

X-ray diffraction from real crystals

In order to obtain a basic understanding of how X-ray diffraction works, and to understand all components of the experimental setup, we had made some drastic simplifications. In particular, we had based our discussion on an infinite, perfect and static crystalline lattice.

Some aspects of real crystals that go beyond these assumptions:

- thermal motion of atoms
- lattice strain
- finite size of crystal
- defects and disorder

In addition, we had assumed that the photons only scatter once before leaving the sample. In the chapter on reflectivity, we had seen that multiple reflections have to be taken into account whenever the reflectivity is close to 1. We will therefore modify our treatment of Bragg diffraction accordingly.

Thermal motion of atoms

Position of atom at lattice site n :

$$\vec{R}_n = \vec{R}_{0n} + \vec{u}_n$$

\uparrow
 equilibrium position

\uparrow
 instantaneous position due to thermally excited lattice vibrations

Approximation: atom moves in harmonic potential $\propto \frac{1}{2} K |\vec{u}|^2$ due to chemical bonding to surrounding atoms.

Harmonic approximation is valid for small $|\vec{u}|$, not too close to the melting point.

Reminder: One-dimensional harmonic oscillator in quantum mechanics.

Energy eigenvalues: $E_n = \left(n + \frac{1}{2}\right) \hbar \omega$ with $n = \text{integer}$, $\omega = \sqrt{\frac{K}{M}}$, $M = \text{mass of atom}$

Energy eigenstates: $|n\rangle$

Raising / lowering operators a^+, a :

$$a^+ |n\rangle = \sqrt{n+1} |n+1\rangle$$

$$a |n\rangle = \sqrt{n} |n-1\rangle$$

$$\text{Position operator: } u = \sqrt{\frac{\hbar}{2M\omega}} (a + a^+)$$

Generalization to three-dimensional lattice of N unit cells:

$$\vec{u}_n = \sqrt{\frac{\hbar}{2M_n N}} \sum_{s, \vec{q}} \frac{\vec{\epsilon}_s(\vec{q})}{\omega_s(\vec{q})} \left[a_{s\vec{q}} e^{i\vec{q} \cdot \vec{R}_{0n}} + a_{s\vec{q}}^\dagger e^{-i\vec{q} \cdot \vec{R}_{0n}} \right]$$

with $\omega_s(\vec{q})$ dispersion relation of phonon in branch s , $\vec{\epsilon}_s$: eigenvector (displacement pattern).

Reminder: A three-dimensional lattice with s atoms/unit cell has 3 acoustic and $3(s-1)$ optical phonon branches.

For simplicity: one atom/unit cell (Bravais lattice) \Rightarrow only acoustic phonons

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= r_0^2 \left\langle \left| \sum_n e^{i\vec{Q} \cdot \vec{R}_n} f(\vec{Q}) \right|^2 \right\rangle \\ &= r_0^2 |f(\vec{Q})|^2 \left\langle \sum_{mn} e^{i\vec{Q} \cdot \vec{R}_m} e^{-i\vec{Q} \cdot \vec{R}_n} \right\rangle \\ &= r_0^2 |f(\vec{Q})|^2 \sum_{mn} e^{i\vec{Q} \cdot (\vec{R}_{0m} - \vec{R}_{0n})} \left\langle e^{i\vec{Q} \cdot (\vec{u}_m - \vec{u}_n)} \right\rangle\end{aligned}$$

with $\langle \dots \rangle$ thermal average.

Time-scale for X-ray scattering experiments \gg period of thermally excited atomic vibrations.

Reminder: thermal average in quantum mechanics:

$$\langle A \rangle = \frac{1}{Z} \sum_n \langle n | A | n \rangle e^{-E_n / k_B T} \quad \text{with } Z = \sum_n e^{-E_n / k_B T} \quad \text{partition function}$$

Theorem for harmonic oscillator: $\langle e^{ix} \rangle = e^{-\frac{1}{2}\langle x^2 \rangle}$

For x small (corresponding to small displacements $|\vec{u}|$, not too close to melting point):

$$\langle e^{ix} \rangle = \left\langle 1 + ix - \frac{1}{2}x^2 - \frac{1}{6}ix^3 + \dots \right\rangle = 1 - \frac{1}{2}\langle x^2 \rangle + \dots \approx e^{-\frac{1}{2}\langle x^2 \rangle}$$

See textbook for rigorous derivation.

$$\langle e^{i\vec{Q} \cdot (\vec{u}_m - \vec{u}_n)} \rangle = \underbrace{e^{-\frac{1}{2}\langle (\vec{Q} \cdot \vec{u}_n)^2 \rangle - \frac{1}{2}\langle (\vec{Q} \cdot \vec{u}_m)^2 \rangle}}_{\textcircled{1}} \underbrace{e^{-\frac{1}{2}\langle (\vec{Q} \cdot \vec{u}_n)(\vec{Q} \cdot \vec{u}_m) \rangle}}_{\textcircled{2}}$$

These two terms are fundamentally different: The thermal average in $\textcircled{1}$ involves only a **single** atom and is independent of interactions between different atoms.

The average in $\textcircled{2}$ is only nonzero if atoms at lattice sites m and n move in a correlated manner. This will be the case if they are nearest neighbors: Due to chemical bonding, atom m will drag atom n along as it moves and vice versa. However for m and n far apart, the atoms move independently, so that

$$\langle (\vec{Q} \cdot \vec{u}_m)(\vec{Q} \cdot \vec{u}_n) \rangle \sim \langle (\vec{Q} \cdot \vec{u}_m) \rangle \langle (\vec{Q} \cdot \vec{u}_n) \rangle \rightarrow 0$$

Separate both terms by writing

$$\frac{d\sigma}{d\Omega} = r_0^2 |f(\vec{Q})|^2 \sum_{mn} \underbrace{e^{i\vec{Q} \cdot (\vec{R}_{0m} - \vec{R}_{0n})}}_{\textcircled{1}} \underbrace{e^{-\frac{1}{2}(\langle (\vec{Q} \cdot \vec{u}_m)^2 \rangle + \langle (\vec{Q} \cdot \vec{u}_n)^2 \rangle)}}_{\textcircled{2}} \left[1 - \frac{1}{2} \langle (\vec{Q} \cdot \vec{u}_n)(\vec{Q} \cdot \vec{u}_m) \rangle + \dots \right]$$

