becomes an insulator at absolute zero. The left of the two semiconductors shown is at a finite temperature, with carriers excited thermally. The other semiconductor is electron-deficient because of impurities.

**Adapted from Kittel**

- No electrons can move in an electric field (energy band is completely filled or empty) – **insulator** ;
- One or more bands are partly filled – **conductor**

**Basic Assumptions:**

- crystal structure is periodic
- periodicity leads to formation of **energy bands** (allowed energy levels)
- energy bands are separated by **energy gaps or band gaps** (region in energy for which no wavelike electron orbital exist)

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## 5.1 Nearly Free Electron Model

In free electron model: all energy values from 0 to infinity are allowed

$$\mathcal{E}_k = \frac{\hbar^2}{2m} \vec{k}^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

Wavefunctions are in the form:  $\psi_{\vec{k}}(\vec{r}) = \exp(i\vec{k} \cdot \vec{r})$ ,

where the components of the wavevector  $\vec{k}$  are:  $k_x = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \dots$

Nearly free electron model: weak perturbation of electrons by periodic potential of ions

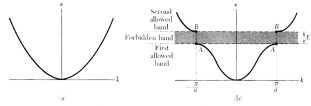


Figure 2 (a) Plot of energy  $\mathcal{E}$  versus wavevector  $k$  for a free electron. (b) Plot of energy versus wavevector for an electron in a sinusoidal lattice of lattice constant  $a$ . The energy gap  $\mathcal{E}_g$  shown is associated with the first Bragg reflection at  $k = \pm \pi/a$ ; other gaps are found at  $\pm n\pi/a$ , for integral values of  $n$ .

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## Nearly Free Electrons

Consider the effects due to a periodic crystal structure

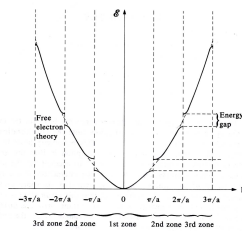


Fig. 10-4 Energy vs. wave vector for free electrons (dashed parabola) and for nearly free electrons (solid lines). Gaps develop at  $k = \pm p\pi/a$  where  $p = \pm 1, \pm 2$ , and so forth.

Under condition  $k = \pm \frac{1}{2} G = \pm \frac{n\pi}{a}$ , the electron wave will undergo Bragg reflection

Energy gaps develop at these  $k$  due to these reflections

At  $k = n\pi/a$  the wavefunctions are **not** the traveling wave of free electrons

The region between  $-\pi/a$  and  $\pi/a$  :  
first Brillouin zone of this 1D lattice

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### 5.1.1 Brillouin Zone in 1D: extended, reduced and repeated

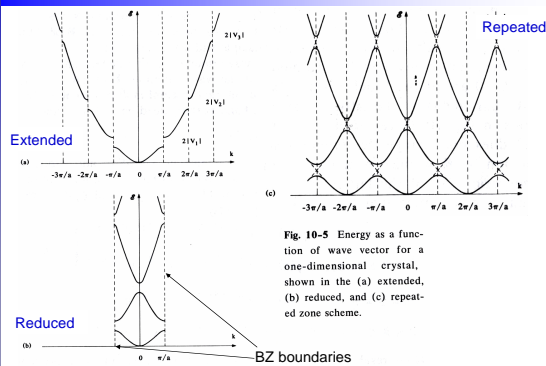


Fig. 10-5 Energy as a function of wave vector for a one-dimensional crystal, shown in the (a) extended, (b) reduced, and (c) repeated zone scheme.

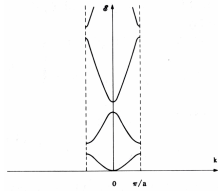
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## Reduction to the first Brillouin zone

This general demand of periodicity implies that the possible electron states are not restricted to a single parabola in  $k$ -space, but can be found on any parabola shifted by any  $G$ -vector:

$$\varepsilon(\vec{k}) = \varepsilon(\vec{k} + \vec{G}) = \frac{\hbar^2}{2m} |\vec{k} + \vec{G}|^2$$

