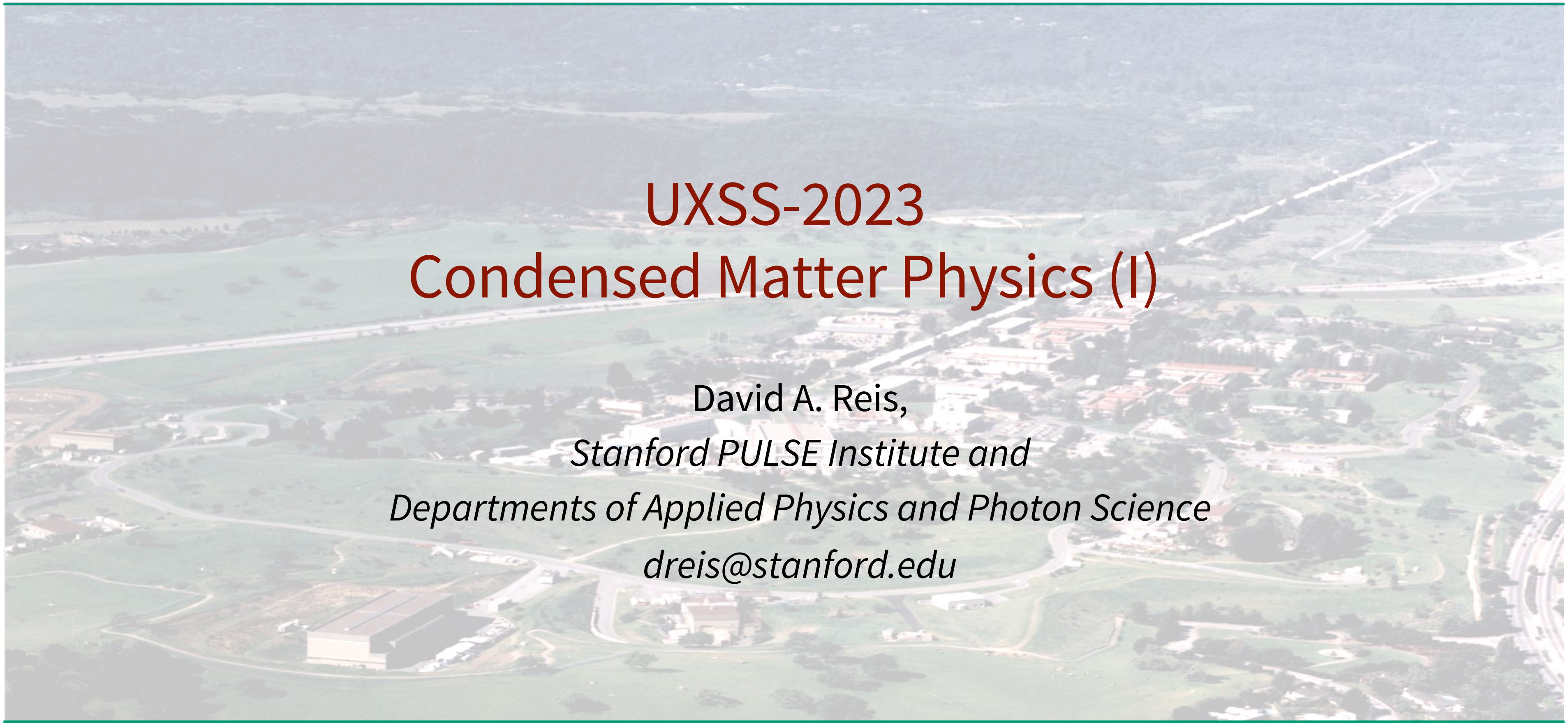


UXSS-2023
Condensed Matter Physics (I)

David A. Reis,

Stanford PULSE Institute and

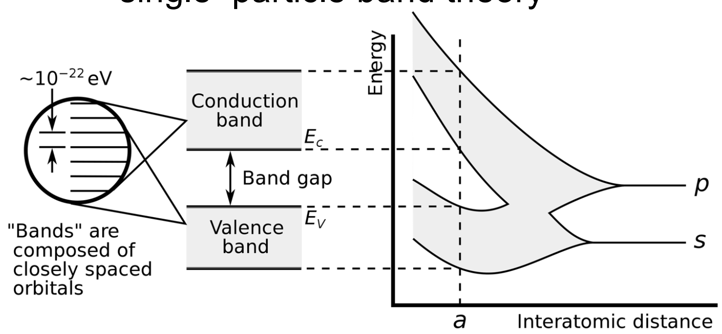
Departments of Applied Physics and Photon Science

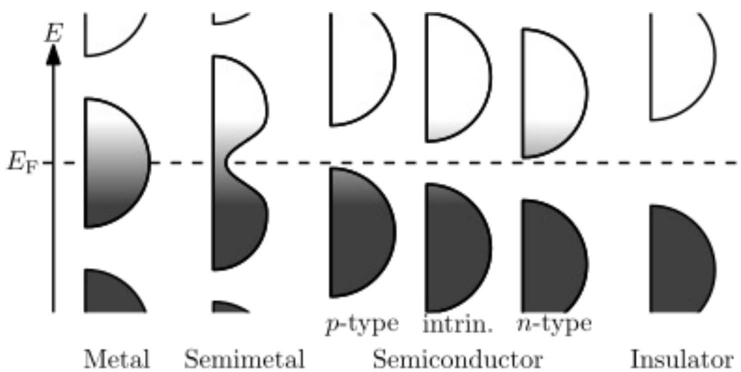
dreis@stanford.edu

17th annual Ultrafast X-ray Summer School, CFEL, Hamburg, Germany June 12–16, 2023