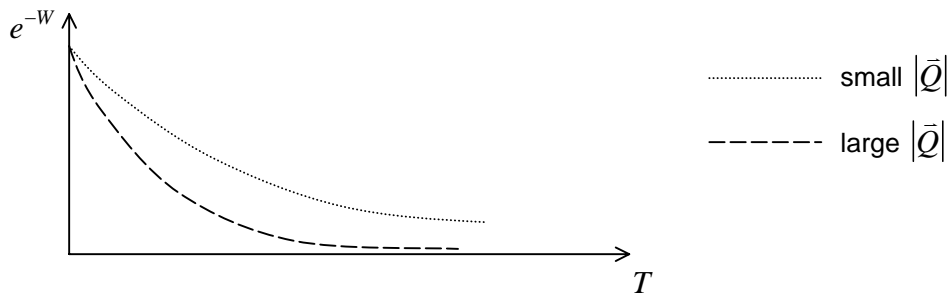
$$\begin{aligned}
W &= \frac{1}{2} \langle (\bar{Q} \cdot \bar{u}_m)^2 \rangle = \frac{1}{2} \langle (\bar{Q} \cdot \bar{u}_n)^2 \rangle \\
&= \frac{\hbar}{4MN} \sum_{\bar{q}s} \frac{(\bar{Q} \cdot \bar{\epsilon}_s)^2}{\omega_s} \langle (a_s e^{i\bar{q} \cdot \bar{R}_{0n}} + a_s^\dagger e^{-i\bar{q} \cdot \bar{R}_{0n}})^2 \rangle \\
\langle a_{qs} a_s \rangle &= \langle a_{qs}^\dagger a_s^\dagger \rangle = 0 \\
\langle n_s | a_{qs} a_{qs}^\dagger | n_s \rangle &= n_s + 1 \\
\langle n_s | a_{qs}^\dagger a_{qs} | n_s \rangle &= n_s \\
\Rightarrow W &= \frac{\hbar}{4MN} \sum_{\bar{q}s} \frac{(\bar{Q} \cdot \bar{\epsilon}_s)^2}{\omega_s} (2\langle n_s \rangle + 1) \quad \text{with } \langle n_s \rangle = \frac{1}{\exp[\hbar\omega_s/k_B T] - 1} \quad \text{Bose factor} \\
&= \frac{\hbar}{4MN} \sum_{\bar{q}s} \frac{(\bar{Q} \cdot \bar{\epsilon}_s)^2}{\omega_s(\bar{q})} \underbrace{\coth \frac{\hbar\omega_s(\bar{q})}{k_B T}}_{\begin{array}{l} \rightarrow 1 \text{ for } T \rightarrow 0 \\ \rightarrow \frac{2k_B T}{\hbar\omega_s} \text{ for } T \rightarrow \infty \end{array}}
\end{aligned}$$

Term ① thus becomes

$$\begin{aligned}
\frac{d\sigma}{d\Omega} &= r_0^2 |f(\bar{Q})|^2 \sum_{mn} e^{-i\bar{Q}(R_{0m} - \bar{R}_{0n})} e^{-2W} \\
&= r_0^2 |f(\bar{Q})|^2 e^{-2W} \frac{(2\pi)^3}{v_0} \sum_{\bar{K}} \delta(\bar{Q} - \bar{K})
\end{aligned}$$

Bragg diffraction, with Bragg peak intensities modified by temperature and \bar{Q} -dependent “Debye-Waller factor” e^{-2W} .

For several atoms / unit cell, replace form factor by $f_n(\bar{Q}) e^{-W_n}$, use same formula as before.



② expand for small $|\vec{u}|$:

$$\frac{d\sigma}{d\Omega} = r_0^2 |f(\vec{Q})|^2 e^{-2W} \sum_{mn} e^{i\vec{Q} \cdot (\vec{R}_{0m} - \vec{R}_{0n})} \langle (\vec{Q} \cdot \vec{u}_m) (\vec{Q} \cdot \vec{u}_n) \rangle$$

In contrast to ①, this contribution to $\frac{d\sigma}{d\Omega}$ is only nonzero as long as the thermal motion of atoms m and n is correlated. This will be the case for nearest neighbours: Due to chemical bonding, atom m will drag atom n along as it moves. However, if m and n are far apart (say at opposite ends of a macroscopic crystal), their motion will be completely uncorrelated, and the term $\langle (\vec{Q} \cdot \vec{u}_m) (\vec{Q} \cdot \vec{u}_n) \rangle$ is zero. The sum thus encompasses a **finite** number of nonzero terms, and therefore does **not** lead to delta-function Bragg reflections as in ①.

Now proceed as above to write

$$\frac{d\sigma}{d\Omega} = r_0^2 |f(\vec{Q})|^2 e^{-2W} \sum_{mn} e^{i\vec{Q} \cdot (\vec{R}_{0m} - \vec{R}_{0n})} \frac{\hbar}{2MN} \sum_{ss' \vec{q} \vec{q}'} \left\langle \frac{\vec{\epsilon}_s \cdot \vec{Q}}{\sqrt{\omega_s(\vec{q})}} (a_{\vec{q}s} e^{i\vec{q} \cdot \vec{R}_{0m}} + a_{\vec{q}s}^+ e^{-i\vec{q} \cdot \vec{R}_{0m}}) \frac{\vec{\epsilon}_{s'} \cdot \vec{Q}}{\sqrt{\omega_{s'}(\vec{q}')}} (a_{\vec{q}'s'} e^{i\vec{q}' \cdot \vec{R}_{0n}} + a_{\vec{q}'s'}^+ e^{-i\vec{q}' \cdot \vec{R}_{0n}}) \right\rangle$$

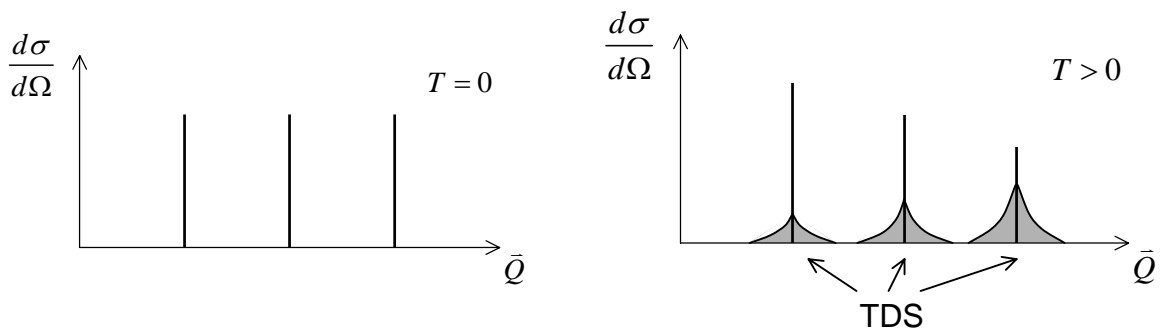
With $\langle a_{\vec{q}'s'} a_{\vec{q}s}^+ \rangle = \langle n_s + 1 \rangle \delta_{s's} \delta_{\vec{q}\vec{q}'}$ and $\langle a_{\vec{q}'s'}^+ a_{\vec{q}s} \rangle = \langle n_s \rangle \delta_{s's} \delta_{\vec{q}\vec{q}'}$

