Anticipatory (trick) question: If you have an x-ray or neutron detector looking at a small sample volume, which will scatter more x-rays or neutrons into the detector 1 atom, 100 atoms or 1000 atoms?

Answer: Depends!
Diffuse Scattering

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Presentation concentrates year graduate-level course into 1 hour

- Skip mathematical complexities
- Expose to range of applications
- Develop "intuition" for length scales
- Talk like x-ray/neutron scattering guru
  - Reciprocal space
  - Debye Temperature
  - Laue monotonic
  - Krivoglaz defects of 1st/2nd kinds!

Great for cocktail parties or impressing attractive strangers-
Important for recognizing origins of diffuse scattering!
Diffuse scattering revolutionized!

- Synchrotron sources/new tools enable new applications
  - Intensity for weak signals
  - High energy for simplified data analysis
  - Small (dangerous) samples
  - Time evolution

- Advanced neutron instruments emerging
  - Low Z elements
  - Magnetic scattering
  - Different contrast

- New theories provide direct link between experiments and first-principles calculations
What you already know- arrangement of atoms redistributes scattering

- Familiar light example
- Practical applications- zero background plates for powder diffraction
- Wave → diffraction

Detector

X-ray or neutron beam
You already know that Bragg reflections occur when scattering amplitudes add *constructively*

- Orientation of sample
- Wavelength
- Bragg Peaks sharp! \(\sim 1/N\) (arc seconds)

Think in terms of *momentum transfer* \(\overline{p}_0 = \frac{h \hat{d}_0}{\lambda}\)
If repeat crystal lattice of atoms leads to Bragg peaks-what happens when an atom is out of place/missing?

- Weakens Bragg peaks
- Redistributes scattering intensity in reciprocal space
Diffuse scattering due to *local* (short ranged) correlations/ fluctuations

- Thermal diffuse scattering (TDS)
- Point defect
  - Site substitution
  - Vacancy
  - Interstitial
- Precipitate
- Dislocations
- Truncated surface - more

All have in common reduced correlation length!
You already know length scales are inverted!

- Big real $\rightarrow$ small reciprocal
- Small real $\rightarrow$ big reciprocal
- **Same behavior for correlation length scales**
  - Long real-space correlation lengths scattering close to Bragg peaks

*If you remember nothing else!*
Krivoglaz classified defects by effect on Bragg Peak

- **Defects of 1st kind**
  - *Atomic displacements remain finite*
  - Bragg width unchanged
  - Bragg intensity decreased
  - Diffuse redistributed in reciprocal space

- **Defects of 2nd kind**
  - No longer distinct Bragg peaks
  - *Displacements continue to grow with crystal size*

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*Graphs showing intensity change with and without defects.*
Who the heck was Krivoglaz?

• Brilliant Ukrainian scientist

• Dissertation – predated Mossbauer’s work

• Pioneered a general way of categorizing and studying defects using x-rays/neutrons
Dimensionality Krivoglaz defect of second kind- influences diffraction

- Small size $\rightarrow$ broad diffraction
- Polycrystalline

\[ \begin{array}{ccc}
\text{a. Amorphous} & \text{b. nanocrystalline} & \text{c. crystalline} \\
\end{array} \]
Cev Noyan and Coworkers Studying Particle Statistics/Using Modern Tools

- Numerical tests of long-time powder diffraction averages

- When are enough particles contributing to satisfy statistical averages

\[
\frac{\sin^2 N x}{\sin^2 x}
\]
Single crystals and surfaces - truncation rods

- Diffuse scattering perpendicular to surface
- Connect to Bragg Peaks
- Intensity falloff indicates roughness
  - Slow (smooth or abrupt)
  - Fast (rough)
Thermal motion-Temperature Diffuse Scattering-
(TDS) -defect of 1st kind

- Atoms coupled through atomic bonding

- Uncorrelated displacements at distant sites
  - (finite)

- Phonons (wave description)
  - Amplitude
  - Period
  - Propagation direction
  - Polarization (transverse/compressional)