For 1D case:  $\vec{G} \rightarrow G = \frac{2\pi}{a}$



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## Brilloiun Zone in 3D

**Brilloiun Zone in 3D:** Wigner-Seitz cell of the reciprocal lattice

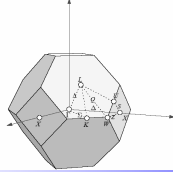
**Recall:** reciprocal lattice vector  $\vec{G} = 2\pi n_1 \vec{b}_1 + 2\pi n_2 \vec{b}_2 + 2\pi n_3 \vec{b}_3$ ,

where  $\vec{b}_1, \vec{b}_2, \vec{b}_3$  are basic vectors such that  $\vec{b}_1 = \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$ ;  $\vec{b}_2 = \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$ ;  $\vec{b}_3 = \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$ ;

**Some properties of reciprocal lattice:**

The direct lattice is the reciprocal of its own reciprocal lattice

The unit cell of the reciprocal lattice need not be a parallelepiped, e.g., Wigner-Seitz cell

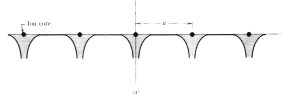


first Brillouin Zone (BZ)  
of the fcc lattice

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## 5.1.2 Origin of the Energy Gap

Crystal Potential -  $U$

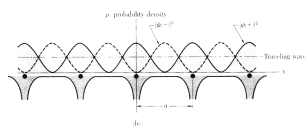


The probability density of the particle is

$$\psi^* \psi = |\psi|^2$$

For pure traveling wave:

$$\rho = \exp(-ikx) \exp(ikx) = 1$$



For plane waves the charge density is not constant:

for the wave  $\psi(+)$ :

$$\rho(+) = |\psi(+)|^2 \propto \cos^2 \frac{\pi x}{a}$$

for the wave  $\psi(-)$ :

$$\rho(-) = |\psi(-)|^2 \propto \sin^2 \frac{\pi x}{a}$$

Figure 3 (a) Variation of potential energy of a conduction electron in the field of the ion cores on a linear lattice. (b) Distribution of probability density  $\rho$  in the lattice for  $\psi = \exp(i k x)$  and  $\psi = \exp(-i k x)$ . The wavefunction  $\psi(+)$  piles up the electronic charge on the cores of the positive ions, thereby lowering the potential energy in comparison with the average potential energy seen by a traveling wave. The wavefunction  $\psi(-)$  piles up charge in the regions between the ions, thereby raising the potential energy in comparison with that seen by a traveling wave. This figure is the key to understanding the origin of the energy gap.

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## Magnitude of the Energy Gap

The potential energy due to the crystal can be approximated as:

$$U(x) = U \cos \frac{2\pi x}{a}$$

This potential has the periodicity of the lattice,  $U(x) = U(x + a)$

The wavefunctions at the Brillouin zone boundary  $k = \pi/a$  (normalized over unit length of line,  $a$ ) are

$$\sqrt{2} \cos \frac{\pi x}{a} \text{ and } \sqrt{2} \sin \frac{\pi x}{a}$$

The difference between the two standing wave states is

The **gap** is equal to the **Fourier component of the crystal potential**

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## 5.2 Translational Symmetry – Bloch's Theorem

**Bloch's theorem:** the wave functions of the electrons in a crystal must be of a special form (the Bloch form)

$$\psi_k(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) u_k(\vec{r})$$

$$u_k(\vec{r}) = u_k(\vec{r} + \vec{T})$$

$u_k(r)$  – the periodicity of the lattice (depends on the wave vector!)

Note: the Bloch function can be decomposed into a sum of traveling waves

**In 1D:** Consider a crystal of length  $L = N a$  ( $N$  primitive u. c. of length  $a$  on a ring)

The periodic boundary condition demands that

Addition of the translational symmetry gives :

$$\text{Therefore } \psi(x) = u_k(x) \exp\left(\frac{i2\pi x}{Na}\right)$$

Kittel, pp.179-180

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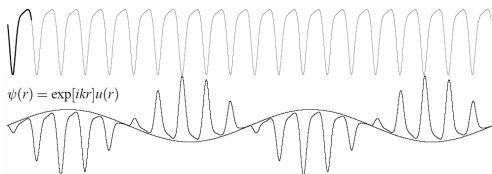
## Bloch's Theorem