this becomes

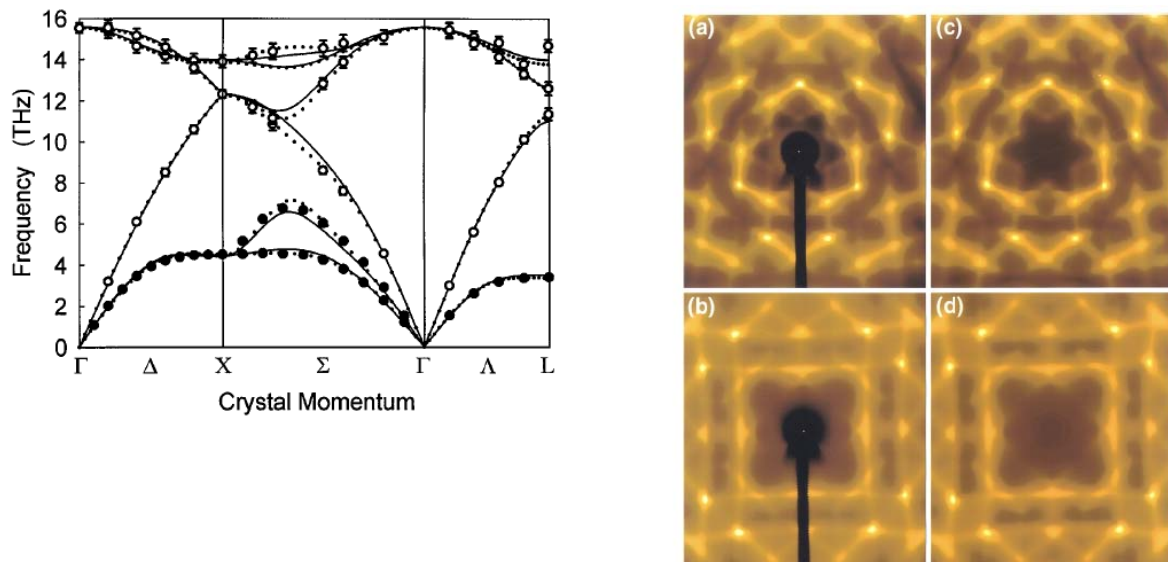
$$\begin{aligned} \frac{d\sigma}{d\Omega} &= r_0^2 |f(\vec{Q})|^2 e^{-2W} \frac{\hbar}{2MN} \sum_{s\vec{q}} \frac{(\vec{\epsilon}_s \cdot \vec{Q})^2}{\omega_s} \sum_{mn} \left[e^{i(\vec{Q} + \vec{q})(\vec{R}_{0m} - \vec{R}_{0n})} \langle n_s + 1 \rangle + e^{i(\vec{Q} - \vec{q})(\vec{R}_{0m} - \vec{R}_{0n})} \langle n_s \rangle \right] \\ &= r_0^2 |f(\vec{Q})|^2 e^{-2W} \frac{\hbar}{2MN} \frac{(2\pi)^3}{v_0} \sum_s \sum_{\vec{q}} \sum_{\vec{K}} \frac{(\vec{\epsilon}_s \cdot \vec{Q})^2}{\omega_s} \left[\langle n_s + 1 \rangle \delta(\vec{Q} + \vec{q} - \vec{K}) + \langle n_s \rangle \delta(\vec{Q} - \vec{q} - \vec{K}) \right] \\ &= r_0^2 |f(\vec{Q})|^2 e^{-2W} \frac{\hbar}{2M} \frac{(2\pi)^3}{v_0} \sum_s \frac{(\vec{\epsilon}_s \cdot \vec{Q})^2}{\omega_s} \coth \frac{\hbar \omega_s}{K_B T} \end{aligned}$$

(Remember that there are N reciprocal lattice vectors \vec{K} for a crystal of N atoms.) As expected, this expression is nonzero at **all** wave vector transfers \vec{Q} , not just at reciprocal lattice vectors \vec{K} . Since it is broadly distributed in reciprocal space and results from thermally excited lattice vibrations, it is called “thermal diffuse scattering” (TDS). Its intensity is nevertheless maximum for $\vec{Q} \rightarrow \vec{K}$, because $\omega_s(\vec{q})$ appears in the denominator and $\omega_s(\vec{q}) \rightarrow 0$ for acoustic phonon branches in the centre of the Brillouin zone.

The total cross section including Bragg peaks and TDS therefore looks qualitatively as follows:



In principle, it is possible to extract the phonon dispersion relations $\omega_s(\vec{q})$ from careful measurements of the TDS. Example:

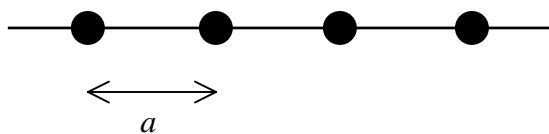


Phonon dispersion relations and Thermal Diffuse Scattering from Si at room temperature.
Note: The color scale is logarithmic. – M. Holt et al., PRL **83**, 3317 (1999)

However, a better method for measuring $\omega_s(\vec{q})$ is inelastic scattering (next semester).

Example: “Peierls transition”:

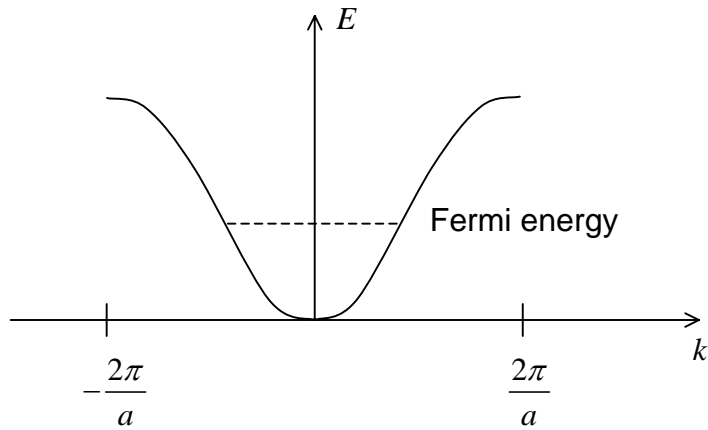
Assume a one-dimensional metal with one atom per unit cell and one electron per atom.