Modern Condensed Matter Physics

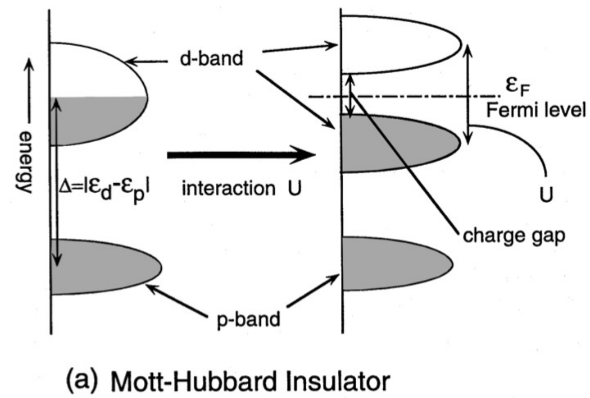
single particle band theory





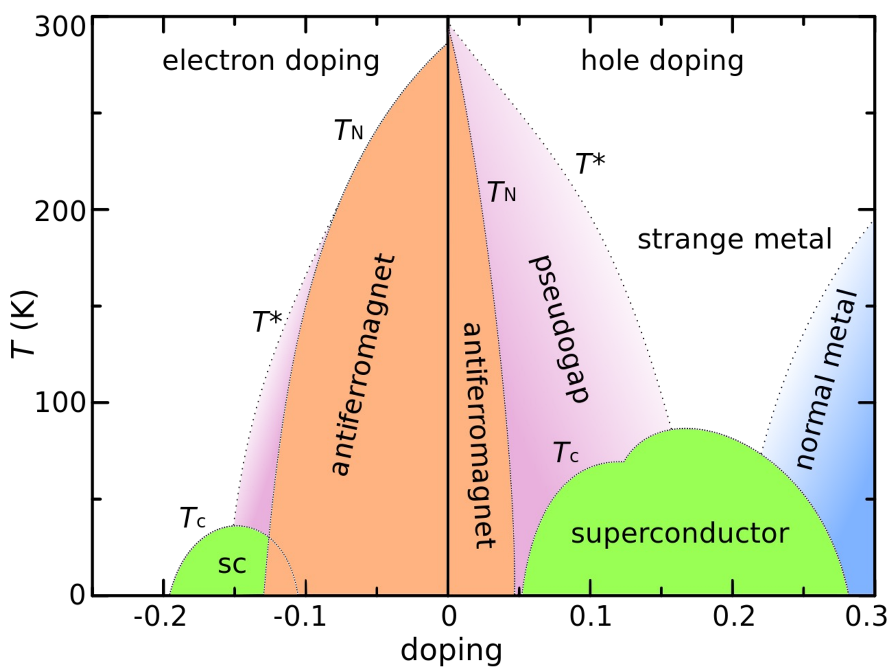
wikepedia

electron correlation

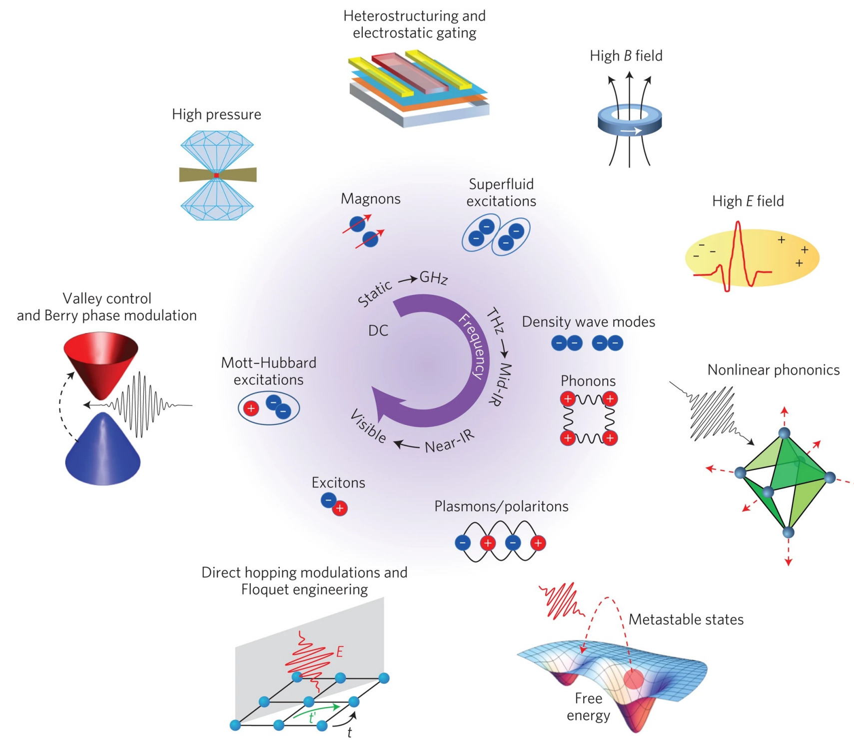


RMP 70, 1998

Controlling properties of Quantum Materials



https://commons.wikimedia.org/wiki/File:Cuprates_phasedigagram_en.svg



Nat. Mat. 16, 2017

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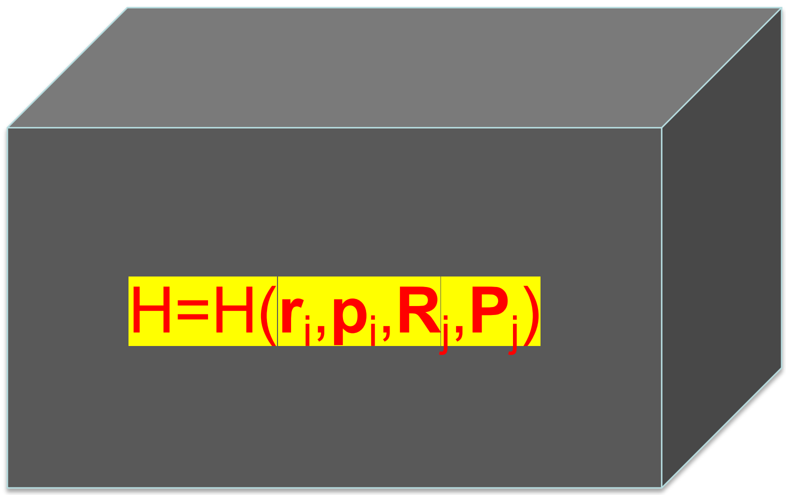
Outline (scope)

- Lecture 1, the "Basics"
  - Hamiltonian and simplifications based on crystal symmetry
  - Low-lying excitations
  - Non-resonant x-ray scattering and structure
  - Inelastic x-ray scattering
- Lecture 2, "ultrafast and time-resolved applications"
  - Time-domain, non-resonant x-ray scattering
  - Lattice dynamics, near and far from equilibrium
  - Other examples…

- Out of scope (for example):
  - Methods to calculate/predict materials properties.
  - Liquids, glasses, low dimensional materials, device physics,…
  - Thermodynamics, Phase transitions
  - X-ray absorption/emission spectroscopy
  - Resonant inelastic x-ray scattering (RIXS)
  - Non x-ray based characterization
  - Coherence
  - And much more…

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_j \frac{P_j^2}{2M_j} + \frac{1}{2}\sum_{j' \neq j} \frac{Z_{j'} Z_j e^2}{|\vec{R}_j - \vec{R}_{j'}|} - \sum_{i,j} \frac{Z_j e^2}{|\vec{r}_i - \vec{R}_j|} + \frac{1}{2}\sum_{i' \neq i} \frac{e^2}{|\vec{r}_i - \vec{r}_{i'}|}$$

electron KE | ion KE | ion-ion PE | ion-electron PE | electron-electron PE

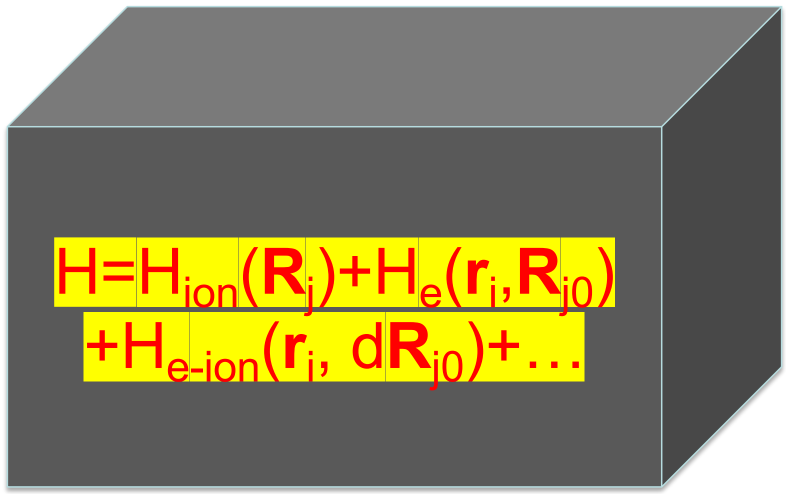


Periodic solids:
Simplifications based on symmetry + approximations

$$\{R|H = H\}$$

- Point group
  (rotations, reflection, inversion, roto-inversion)
- Space group =
  Point group +
  discrete translations

(+ (possibly) time reversal)



- Separate ion and electron degrees of freedom
- Electrons depend to lowest order on average ion position
- Ions only see electrons on average.
- Higher order gives couplings

Lattice periodicity and Bloch Theorem

Direct Lattice Vector

$$\boldsymbol{R}_{uvw} = u\boldsymbol{a}_1 + v\boldsymbol{a}_2 + w\boldsymbol{a}_3$$

Equilibrium Positions of ion of type "s"