For non-interacting electrons moving in a **periodic potential**,  $U(r)$

$$U(\vec{r} + \vec{R}) = U(\vec{r})$$

Bloch wave functions are periodic functions  $u(r)$  modulated by a plane wave of a longer period

Periodic function  $u(r)$



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## Translation Operators

Let  $\hat{T}_{\vec{R}}$  translate wave function by  $\vec{R}$ :  $\hat{T}_{\vec{R}} = e^{-\frac{i\vec{p}\vec{R}}{\hbar}}$

**Theorem:** if one has a collection of Hermitian operators that commute with one another, they can be diagonalized simultaneously

Any eigenvector of the Hamiltonian can be taken as an eigenfunction of all the translational operators as well:

Use theorem:

$$\begin{aligned}\hat{T}_{\vec{R}}|\psi\rangle &= e^{-\frac{i\vec{p}\vec{R}}{\hbar}}|\psi\rangle = C_{\vec{R}}|\psi\rangle \\ \psi(\vec{r} + \vec{R}) &= C_{\vec{R}}\psi(\vec{r})\end{aligned}$$

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## Translation Operators

Operating with eigenfunction of momentum:

$$\begin{aligned}e^{i\vec{k}\vec{R}}\langle\vec{k}|\psi\rangle &= C_{\vec{R}}\langle\vec{k}|\psi\rangle \\ \Rightarrow \text{either } C_{\vec{R}} &= e^{i\vec{k}\vec{R}} \quad \text{or} \quad \langle\vec{k}|\psi\rangle = 0\end{aligned}$$

$\vec{k}$ : Bloch wave vector  
 $\hbar\vec{k}$ : Crystal momentum  
 $n$ : Band index

For a given value of Bloch wavevector, there is still the possibility of many energy eigenvalues (can be labeled by the band index  $n$ )

The eigenfunctions made possible by periodicity is:  $\hat{H}|\psi_{n\vec{k}}\rangle = E_{n\vec{k}}|\psi_{n\vec{k}}\rangle$   
 $\hat{T}_{\vec{R}}|\psi_{n\vec{k}}\rangle = e^{i\vec{k}\vec{R}}|\psi_{n\vec{k}}\rangle$

$$\begin{aligned}\psi_{n\vec{k}}(\vec{r} + \vec{R}) &= e^{i\vec{k}\vec{R}}\psi_{n\vec{k}}(\vec{r}) \quad \text{or} \\ u_{n\vec{k}}(\vec{r}) &= e^{-i\vec{k}\vec{r}}\psi_{n\vec{k}}(\vec{r})\end{aligned}$$

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## Allowed values of k

If crystal is periodic with (macroscopic) dimensions  $M_1\vec{a}_1, M_2\vec{a}_2, M_3\vec{a}_3$  then requiring  $\exp[i\vec{k}\cdot\vec{r}]$  to be periodic constrains  $\vec{k}$  to

$$\vec{k} = \sum_{i=1}^3 \frac{m_i}{M_i} \vec{b}_i, 0 \leq m_i \leq M_i, \text{ where } \vec{b}_1, \vec{b}_2, \vec{b}_3 \text{ are such that } \vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$$

Periodic boundary condition place a condition on how small  $k$  can be

Demanding that  $C_{\vec{R}} = e^{i\vec{k}\vec{R}}$  be unique places conditions on how big  $k$  can be

Number of points in crystal equals number of unique Bloch wave vectors

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## Energy Bands and Group Velocities

Velocity of electrons in the  $n$ th band with wave number  $k$  is:

$$\vec{v}_{nk} = \frac{1}{\hbar} \nabla_{\vec{k}} E_{nk}$$

Note: this is similar to the solution of wave equations for a group velocity:  $v = \frac{\partial \omega}{\partial k}$