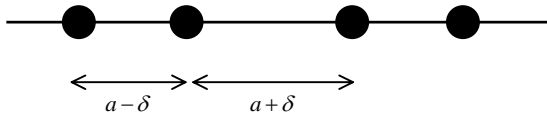
$$\frac{d\sigma}{d\Omega} = \frac{2\pi}{a} \sum_K \delta(Q - K)$$

$$K = n \frac{2\pi}{a}$$

band dispersions:

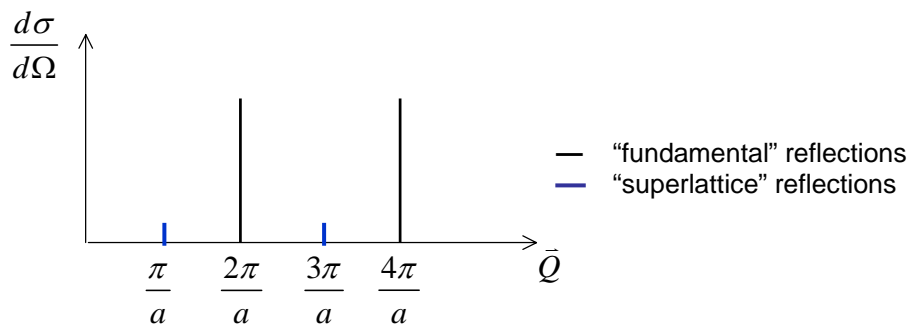


Now assume that the unit cell doubles by virtue of a small lattice distortion δ :

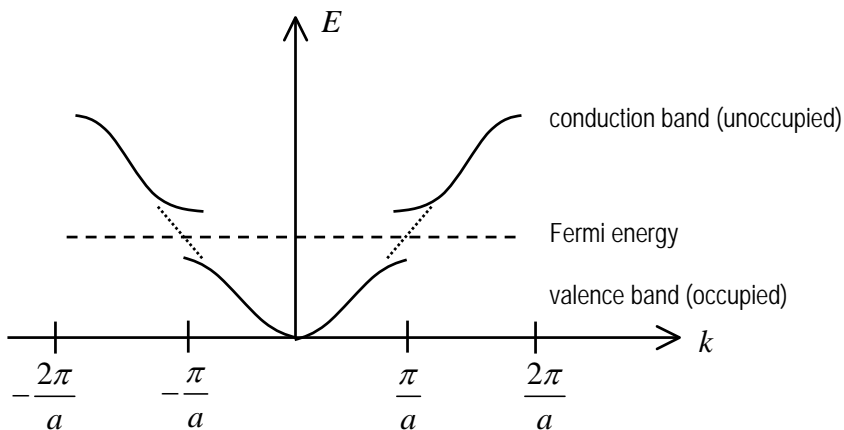


$$\frac{d\sigma}{d\Omega} = \frac{2\pi}{a} \sum_K |F(K)|^2 \delta(Q-K)$$

$$|F|^2 = \cos^2(Qa - \delta) \approx \begin{cases} 1 & \text{for } K = 2n \frac{\pi}{a} \\ (Q\delta)^2 & \text{for } K = (2n+1) \frac{\pi}{a} \end{cases}$$



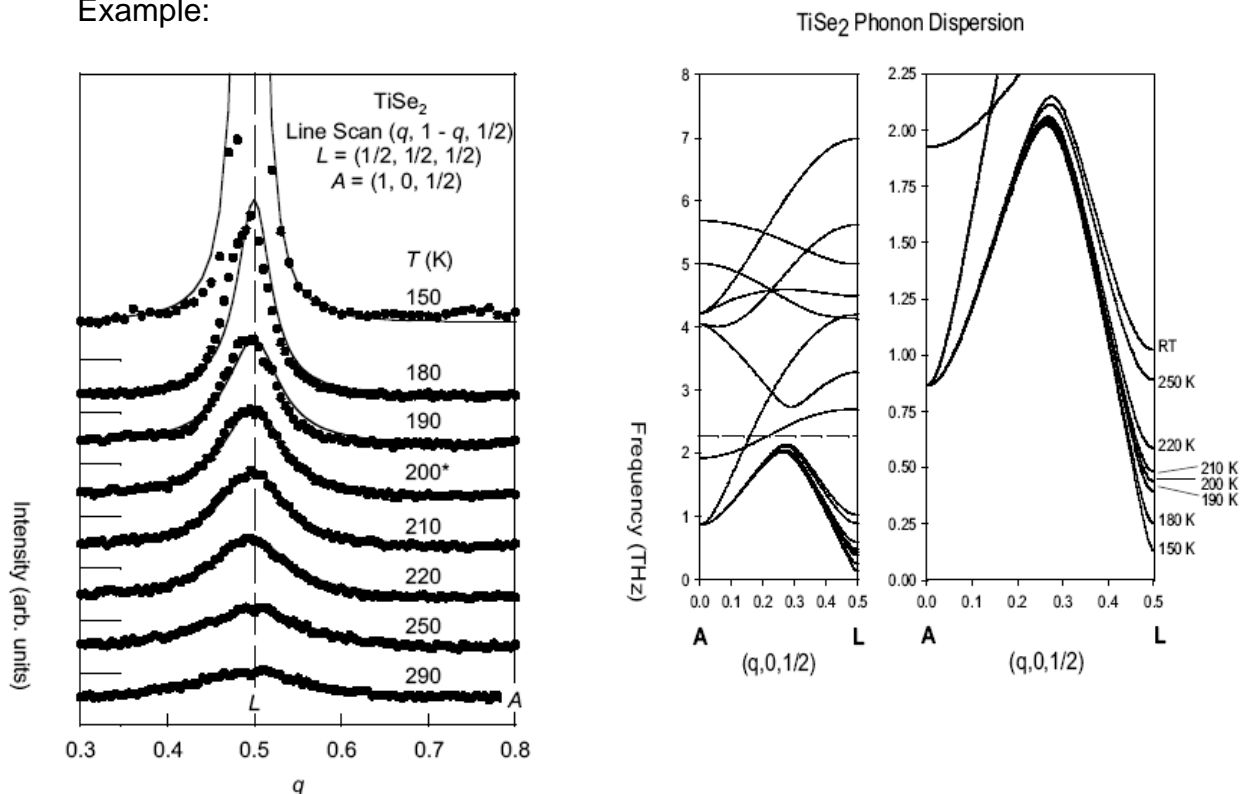
band dispersions:



⇒ A band gap opens up at the Fermi surface, and the material becomes insulating. As all the occupied states are lower in energy than those in the metal, the electronic energy is lower than in the metal. It can be shown that this gain in electronic energy outweighs the energy it takes to create the lattice distortion. One-dimensional metals therefore do not exist at zero temperature.