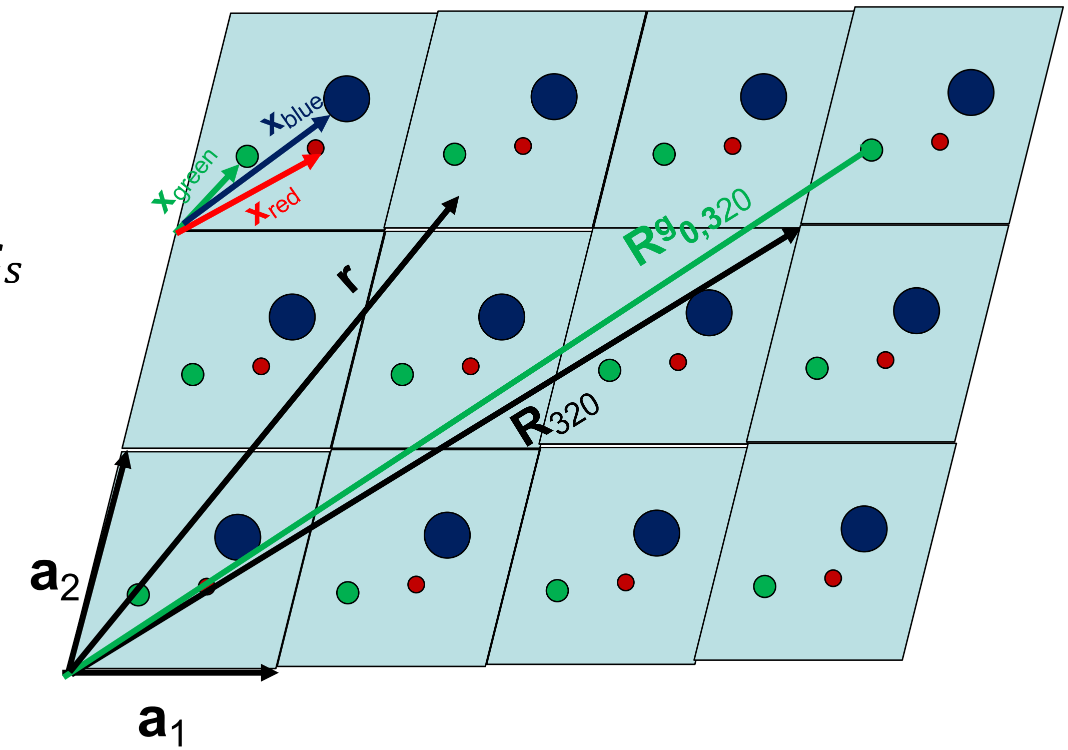
$$\boldsymbol{R}_{0,uvw}^{(s)} = u\boldsymbol{a}_1 + v\boldsymbol{a}_2 + w\boldsymbol{a}_3 + \boldsymbol{x}_s$$

$$H(\boldsymbol{r}) = H(\boldsymbol{r} + \boldsymbol{R}_{uvw})$$

$$\rho(\boldsymbol{r}) = \rho(\boldsymbol{r} + \boldsymbol{R}_{uvw})$$

$$\chi(\boldsymbol{r}) = \chi(\boldsymbol{r} + \boldsymbol{R}_{uvw})$$

etc.



What about excited states?

Lattice periodicity and Bloch Theorem

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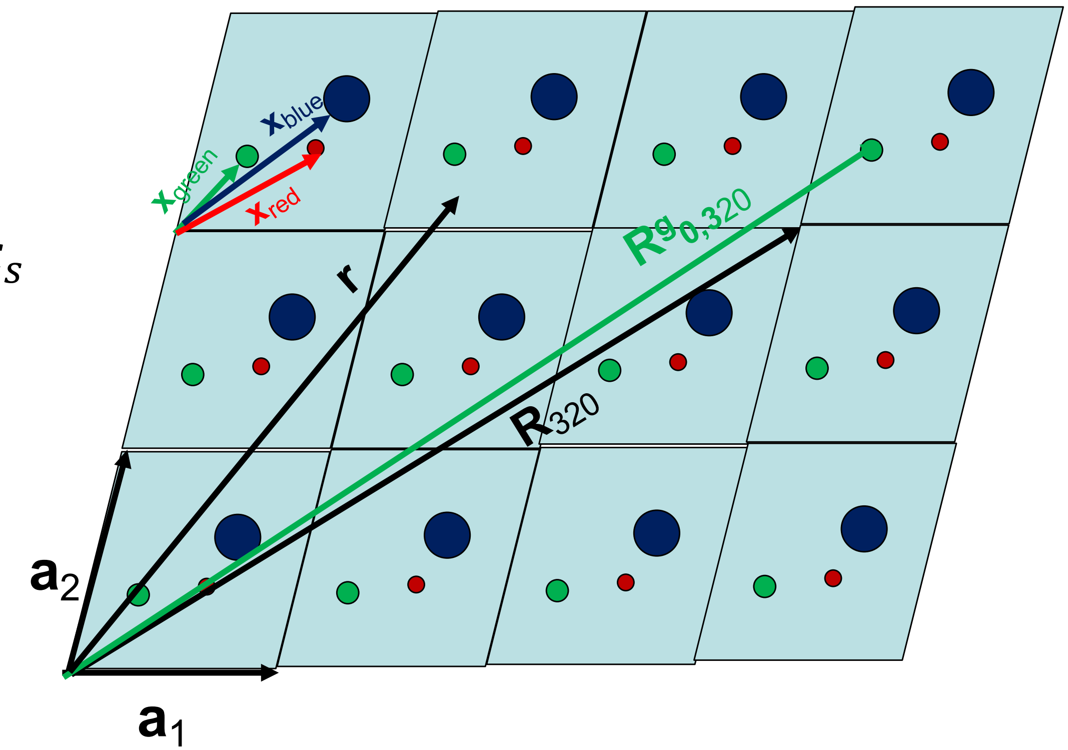
Equilibrium Positions of ion of type ”s”

$$\boldsymbol{R}^{(s)}_{0,uvw} = u\boldsymbol{a}_1 + v\boldsymbol{a}_2 + w\boldsymbol{a}_3 + \boldsymbol{x}_s$$

$$H\psi_k(\boldsymbol{r}) = E_k\psi_k(\boldsymbol{r})$$

$$\psi_k(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{\boldsymbol{k}}(\boldsymbol{r})$$

$$u_k(\boldsymbol{r}) = u_k(\boldsymbol{r}+\boldsymbol{R})$$



What about excited states?

Reciprocal Lattice

Direct Lattice Vector

$$\boldsymbol{R}_{uvw} = u\boldsymbol{a}_1 + v\boldsymbol{a}_2 + w\boldsymbol{a}_3$$

Define some

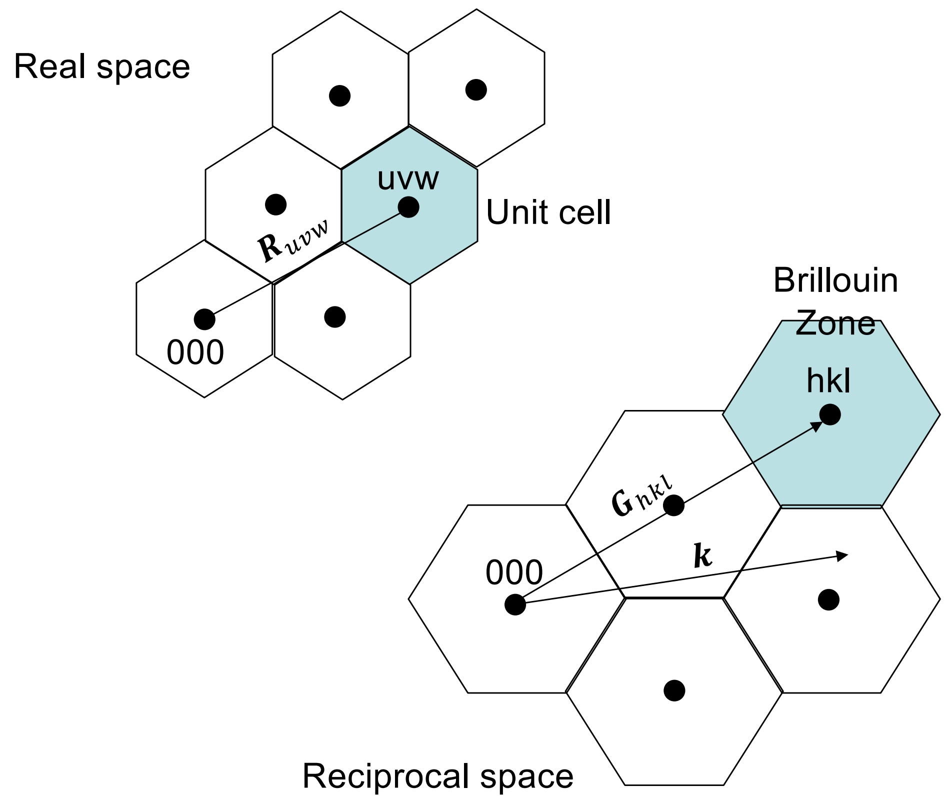
$$\boldsymbol{G}_{hkl} = h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3$$