Wave packet: 
$$W(\vec{r}, \vec{k}, t) = \int w(\vec{k}' - \vec{k}) \cdot e^{i(\vec{k}' - \vec{k}) \cdot \vec{r} - i(E_{\vec{k}'} - E_{\vec{k}})t/\hbar} \psi_{\vec{k}'} e^{-i\vec{k}' \cdot \vec{r}} d\vec{k}' \approx$$
  

$$\approx e^{i(\vec{k} - \vec{r}) \cdot \vec{r} - iE_{\vec{k}}t/\hbar} \int w(\vec{k}') d\vec{k}' \approx e^{i(\vec{k} - \vec{r}) \cdot \vec{r} - iE_{\vec{k}}t/\hbar}$$

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## 5.3 Kronig-Penney Model

The wave equation is 
$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + U(x) \psi = E \psi$$

In the region  $0 < x < a$  ( $U = 0$ ), the eigenfunction is a linear combination of plane waves traveling to the right and to the left with energy  $E = \frac{\hbar^2 K^2}{2m}$

$$\psi = A e^{iKx} + B e^{-iKx}$$

In the region  $-b < x < 0$  within the barrier the solution is

$$\psi = C e^{Qx} + D e^{-Qx}$$

where  $U_0 - E = \frac{\hbar^2 Q^2}{2m}$

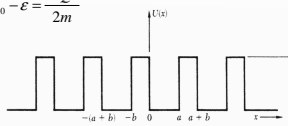


Figure 4 Square-well periodic potential as introduced by Kronig and Penney.

## Kronig-Penney Model

Solution must be in the Bloch form:

$$\psi(a < x < a+b) = \psi(-b < x < 0) e^{ik(a+b)}$$

The constants  $A, B, C, D$  are chosen so that wavefunction and its derivative are continuous at  $x = 0$  and  $x = a$

At  $x = 0$  
$$A + B = C + D$$
  

$$iK(A - B) = Q(C - D)$$

At  $x = a$  
$$A e^{iKa} + B e^{-iKa} = (C e^{-Qb} + D e^{Qb}) e^{ik(a+b)}$$
  

$$iK(A e^{iKa} - B e^{-iKa}) = Q(C e^{-Qb} - D e^{Qb}) e^{ik(a+b)}$$

Solution: 
$$[(Q^2 - K^2) 2QK] \sinh Qb \sin Ka + \cosh Qb \cos Ka = \cos k(a+b)$$
  
 In the limit  $Q \gg K$  and  $Qb \ll 1$

$$\frac{P}{Ka} \sin Ka + \cos Ka = \cos ka$$

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## Functions and Energy for the K-P potential

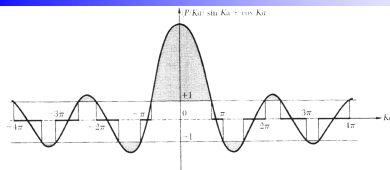
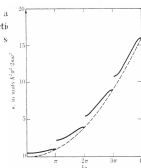


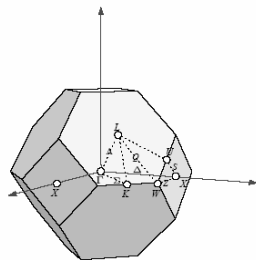
Figure 5 Plot of the function  $(P/Ka) \sin Ka + \cos Ka$ , for  $P = 3\pi/2$ . The energy  $\epsilon$  are given by those ranges of  $Ka = (2me\hbar^2)^{1/2}a$  for which the function is between -1 and 1. For other values of the energy there are no traveling wave or Bloch-like solutions, so that forbidden gaps in the energy spectrum are formed.



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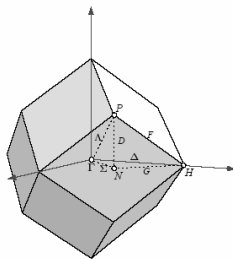
Figure 6 Plot of energy  $\epsilon$  vs. wave number for the Kronig-Penney potential

## First Brillouin Zone for fcc lattice



In units of  $2\pi/a$ ,  $\Gamma = (0\ 0\ 0)$ ,  $X = (0\ 1\ 0)$ ,  $L = (1/2\ 1/2\ 1/2)$ ,  $W = (1/2\ 1\ 0)$ ,  $K = (3/4\ 3/4\ 0)$ , and  $U = (1/4\ 1\ 1/4)$ .