Sophisticated theories from James, Born Von Karmen, Krivoglaz
A little math helps for party conversation

- Decrease in Bragg intensity scales like $e^{-2M}$, where

$$2M = 16\pi^2 \left\langle u_s^2 \right\rangle \frac{\sin^2 \theta}{\lambda^2}$$

- Small $\theta \rightarrow$ Big reflections

- $e^{-2M}$ shrinks (bigger effect) with $\theta (q)$

Displacements, $u_s$ depend on Debye Temperature $\theta_D$ - Bigger $\theta_D$  
$\rightarrow$ smaller displacements!
TDS makes beautiful patterns reciprocal space

- Iso-intensity contours
  - Butterfly
  - Ovoid
  - Star

- Transmission images reflect symmetry of reciprocal space and TDS patterns

X-rays scattering measurements infer phonon dispersion from quasi-elastic scattering

- Phonon energies \textit{milli-eV}
- Synchrotron based high-E resolution X-ray beamlines can measure phonons \textit{in some cases}
- Emerging area for high-brilliance x-ray sources

**Phonon spectrum gives natural vibration frequencies in different crystal directions!**
Inelastic neutron/x-ray scattering directly measures phonon spectra in symmetry directions

- Inelastic neutron scattering confirms origins of negative Grüneisen coefficient in cubic ZrW$_2$O$_8$ (negative thermal expansion)-disordering phase transition.

- Unusual thermal displacements often associated with phase transitions.

Phonon energies similar to meV neutron energies.
Extra diffuse scattering often observed from materials near phase transitions

- Distribution of configurations at finite temperature
  - Mixed phases (1st order)

- Extended displacements

- High-pressure
  - higher-co-ordination
  - Longer NN bond distance
  - Smaller volume/atom
R-3c→I2/a displacive transition observed in a single crystal of Cr$_2$O$_3$ at 80 GPA
C22→C23 transition in Fe$_2$P at 10 GPa


Complete transformation induced by heating the sample to 2000 K

Diffuse scattering before the transformation occurs, heating at ~1000 K
High-energy Synchrotron X-rays are revolutionizing TDS measurements

- Small samples
- Fast (time resolved/combinatorial)
  - Experiments in seconds rather than days
- Materials that cannot be studied with neutrons

Pu experiment

Pu theory
Neutrons uniquely sensitive to low Z

- Deuterium cross section large
- Phonon energy comparable to neutron energy
- New insights into dynamics of “molecular crystals” splitting

Welberry et al. ISIS

Experiment

Theory
Often TDS mixed with additional diffuse scattering

- Experiment
- Strain contribution
- Combined theoretical TDS and strain diffuse scattering

TDS must often be removed to reveal other diffuse scattering
Alloys can have another type 1 defect-site substitution

- Long range
  - Ordering (unlike neighbors)
  - Phase separation (like neighbors)

- Short ranged
  - Ordering
  - Clustering (like neighbors)

Each Au has 8 Cu near-neighbors

Alternating planes of Au and Cu
Redistribution depends on kind of correlation

Clustering intensity → fundamental sites

Random causes Laue monotonic

Short-range ordering → superstructure sites
**Neutron/ X-rays Complimentary For Short-range Order Measurements**

- Chemical order diffuse scattering proportional to contrast \((f_A - f_B)^2\)

- Neutron scattering cross sections
  - Vary wildly with isotope
  - Can have + and - sign
  - Null matrix
  - Low Z, high Z comparable

- X-ray scattering cross section
  - Monotonic like \(Z^2\)
  - Alter by anomalous scattering
Neutrons can select isotope to **eliminate** Bragg scattering

- Total scattering $c_a f_a^2 + c_b f_b^2 = 3$
- Bragg scattering $(c_a f_a + c_b f_b)^2 = 0$
- Laue (diffuse) scattering $c_a c_b (f_a - f_b)^2 = 3$

*Isotopic purity important as different isotopes have distinct scattering cross sections- only one experiment ever done!*
X-ray anomalous scattering can change x-ray contrast