However, lattice fluctuations can induce a “Peierls transition” into a metallic state with undimerized lattice when the temperature is increased. At the critical temperature, T_c , the “superlattice” reflections disappear. However, thermal diffuse scattering due to “soft” optical phonons remains up to temperatures well above T_c . Peierls transitions are also observed in some two-dimensional metals.

Example:



Thermal diffuse scattering from TiSe_2

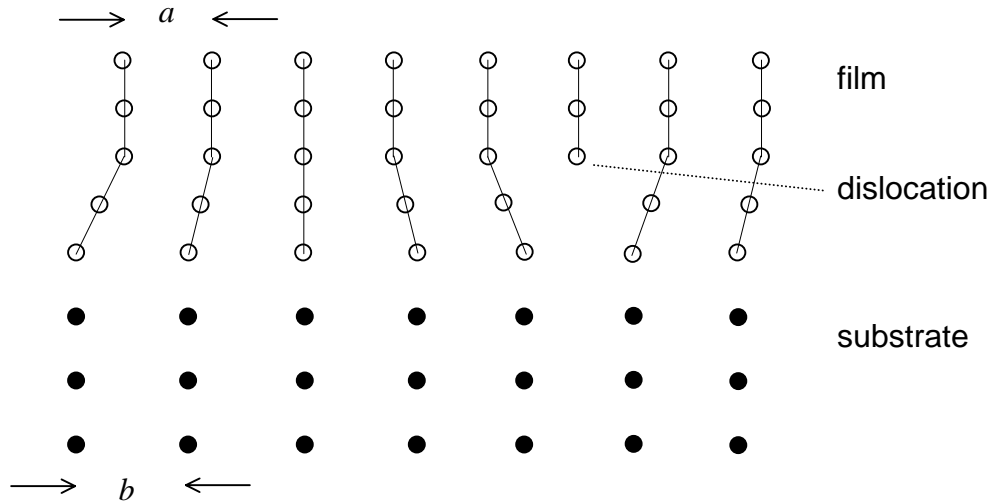
TiSe_2 has a two-dimensional electronic structure and changes its lattice structure around 200 K due to a Peierls distortion. Above the transition, a particular phonon branch lowers its energy (“softening”). This gives rise to pronounced thermal diffuse scattering.

<http://www.aps.anl.gov/xfd/communicator/user2000/holtm2.pdf>

M. Holt et al., Phys. Rev. Lett. **86**, 3799 (2001)

Lattice strain

Deviations from perfect periodicity can also occur by virtue of static, non-thermal lattice displacements \bar{u} , for instance in materials under local compression or extension (machine parts, etc.) or around lattice defects (dopant atoms in semiconductors, etc.) A very common situation is a film with natural lattice constant a on a substrate with lattice constant b :



Static lattice strain can be treated in a formalism similar to the effects of thermal displacements. In particular, the Bragg are reduced in a manner characteristic of the static strain field \bar{u} : $e^{-\langle (\bar{Q} \cdot \bar{u})^2 \rangle}$ is also called “static Debye-Waller factor”. It is temperature independent and can thus be distinguished from the strongly temperature dependent thermal Debye-Waller factor. Likewise, lattice strain generates temperature independent diffuse scattering, in analogy to the thermal diffuse scattering discussed above.

Finite-sized crystals

Motivation:

- Powders are built up of small crystallites; take finite size into account for accurate description of diffraction pattern.
- Nanometer-sized features of solids important for cutting-edge technology
- Related formalism for X-ray scattering from nanometer-sized “soft matter” or biological objects (macromolecules in solution, vesicles, micelles, etc.)

for simplicity: 1 atom / unit cell

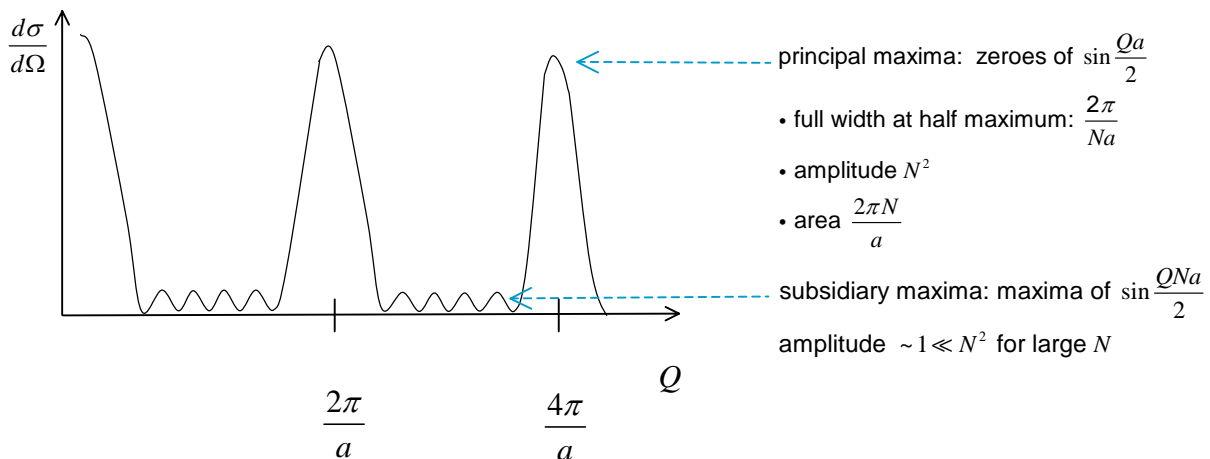
$$\frac{d\sigma}{d\Omega} = r_o^2 |f(\vec{Q})|^2 \left| \sum_{\vec{R}} e^{i\vec{Q} \cdot \vec{R}} \right|^2$$

$$\rightarrow \frac{N(2\pi)^3}{v_o} \sum_{\vec{K}} \delta(\vec{Q} - \vec{K}) \text{ for } N \rightarrow \infty$$

for finite N : one-dimensional example

$$\left| \sum_{n=1}^N e^{iQna} \right|^2 = \left| \sum_{n=1}^N (e^{iQa})^n \right|^2 = \left| \frac{e^{iQNa} - 1}{e^{iQa} - 1} \right|^2 = \frac{\sin^2 \frac{QNa}{2}}{\sin^2 \frac{Qa}{2}} \rightarrow N \frac{2\pi}{a} \sum_K \delta(Q - K) \text{ for } N \rightarrow \infty$$

as before.

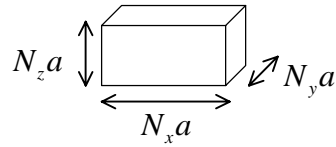


For finite-sized crystallites: T -independent broadening of Bragg reflections.