$$\boldsymbol{b}_i = 2\pi \frac{\boldsymbol{a}_j \times \boldsymbol{a}_k}{\boldsymbol{a}_i \cdot \boldsymbol{a}_j \times \boldsymbol{a}_k} \epsilon_{ijk}$$

$$\boldsymbol{a_i} \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}$$

$$E_k = E_{k+G}$$

$$e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{R}}$$



Alphabet soup of elementary excitations (quasi-particles, collective excitations)

$$H\psi_k(\boldsymbol{r}) = E_k\psi_k(\boldsymbol{r})$$

Adapted from A. Warhol

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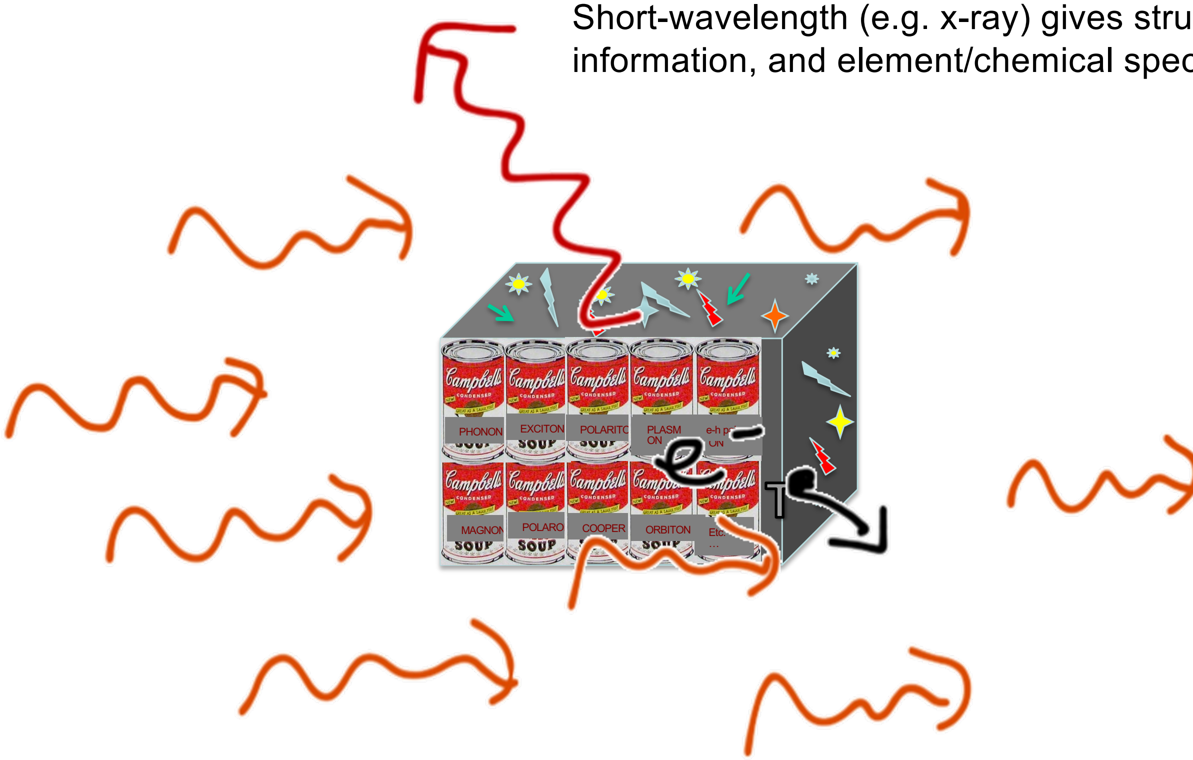
Light scattering and spectroscopy

Short-wavelength (e.g. x-ray) gives structural information, and element/chemical specificity



Adapted from A. Warhol

X-ray interaction with matter primarily through electrons

photon in-electron out

photoelectric absorption (p•A)
primarily off core electrons, element specific and sensitive to local environment (photoemission,EXAFS,…)

Leaves material in highly excited state
relaxation via fluorescence of Auger emission.

photon in-photon out

elastic, (Thomson, Bragg, …)
initial and final state the same (A^2)
finite dispersion due to $(A \cdot p)^2$ term

inelastic,
Compton, IXS (A^2 & $(A \cdot p)^2$)
Raman/RIXS… $(A \cdot p)^2$
leaves material in excited state
outgoing photon shifted in energy

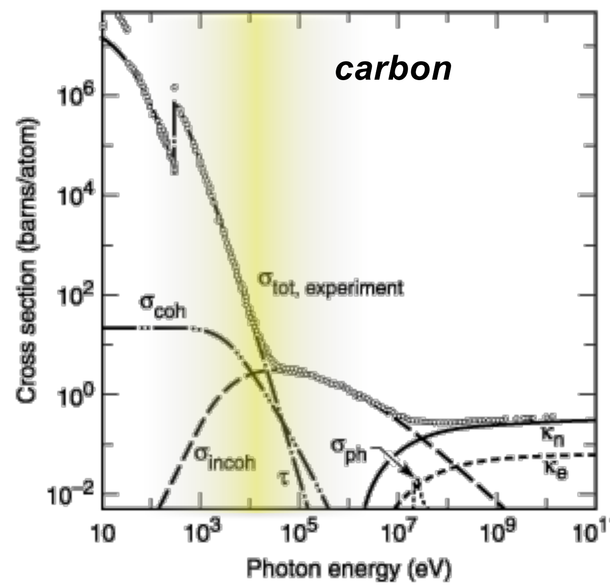


Fig. 3-1. Total photon cross section in carbon, as a function of energy, showing the contributions of different processes: τ, atomic photo-effect (electron ejection, photon absorption); σ_{coh}, coherent scattering (Rayleigh scattering—atom neither ionized nor excited); , σ_{incoh}incoherent scattering (Compton scattering off an electron); κ_n, pair production, nuclear field; κ_e , pair production, electron field; , σ_{ph} photonuclear absorption (nuclear absorption, usually followed by emission of a neutron or other particle). (From Ref. 3; figure courtesy of J. H. Hubbell.)

adapted from xdb.lbl.gov/

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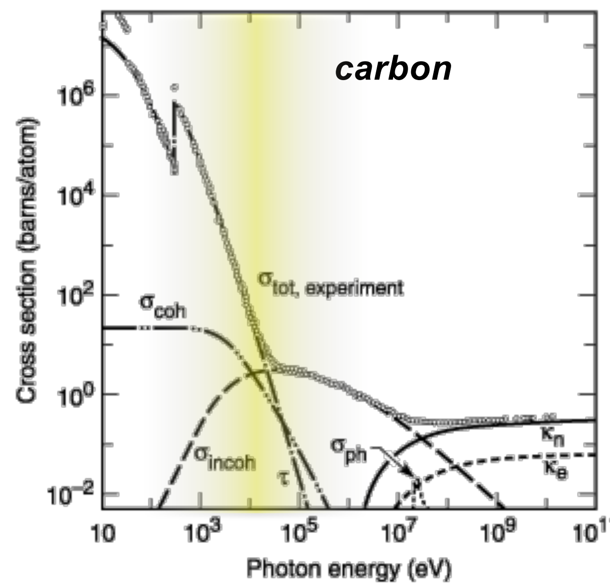