- Chemical SRO scattering scales like \((f_a-f_b)^2\)
- Static displacements scale like \((f_a-f_b)\)
- TDS scales like \(\sim f_{\text{average}}^2\)
Atomic size (static displacements) affect phase stability/properties

- **Ionic materials (Goldschmidt)**
  - Ratio of Components
  - Ratio of radii
  - Influence of polarization

- **Metals and alloy phases (hume-Rothery)**
  - Ratio of radii
  - Valence electron concentration
  - Electrochemical factor

**Grand challenge**: include deviations from lattice in modeling of alloys
Measurement *and* theory of atomic size are hard!

- **Theory** - violates repeat lattice approximation - every unit cell different!

- **Experiment**
  - EXAFS marginal (0.02 nm) in dilute samples
  - Long-ranged samples have balanced forces

**Important!**
Systematic study of bond distances in Fe-Ni alloys raises interesting questions

- Why is the Fe-Fe bond distance stable?
- Why does Ni-Ni bond swell with Fe concentration?
- Are second near neighbor bond distances determined by first neighbor bonding?
High-energy x-ray measurements revolutionize studies of phase stability

- Data in \textit{seconds} instead of \textit{days}
- Minimum absorption and stability corrections
- New analysis provides direct link to first-principle

\textit{Max Planck integrates diffuse x-ray scattering elements!}
Measurements show competing tendencies to order

- Both $L_{12}$ and $Z_1$ present

- Compare with first principles calculations

Short-range and long-range order can also impact functional materials

- Interest in AgSbTe$_2$ because of very low thermal conductivity in a nominal rock-salt system: $\kappa_{\text{lat}} = 0.7$ W/m/K at 300K.
  [Morelli, Jovovic, Heremans, PRL 2008].

- Strong Ag, Sb ordering predicted on sublattice by DFT
Single-crystals reveal nano-scale ordering

- **Superlattice peaks**, indicating **doubling of periodicity along <111>**, associated with cation ordering (compatible with DFT predictions).
- Superlattice peaks are broad, ordering **correlation length** \( \xi \sim 3\text{nm} \).
- Diffuse streaks along <111> from sharp interfaces (APBs).
- Agreement with XRD (Quarez JACS 2005), and TEM (Manolikas Mat. Res. Bull. 1977).

TEM diffraction single-crystal \((\text{Ag}_{0.8}\text{Sb}_{1.2}\text{Te}_{2.2})\) in \((1,-1,0)\) reciprocal plane.

Neutron scattering on single-crystal \((\text{Ag}_{0.8}\text{Sb}_{1.2}\text{Te}_{2.2})\) in \((1,-1,0)\) reciprocal plane.

-1 < \(E\) < 1 meV

same results in \(\text{AgSbTe}_2\) and \(\text{Ag}_{0.8}\text{Sb}_{1.2}\text{Te}_{2.2}\).
TEM and synchrotron x-ray scattering

• Diffuse synchrotron x-ray scattering on single-crystals reveals complex intensity patterns related to nanostructure (APS 33BM).
  – Superlattice peaks, <111> rods, and lobes around Bragg peaks from strain.

• TEM imaging reveals tweed-like nanodomains (crystallographic variants of ordered domains)
  – Domains appear like platelets, with dimensions of few nanometers.
Dislocations - Krivoglaz defect of the second kind

• Unbounded displacement with increased number

• Broaden Bragg peak

• Fundamental to plasticity
Influence of number and orientation of dislocations can be quantified

\[ x_1 = [1-2-1], \quad n = [-1-11], \quad b = [110] \]

\[ y_2 = [-1-21], \quad n = [-111], \quad b = [101] \]

\[ x_3 = [-11-2], \quad n = [1-1-1], \quad b = [110] \]

\[ y_4 = [1-1-2], \quad n = [1-11], \quad b = [110] \]
Intense microbeams/area detectors provide new direction in diffuse scattering

- Tiny crystals (20 \( \mu \)m)
  - Natural polycrystals
  - No special sample prep