Finite-size width of **all** Bragg peaks is **identical**: $\Delta Q \sim \frac{2\pi}{Na}$

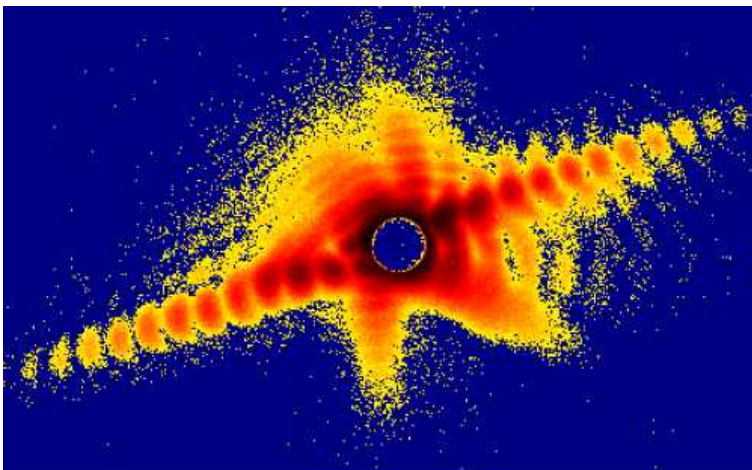
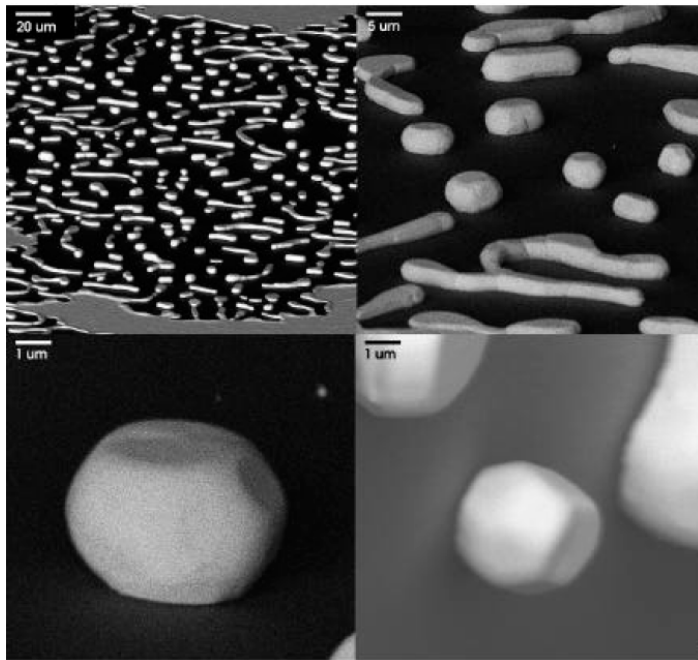
\Rightarrow can separate diffuse scattering from lattice displacements (TDS, strain) from finite-size broadening by comparing Bragg reflections of different order.

Generalization for 3D cubic crystal:



$$\left| \sum_{\vec{R}} e^{i\vec{Q} \cdot \vec{R}} \right|^2 = \frac{\sin^2 \frac{Q_x N_x a}{2}}{\sin^2 \frac{Q_x a}{2}} \frac{\sin^2 \frac{Q_y N_y a}{2}}{\sin^2 \frac{Q_y a}{2}} \frac{\sin^2 \frac{Q_z N_z a}{2}}{\sin^2 \frac{Q_z a}{2}}$$

⇒ can determine **shape** of crystal by monitoring **anisotropic** finite-size broadening of Bragg peaks.



TEM micrographs and x-ray diffraction pattern of Au nanocrystals

I.K. Robinson et al., Phys. Rev. Lett. **87**, 195505 (2001)

<http://www-esg.lbl.gov/esg/meetings/phasing/viewgraphs/VGRobinson.pdf>

For particles with irregular internal structure (e.g. macromolecules in solution, oil droplets in water): no Bragg peaks at nonzero Q , but “zeroth-order” reflection of width $\sim \frac{2\pi}{Na}$ still exists (“form factor” of object).

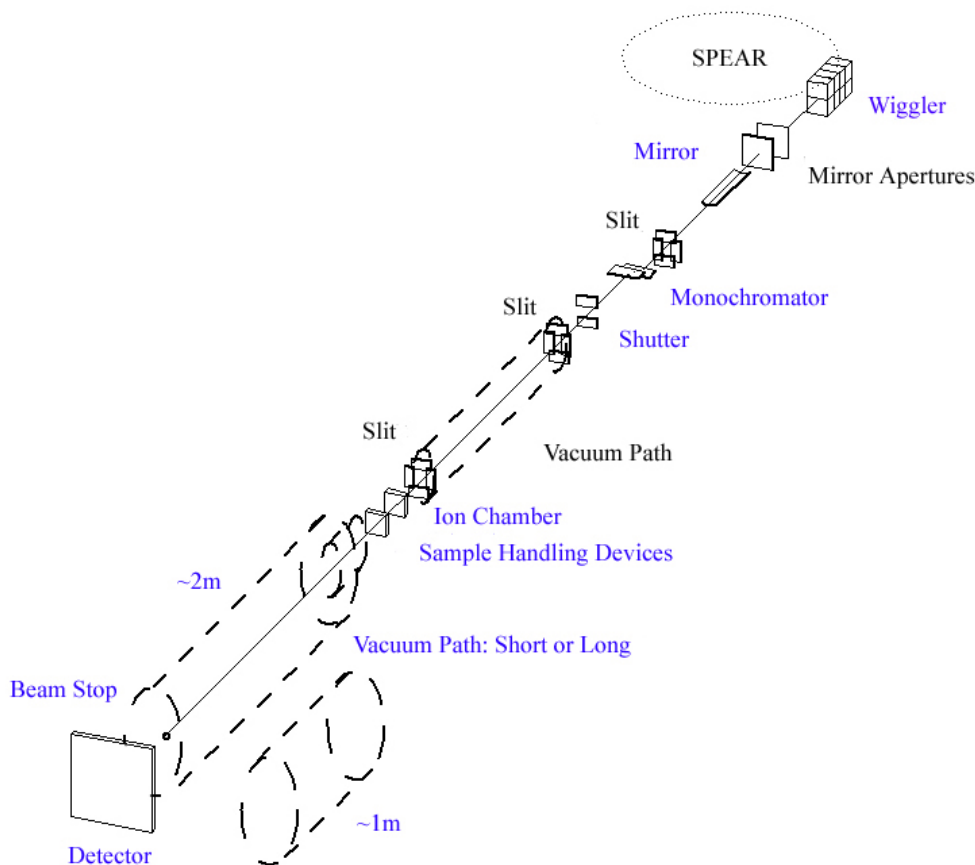
Often approximated by Gaussian of same width, amplitude:

$$\frac{\sin^2 Nx}{\sin^2 x} \rightarrow N^2 e^{-(Nx)^2/\pi} \sim N^2 e^{-Q^2 R_g^2/3} \quad \text{with} \quad \frac{4}{3} \pi R_g^3 = (Na)^3 \quad R_g = \text{radius of gyration}$$

Guinier's law

can measure characteristic size of nanometer-sized objects by small angle X-ray scattering.