## First Brillouin Zone for bcc lattice

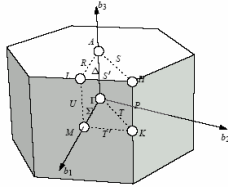


In units of  $\frac{4\pi}{a}$ ,  $\Gamma = (0\ 0\ 0)$ ,  $H = (0\ 1\ 0)$ ,  $N = (1/2\ 1/2\ 0)$ , and  $P = (1/2\ 1/2\ 1/2)$ .

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## First Brillouin Zone for hcp lattice



In units of  $4\pi/a\sqrt{3}$ ,  $4\pi/a\sqrt{3}$ , and  $2\pi/c$ , along the three primitive vectors  $\vec{b}_1$ ,  $\vec{b}_2$ , and  $\vec{b}_3$ ;  $\Gamma = (0\ 0\ 0)$ ,  $A = (0\ 0\ 1/2)$ ,  $M = (1/2\ 0\ 0)$ ,  $K = (1/3\ 1/3\ 0)$ ,  $H = (1/3\ 1/3\ 1/2)$ , and  $L = (1/2\ 0\ 1/2)$ .

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## Example: Nearly Free Electron in 1D

Electrons of mass  $m$  are confined to one dimension. A weak periodic potential is applied:

$$V(x) = V_0 + V_1 \cos \frac{2\pi x}{a} + V_2 \cos \frac{4\pi x}{a}$$

- Under what conditions will the nearly free-electron approximation work?
- Sketch the three lowest energy bands in the first Brillouin zone. Number the energy bands (starting from one at the lowest band)
- Calculate (to first order) the energy gap at  $k = \pi/a$  (between the first and second band) and  $k = 0$  (between the second and third band)

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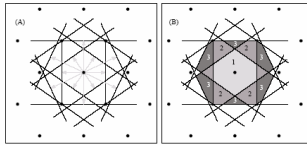
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## N<sup>th</sup> Brillouin zone: geometrical view

N<sup>th</sup> Brillouin zone: geometrical view

$$\vec{k} \cdot \frac{\vec{K}}{K} = \frac{1}{2}K$$



Procedure:

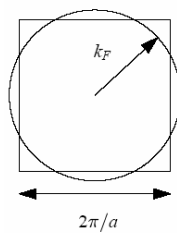
- perpendicular bisectors are drawn between the origin and all nearby reciprocal lattice points  $\Rightarrow$  zone boundaries
- the 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> BZ are shaded in different color (same volume)

- electron response to the external electric field same as for free electron till it approaches a zone boundary plane
- an electron once in the n<sup>th</sup> BZ remains in the n<sup>th</sup> BZ

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## Example in two dimensions



Suppose 2D lattice has two conduction el. per lattice sites

The # of  $k$ -states in BZ = the # of lattice points

For a weak potential, shape of the energy surface ~ sphere

$$\pi k_F^2 = 4\pi^2/a^2$$

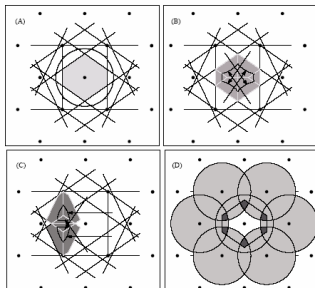
$$\Rightarrow k_F = 2\pi/\sqrt{\pi}a = 1.128\pi/a$$

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## Example in two dimensions

- Fermi surface completely enclosing the 1<sup>st</sup> BZ
- shape of surface is modified near the zone boundary



- portion of the Fermi surface in 2<sup>nd</sup> BZ is mapped back into the 1<sup>st</sup> zone

- portion of the Fermi surface in 3<sup>rd</sup> BZ is made continuous by translation through reciprocal lattice vectors

Harrison construction:  
n<sup>th</sup> BZ mapped into 1<sup>st</sup> BZ

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## Nearly Free Electron Fermi Surface Gallery

Brillouin zone	1 electron/cell	2 electrons/cell	3 electrons/cell
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First



Second



Third



[http://www.phys.ufl.edu/fermisurface/periodic\\_table.html](http://www.phys.ufl.edu/fermisurface/periodic_table.html)

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