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adapted from xdb.lbl.gov/

"Elastic" scattering from single electron

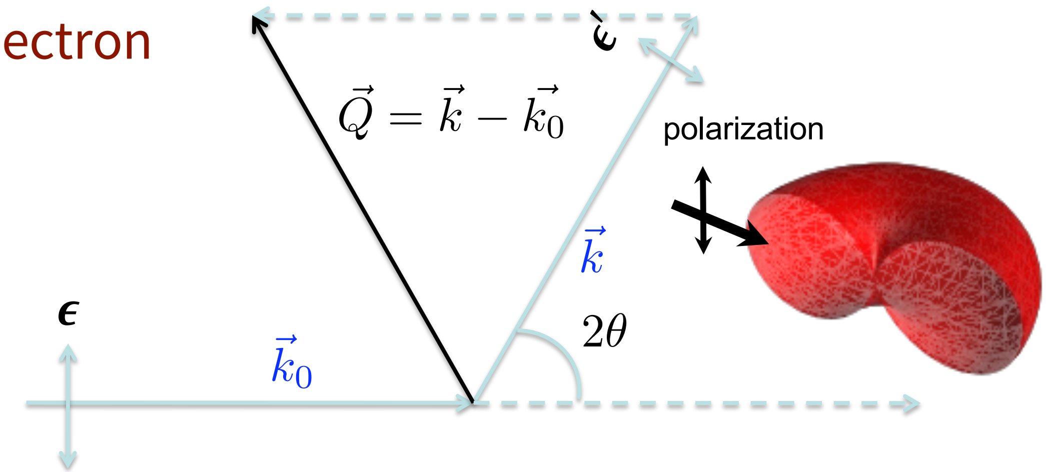
where $|k| = |k|_0 = 2\pi/\lambda$

$$Q = \frac{4\pi}{\lambda} \sin\theta$$

$$E_e = E_0 \frac{r_e}{r} e^{i(\boldsymbol{Q}\cdot\boldsymbol{r} - \omega t)} \sin\Theta$$

$$I_e = I_0 \frac{r_e^2}{r^2} \sin^2\Theta$$

$$\sin\Theta = |\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'|$$



Elastic scattering from single atom, far from resonance

$$E_e = E_0 \frac{r_e}{r} f(\boldsymbol{Q}) e^{i(\boldsymbol{Q}\cdot\boldsymbol{r} - \omega t)} \sin\Theta$$

$$r_e = \frac{e^2}{mc^2} \approx 2.8\ 10^{-15} m$$

$$\frac{d\sigma}{d\Omega} = r_e^2\, |\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'|^2$$

$$f(\boldsymbol{Q}) = \int d^3r\, \rho_{atom}(\boldsymbol{r}) e^{i\boldsymbol{Q}\cdot\boldsymbol{r}}$$

Thomson

$\hbar\vec{Q}$ is the momentum transfer for scattering of a photon

Quiz, can we have elastic scattering from a free-electron?

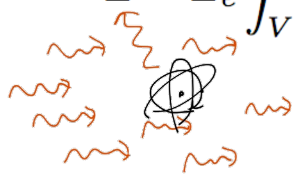
No cannot satisfy energy and momentum conservation
(Compton Scattering, $\omega' < \omega$)

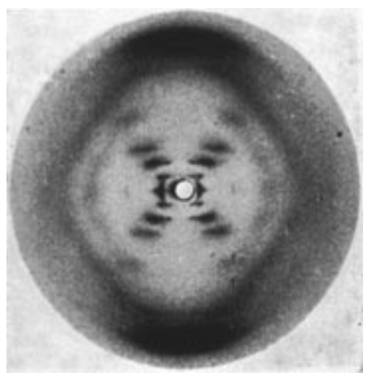
Then why can we have elastic scattering from an atom?

Recoil insignificant since $M_{ion} \gg m_e$

Coherent-Scattering

$$E \approx E_e \int_V \rho(\vec{r}) e^{i((\vec{k}-\vec{k_0})\cdot\vec{r})} d^3r$$



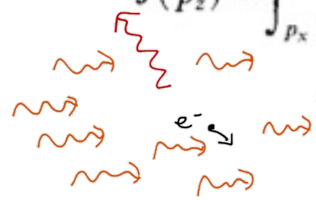


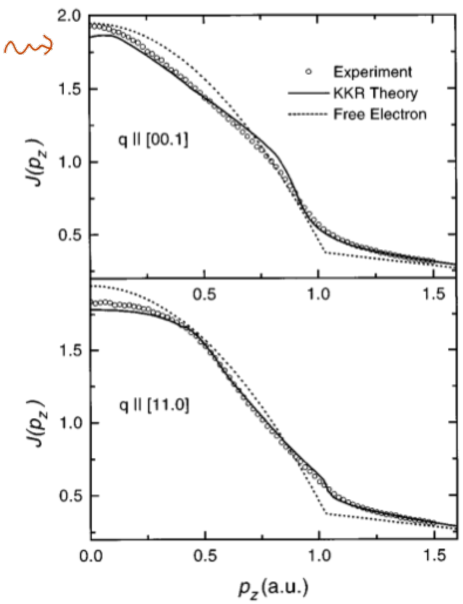
Franklin R. and Gosling R.G. *Nature* 171, 740-741 (1953)

Watson J.D. and Crick F.H.C. *Nature* 171, 737-738 (1953)

Incoherent-Scattering

$$J(p_z) = \int_{p_x} \int_{p_y} n(p_x, p_y, p_z)\, dp_x\, dp_y.$$





Hämäläinen et al., PRB 54, 5453, 1996

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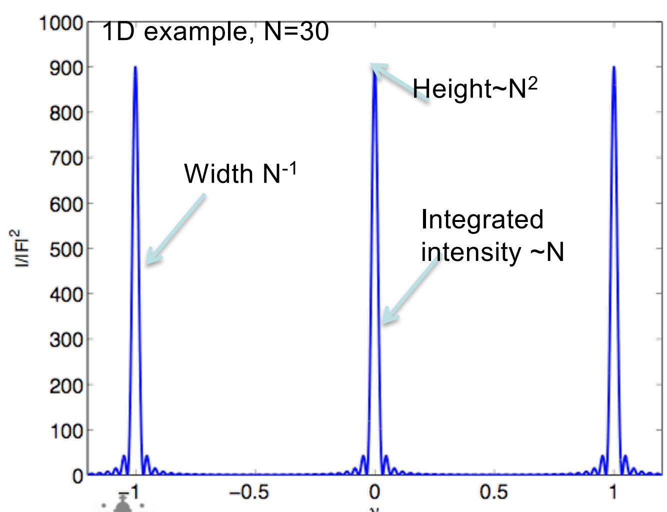
Elastic scattered field Fourier transform of crystal (far from resonance)

$$E(\boldsymbol{Q}) \approx E_e \int d^3r\, \rho(\boldsymbol{r}) e^{i\boldsymbol{Q}\cdot\boldsymbol{r}} \approx E_a \int d^3r\, \sum_{s,j} f_s\, \delta(\boldsymbol{r} - \boldsymbol{R}_j^s) e^{i\boldsymbol{Q}\cdot\boldsymbol{r}}$$

$$E(\boldsymbol{Q}) \approx E_e \sum_j F(\boldsymbol{Q})\, e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_j} \qquad \mathrm{F}(\boldsymbol{Q}) = \sum_s f(\boldsymbol{Q})\, e^{i\boldsymbol{Q}\cdot\boldsymbol{x}_s}$$

(Molecular) Structure Factor



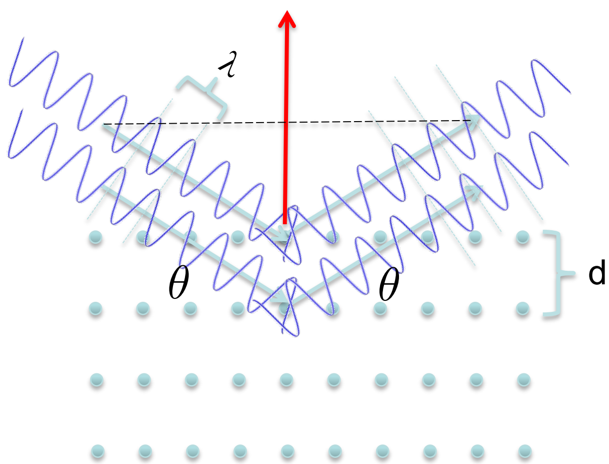
$$E(\boldsymbol{Q}) \approx N E_e F(\boldsymbol{Q}) \delta(\boldsymbol{Q} - \boldsymbol{G})$$

$$I(\boldsymbol{Q}) \approx N^2 I_e |F(\boldsymbol{Q})|^2 \delta(\boldsymbol{Q} - \boldsymbol{G})$$