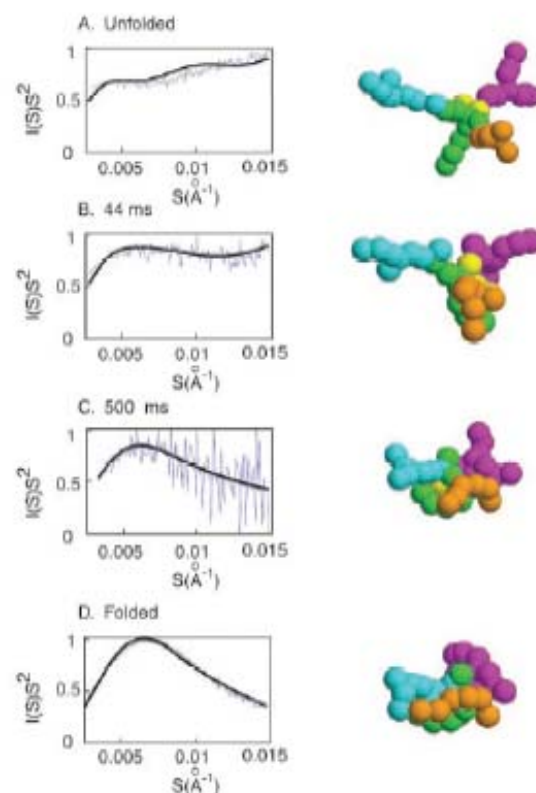
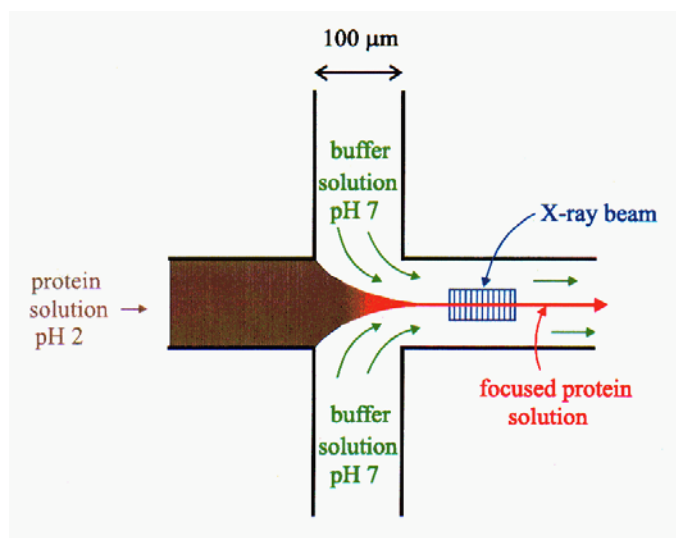
Long distance between sample and detector: can resolve scattering angles of order 0.01°



Small angle x-ray scattering beamline

<http://www-ssrl.slac.stanford.edu/~saxs/>

Examples from frontier research



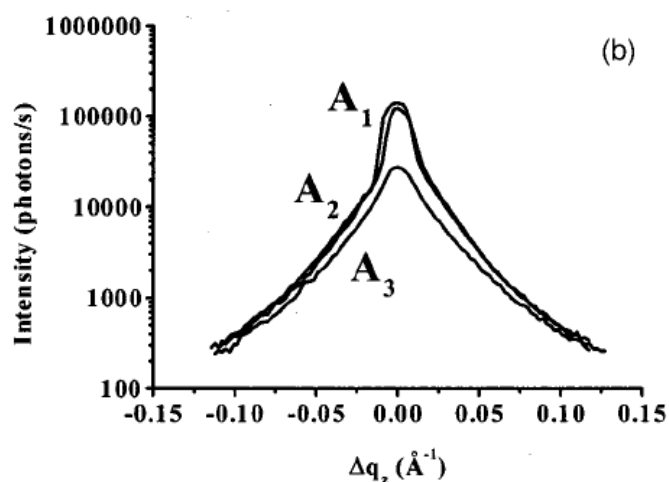
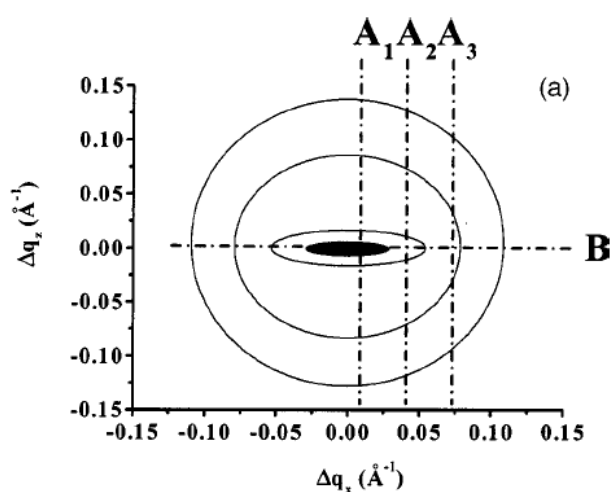
Time resolved small angle x-ray scattering study of protein folding

Note: Intensity is plotted as $I(S)S^2$ with $S=2\sin\Theta/\lambda$.

R. Russell et al., PNAS **99**, 4266 (1999)

http://www.chess.cornell.edu/Research/Highlights/Nanofabricated_flow_cell_1999.htm

T



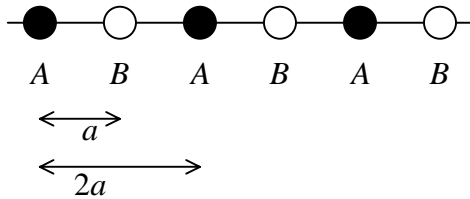
X-ray diffuse scattering around a Bragg reflection of porous silicon

The size and shape distribution of crystallites in porous Si help explain the unusual luminescence properties of this material.