- Combinatorial

- Dangerous samples
Small irradiated volumes simplify handling/preparation

- Activity ~volume ($10^{-5}$)
- Much less waste ($10^{-7}$)
- Polycrystalline samples easier obtain—closer to real materials

![Diagram showing traditional diffuse sample ~300 mm$^3$ and microsample ~$10^{-3}$ mm$^3$, indicating 100-1000 samples.]
Diffuse microdiffraction holds promise for irradiated materials

- Powerful single crystal techniques applied to polycrystals
- ~4-6 Orders of magnitude lower activity
  - Safer/lower backgrounds
- Cryocooled samples to study initial defects
- New information about point/line/mesoscale defect interactions

Successful demonstration experiments!
Corelli SNS beamline specialized for diffuse scattering with elastic Discrimination

- Complex disorder and short-range correlations
Correlation Chopper efficiently determines incident/final neutron wavelengths

- Probability that beam can pass ~50%
- Probability independent of wavelength
Time to detector depends on speed/distance traveled for incident \textit{and} scattered neutron

- Distances known
- Contributions from wrong set of neutron speeds cancel statistically
- Contributions from correct set of neutron speeds add constructively

Up to 50 x gain! Distinguishes static/dynamic contributions.
X-ray diffuse scattering at Femtosecond Resolution

- Ultra-brilliant LCLS opens new experimental possibilities
- Transient behaviors at femtosecond time scales demonstrated.

New directions in diffuse scattering

- High-energy x-ray

- Microdiffuse x-ray scattering
  - Combinatorial
  - Easy sample preparation

- Diffuse neutron data from every sample

- Time-evolution and diffuse scattering

- Interpretation more closely tied to theory
  - Modeling of scattering x-ray/neutron intensity
Intense synchrotron/neutron sources realize the promise envisioned by pioneers of diffuse x-ray scattering

- M. Born and T. Von Karman 1912-1946 - TDS
- Andre Guiner (30’ s-40’ s)- qualitative size
- I. M. Lifshitz *J. Exp. Theoret. Phys. (USSR)* **8** 959 (1937)
- J. M Cowley (1950) *J. Appl. Phys.* - local atomic size
- Krivoglaz *JETP* **34** 139 1958 chemical and spatial fluctuations

Other references:

- [http://www.uni-wuerzburg.de/mineralogie/crystal/teaching/dif_a.html](http://www.uni-wuerzburg.de/mineralogie/crystal/teaching/dif_a.html)
- Krivoglaz vol. I and Vol II.
Diffuse scattering done by small community

- Warren school
  - A. Gunier
  - Warren school
  - S. Cowley, Arizona St.
  - Bernie Borie, ORNL
  - Jerry Cohen, Northwestern

- Krivoglaz school
  - Simon Moss, U. Of Houston
  - B. Schoenfeld, ETH Zurich
  - W. Schweika, KFA Jülich
  - H. Reichert, Max Planck
  - Peisl, U. München
  - Gitgarts, Minsk
  - Rosa Barabash, ORNL
  - Rya Boshupka, IMP
Diffuse scattering song

Come eager young scholars- so tender and new
I’ll teach you diffraction- what I says mostly true
Between the Bragg Peaks lies a world where you see
Fluctuations and defects- they stand out plane-ly

Chorus
For its dark as a dungeon between the Bragg peaks
But here in the darkness- each defect speaks
It gathers- from throughout- reciprocal space
And re-distributes all over the place.

Between the Bragg peaks - one thing that we see
Is TDS on our CCD
Intensity totals are conserved- you can’t win
It steals from the Bragg peaks that stay very thin

Substitutional alloys can cause quite a stir
The shorter the length scale the greater the blur
With care you can find out the bond length between
Each atom pair type-the measurements clean

Dislocations and other- type 2 defects
Destroy the Bragg peaks -they turn them to wrecks
But near the Bragg peaks- you still can see
Intense diffraction continuously

Many -are- the defects you find
Between the Bragg peaks where others are blind
So go tell your friends and impress your boss
You’ve new understanding -with one hours loss