Crystallography

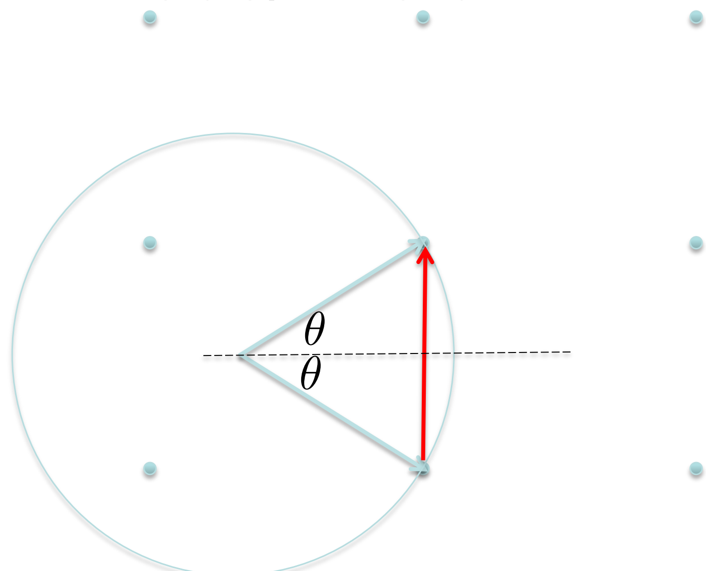
*of course, don't measure E but $|E|^2$

Bragg



$$\sin\theta = \frac{\lambda}{2d}$$

Laue/Ewald



$$\vec{k_0} + \vec{G}_{hkl} = \vec{k}$$

$$|k| = |k_0| = \frac{2\pi}{\lambda}, d = \frac{2\pi}{|G_{hkl}|}$$

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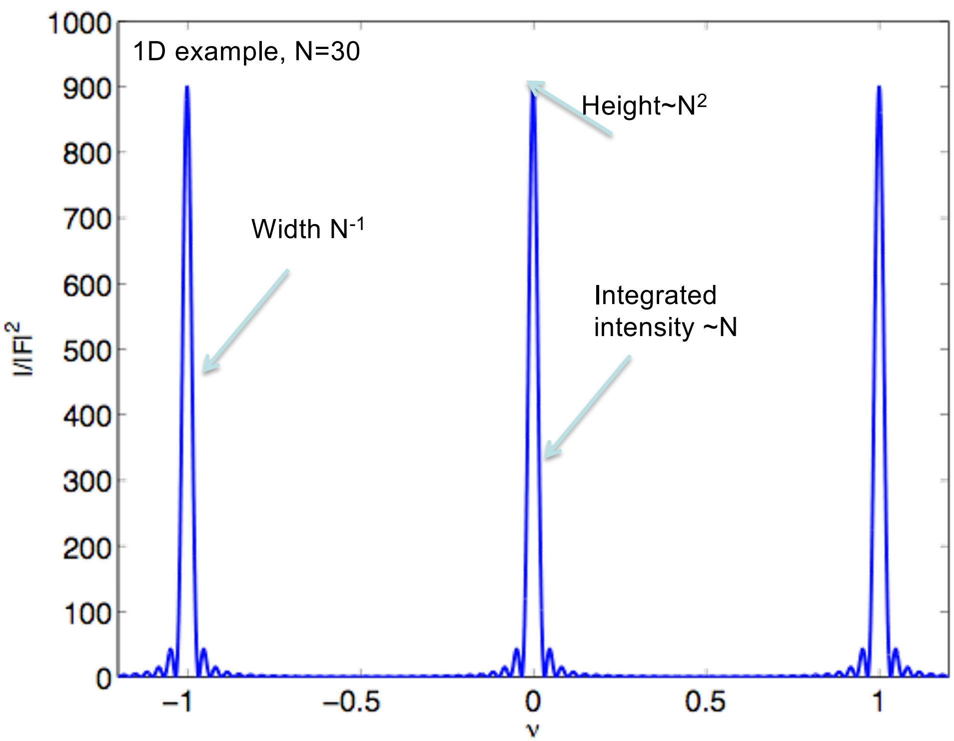
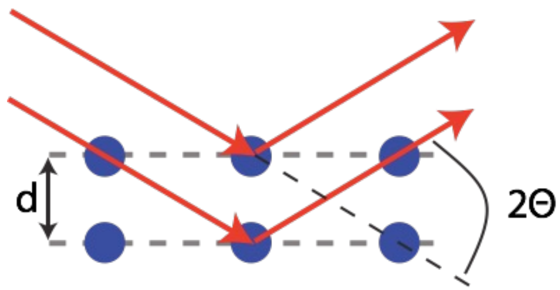


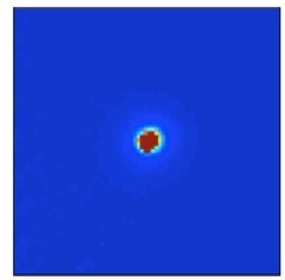
What happens on “Bragg” as $N \rightarrow \infty$?

X-ray scattering from disordered materials

Bragg Scattering

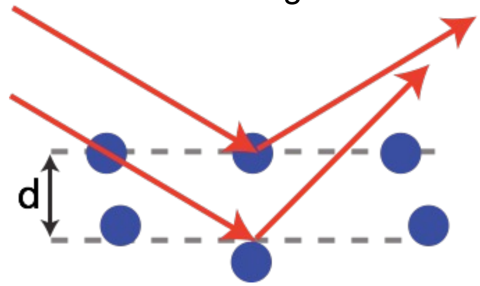


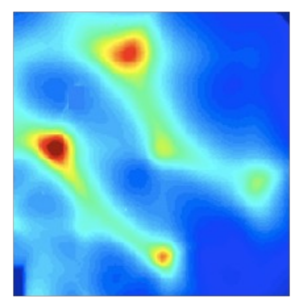
Bragg peak



strong peak
in
defined
direction

Diffuse Scattering





weak signal
“in between”
Bragg peaks
(in reciprocal
space)

Recall

$$H\psi_k(\boldsymbol{r}) = E_k\psi_k(\boldsymbol{r})$$

$$\{R|H = H\}$$

- Point group (rotations, reflection, inversion, roto-inversion)
- Space group = Point group + **discrete translations**

(+ (possibly) time reversal)

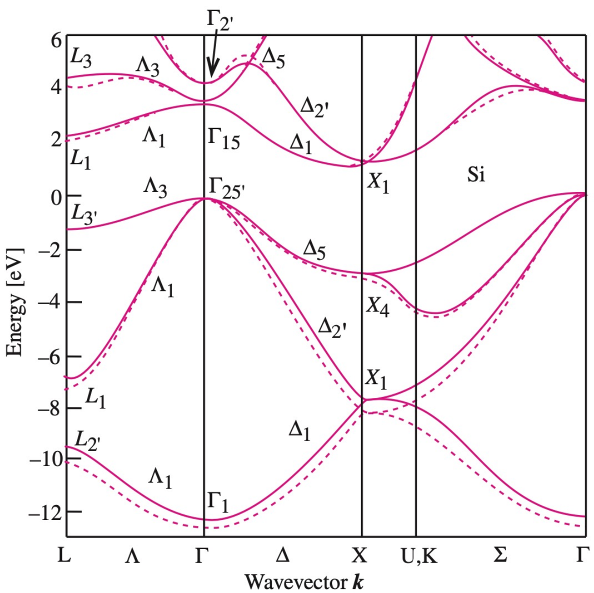
$$H=H_{ion}(\mathbf{R}_j)+H_e(\mathbf{r}_i,\mathbf{R}_{j0})$$
$$+H_{e\text{-}ion}(\mathbf{r}_i,\, d\mathbf{R}_{j0})+\ldots$$

- Separate ion and electron degrees of freedom
- Electrons depend to lowest order on average ion position
- Ions only see electrons on average.
- Higher order gives couplings