D. Butard et al., J. Appl. Phys. **91** (2002)

Diffuse scattering from disorder

Example: one-dimensional solid with two types of atoms



basis vector $d = a$

reciprocal lattice vectors $K = \frac{n\pi}{a}$

if lattice is perfectly ordered:

$$\frac{d\sigma}{d\Omega} = r_0^2 N \frac{2\pi}{2a} \sum_K |F(K)|^2 \delta(Q - K)$$

N = number of unit cells in crystal

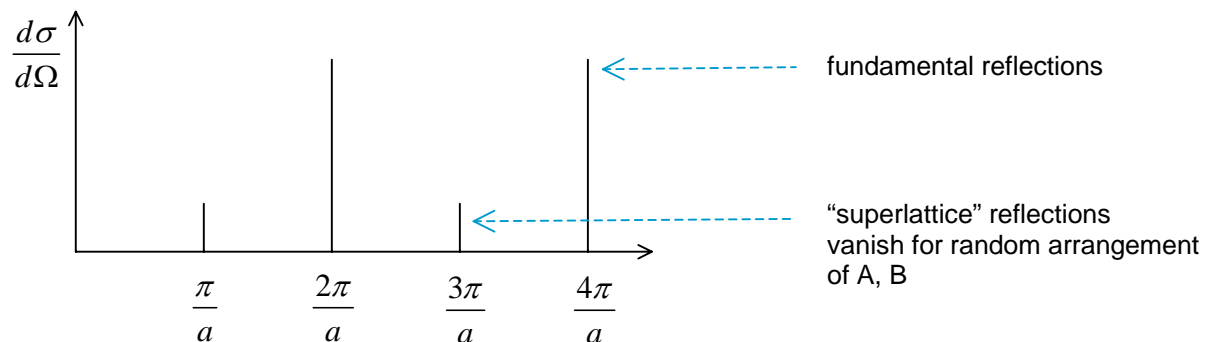
Structure factor:

$$F(K) = f_A(Q) + f_B(Q) e^{iKa}$$

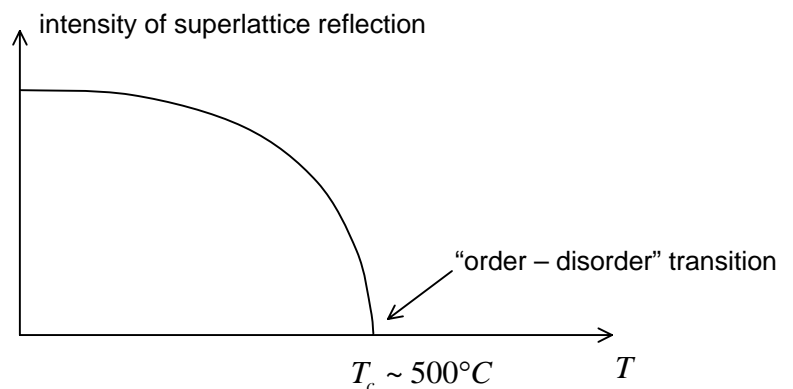
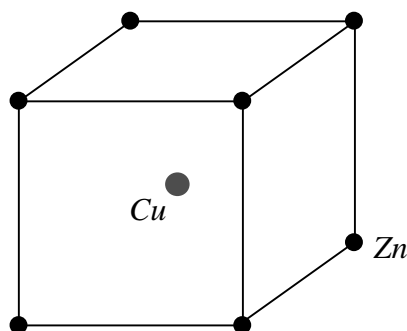
$$= f_A + f_B e^{in\pi}$$

$$n \text{ even: } |F|^2 = (f_A + f_B)^2$$

$$n \text{ odd: } |F|^2 = (f_A - f_B)^2$$



realistic example: alloys, e.g. CuZn (“ β -brass”)



above T_c : “short range order” persists. A atoms prefer B atoms as nearest neighbor, and vice versa.

below T_c : defects in real crystals (A atoms on B sites, and vice versa)

Both effects lead to diffuse X-ray scattering.

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= r_0^2 \left\langle \sum_{mn} f_m f_n e^{i\vec{Q}(\vec{R}_m - \vec{R}_n)} \right\rangle \\ &= r_0^2 \sum_{mn} \langle f_m f_n \rangle e^{i\vec{Q}(\vec{R}_m - \vec{R}_n)} \quad \text{assume static lattice for simplicity}\end{aligned}$$

$\langle \dots \rangle$ = average over sample volume

Rapid fluctuations of occupancy on each site \Rightarrow

$T \gg T_c$: no correlations between A, B

$$\rightarrow \langle f_m f_n \rangle = \langle f_m \rangle \langle f_n \rangle = \left(\frac{1}{2} f_A + \frac{1}{2} f_B \right)^2$$

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= \frac{1}{4} r_0^2 (f_A + f_B)^2 \sum_{mn} e^{i\vec{Q}(\vec{R}_m - \vec{R}_n)} \\ &= \frac{1}{4} r_0^2 (f_A + f_B)^2 N \frac{2\pi}{a} \sum_K \delta(Q - K) \quad N = \text{\# of unit cells, twice as large as in expression above}\end{aligned}$$

same result as for fundamental reflections above.

T_c approached from above: fluctuations become slower, configurations $\bigcirc \bullet \bigcirc$ and $\bullet \bigcirc \bullet$ adopted more often than $\bigcirc \bigcirc \bigcirc$ or $\bullet \bullet \bullet$ etc.

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= \sum_{mn} r_0^2 \underbrace{\left(\langle f_m f_n \rangle - \frac{1}{4} (f_A + f_B)^2 \right)}_{\text{diffuse scattering}} e^{i\vec{Q}(\vec{R}_m - \vec{R}_n)} \\ &\quad + \underbrace{\sum_{mn} \frac{1}{4} (f_A + f_B)^2 e^{i\vec{Q}(\vec{R}_m - \vec{R}_n)}}_{\text{Bragg reflections}}\end{aligned}$$

$$\langle f_m f_n \rangle \rightarrow \frac{1}{4} (f_A + f_B)^2 \text{ for } \vec{R}_m, \vec{R}_n \text{ far apart.}$$

First term is **finite** sum \Rightarrow no δ -function

\Rightarrow “diffuse scattering”

$$\text{diffuse intensity} \propto \sum_{\Delta} \underbrace{\left[\langle f_m f_n \rangle_{\Delta} - \frac{1}{4} (f_A + f_B)^2 \right]}_{\text{empirical correlation parameters}} \cos Q\Delta \quad \text{with } \Delta \equiv |\vec{R}_m - \vec{R}_n|$$

A similar expansion can be made for scattering from substitutional defects below T_c .

As for finite-size effects, short range order diffuse scattering is the same in every Brillouin zone. However, lattice displacements always go along with substitutional disorder (“Huang scattering”). This leads to an intensity increase with increasing $|\vec{Q}|$, as for TDS and strain effects.