Alphabet soup of elementary excitations (quasi-particles, collective excitations)

$$H\psi_k(\boldsymbol{r}) = E_k\psi_k(\boldsymbol{r})$$

Electron Band Structure (Si)



Cardon & Yu, Fundamental of Semiconductors

Adapted from A. Warhol

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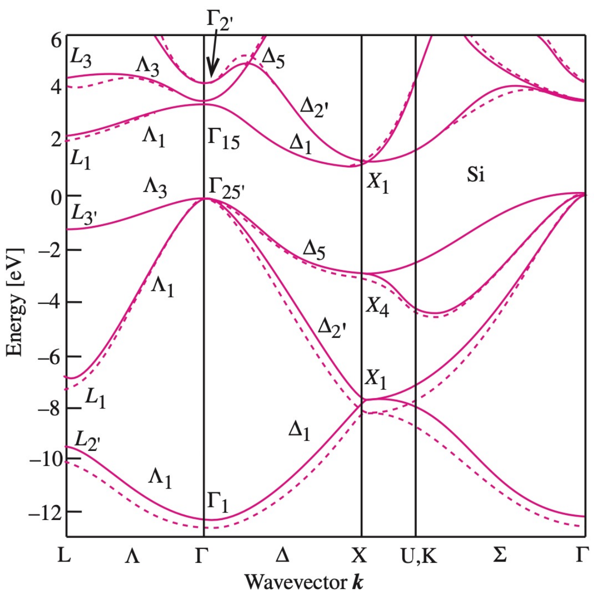
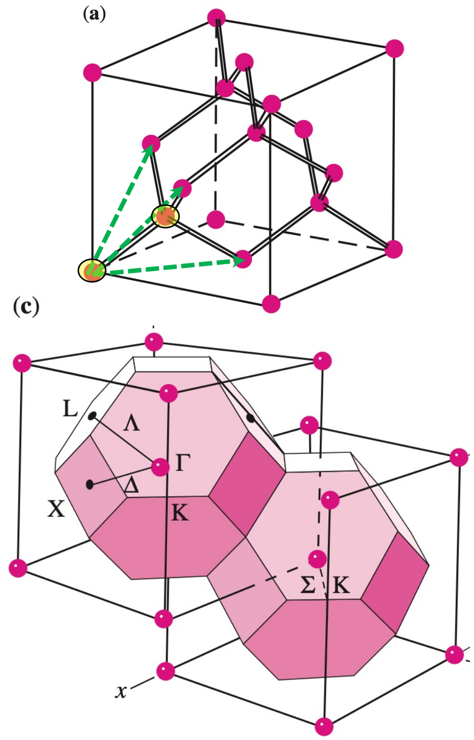
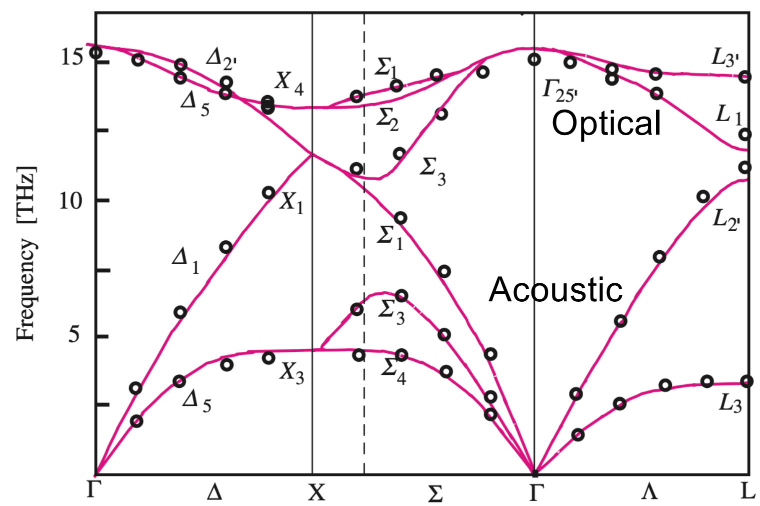




Phonon Dispersion (Si)



Cardon & Yu, Fundamental of Semiconductors

3 acoustic
3n -3 = 3 (n=2) optical

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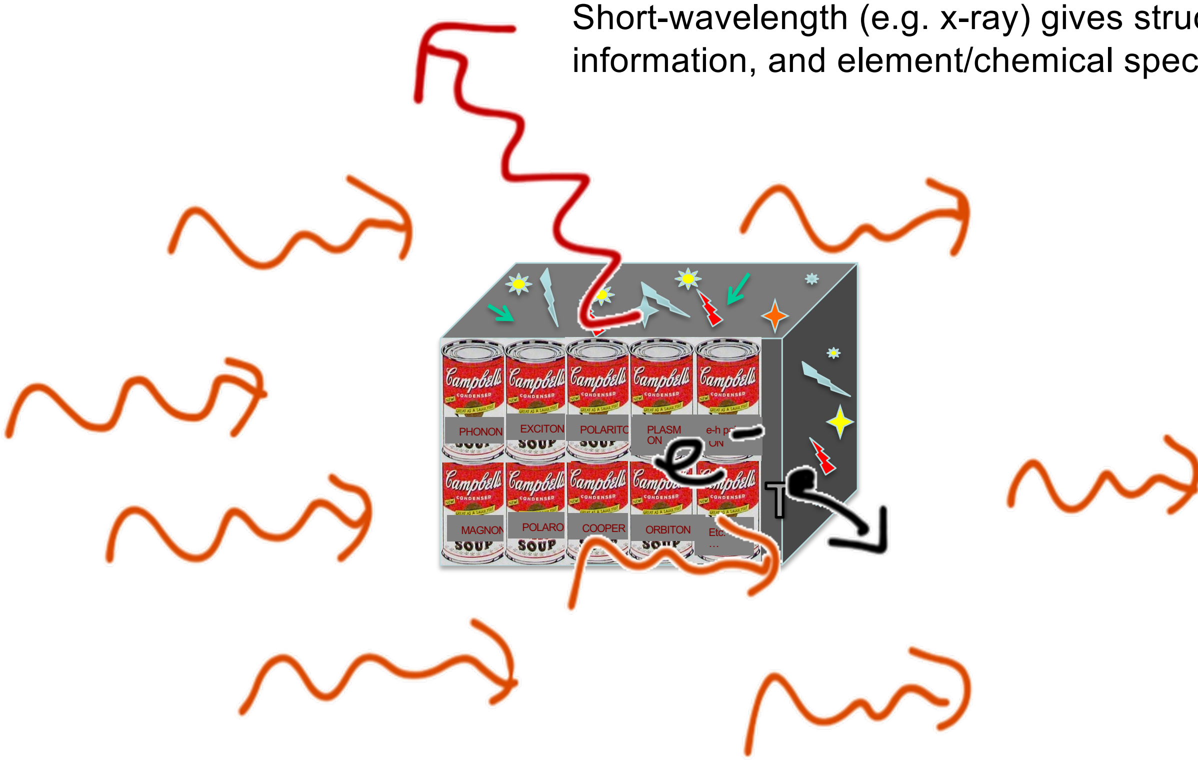
Light scattering and spectroscopy

Short-wavelength (e.g. x-ray) gives structural information, and element/chemical specificity



Adapted from A. Warhol

Dynamical Structure Factor

PHYSICAL REVIEW VOLUME 95, NUMBER 1 JULY 1, 1954

Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles

Léon Van Hove
Institute for Advanced Study, Princeton, New Jersey
(Received March 16, 1954)

$$\frac{d^2\sigma}{dE\,d\Omega} = A S(\boldsymbol{Q}, E)$$

$$S(\boldsymbol{Q}, \boldsymbol{E}) = \frac{N}{2\pi} \int e^{i\boldsymbol{Q}\cdot\boldsymbol{r} - \frac{\boldsymbol{E}t}{\hbar}} G(\boldsymbol{r}, t)\, d^3r\, dt$$

Related to poles in susceptibility (excitations)

$$G(\boldsymbol{r}, t) = \frac{1}{N(2\pi)^3} \sum_{R_j R_l} d^3Q \int e^{-i\boldsymbol{Q}\cdot\boldsymbol{r}} < e^{-i\boldsymbol{Q}\cdot\boldsymbol{R}_l(0)} e^{-\boldsymbol{Q}\cdot j(t)} >$$

Time and spatial Fourier transform of density-density correlation

S(Q,ω) Related to the imaginary part of density-density response function

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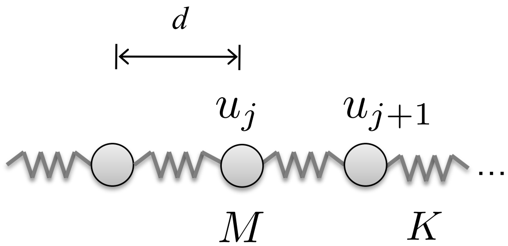
Phonons: quantized normal vibrational modes of lattice

Phonons in 1D



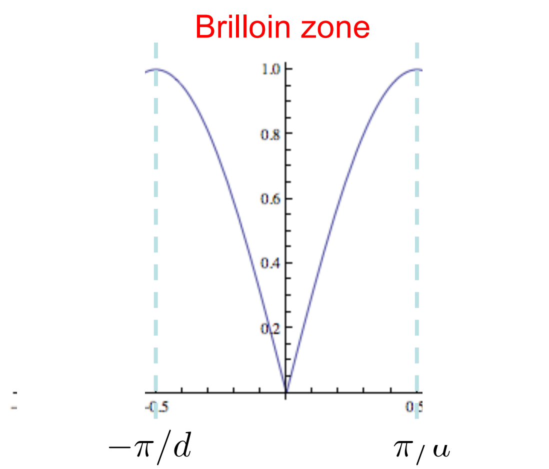
$$M\frac{d^2u}{dt^2} = K(u_{j+1} - 2u_j + u_{j-1})$$

Propose solutions: $u_j = \epsilon e^{i(qR_j - \omega t)}$

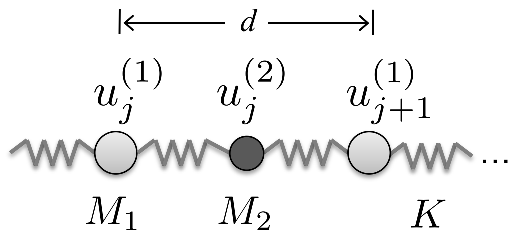
relationship between ω and **q**,
dispersion relation:

$$\omega = 2\sqrt{\frac{K}{M}}|\sin(qd/2)|$$

ω linear for $|q| << 1/d$: acoustic phonons



Phonons: quantized normal vibrational modes of lattice



Now $M_1 \neq M_2$

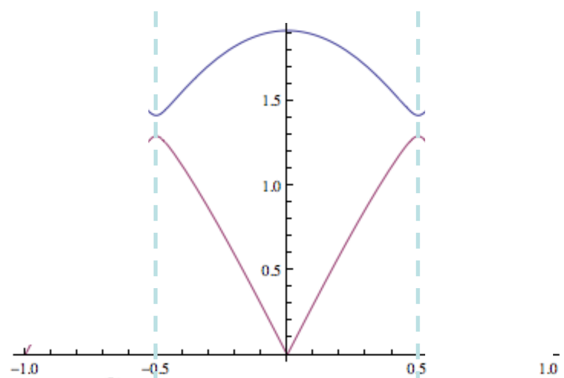
$$M_1 \frac{d^2 u^{(1)}}{dt^2} = K(u_j^{(2)} - 2u_j^{(1)} + u_{j-1}^{(2)})$$

$$M_2 \frac{d^2 u^{(2)}}{dt^2} = K(u_{j+1}^{(1)} - 2u_j^{(2)} + u_j^{(1)})$$

Propose solutions: $u_j^{(1,2)} = \epsilon^{(1,2)} e^{i(qR_j - \omega t)}$

dispersion relation:

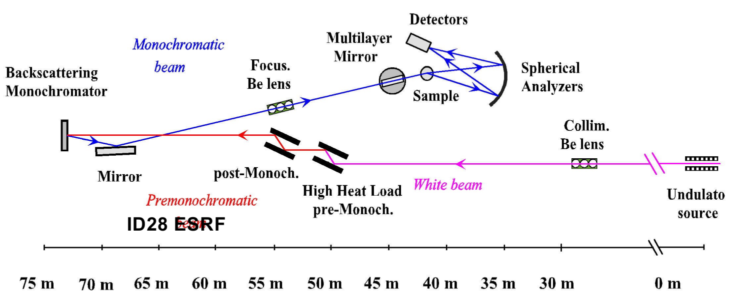
Brilloin zone



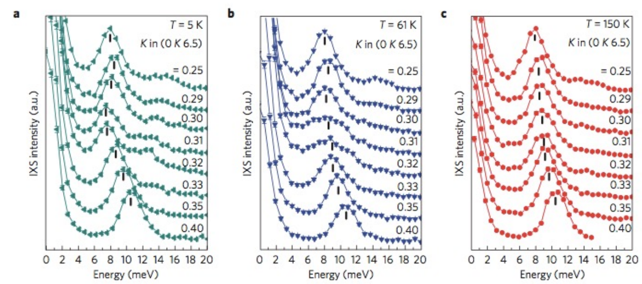
Here u is displacement from equilibrium

Inelastic X-ray Scattering:

$$S(\vec{Q},\omega) \propto \sum_j \int dt e^{i\omega t} \langle u_{j,\vec{Q}}(0) u_{j,-\vec{Q}}(t) \rangle \qquad \omega = E/\hbar$$



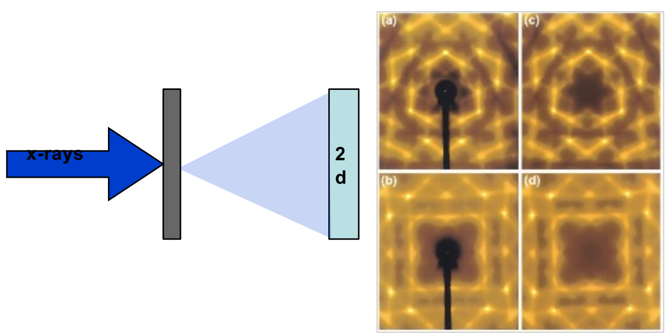
Underdoped YBCO



M. Le Tacon et. al, Nat. Phys. 10,52 (2014)

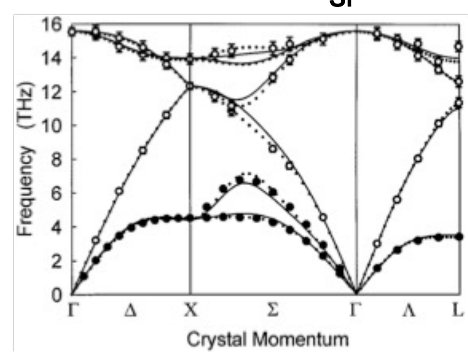
X-ray Diffuse Scattering:

$$S(\vec{Q}) \propto \sum_j \langle u_{j,\vec{Q}}(0) u_{j,-\vec{Q}}(0) \rangle$$



fit to Bose-Einstein distribution.

Si



M. Holt et al., PRL 83 (1999).

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Outline (scope)

- Lecture 1, the "Basics"
  - Hamiltonian and simplifications based on crystal symmetry
  - Low-lying excitations
  - Non-resonant x-ray scattering and structure
  - Inelastic x-ray scattering
- Lecture 2, "ultrafast and time-resolved applications"
  - Time-domain, non-resonant x-ray scattering
  - Lattice dynamics, near and far from equilibrium
  - Other examples…

- Out of scope (for example):
  - Methods to calculate/predict materials properties.
  - Liquids, glasses, low dimensional materials, device physics,…
  - Thermodynamics, Phase transitions
  - X-ray absorption/emission spectroscopy
  - Resonant inelastic x-ray scattering (RIXS)
  - Non x-ray based characterization
  - Coherence
  - And much more…

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