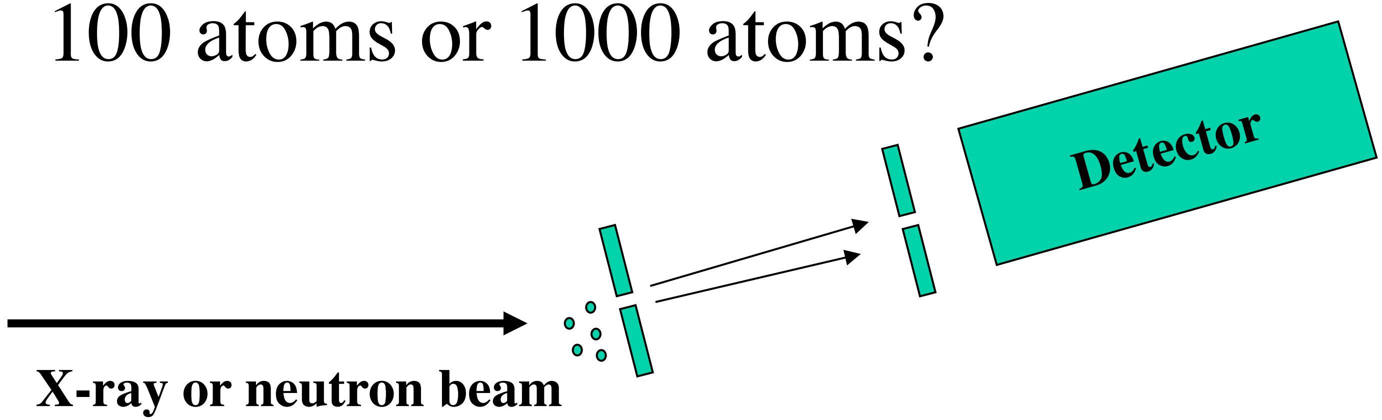
# Diffuse Scattering

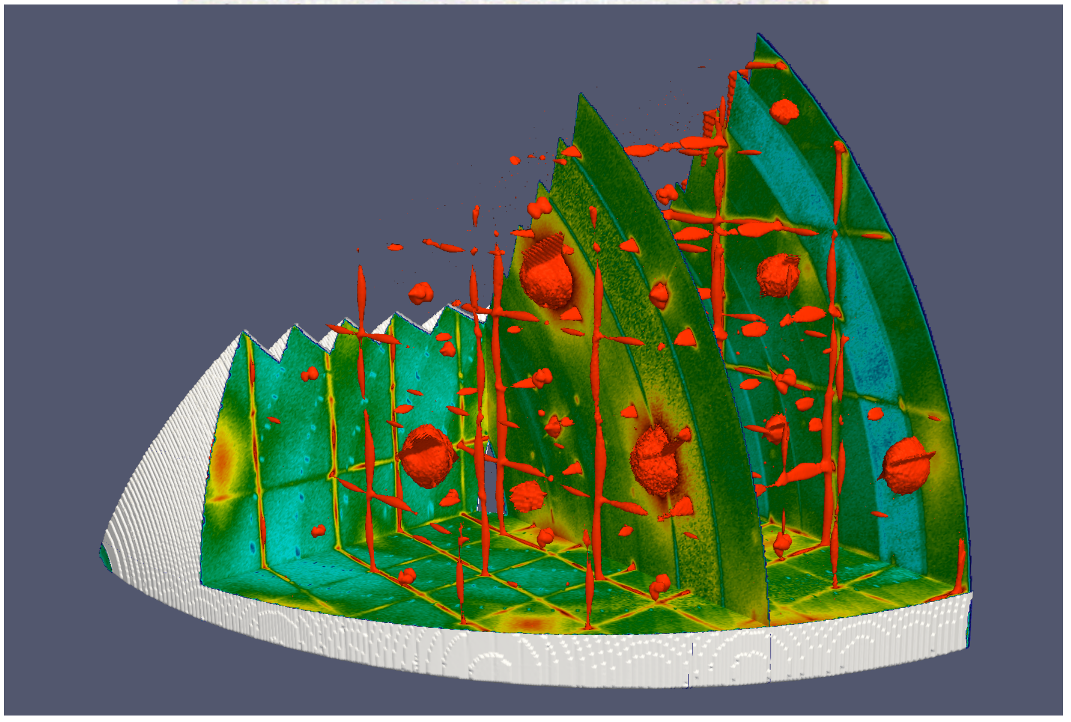
- Anticipatory (trick) question: If you have an x-ray or neutron detector looking at a small sample volume, which will scatter more x-rays or neutrons into the detector 1 atom 100 atoms or 1000 atoms?




***Answer**: Depends!*

# Diffuse Scattering

**Gene E. Ice**
*Materials Science and Technology Division*
*Oak Ridge National Laboratory, USA*



National School on Neutron and X-ray Scattering
ORNL/SNS June 2014

# 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-***

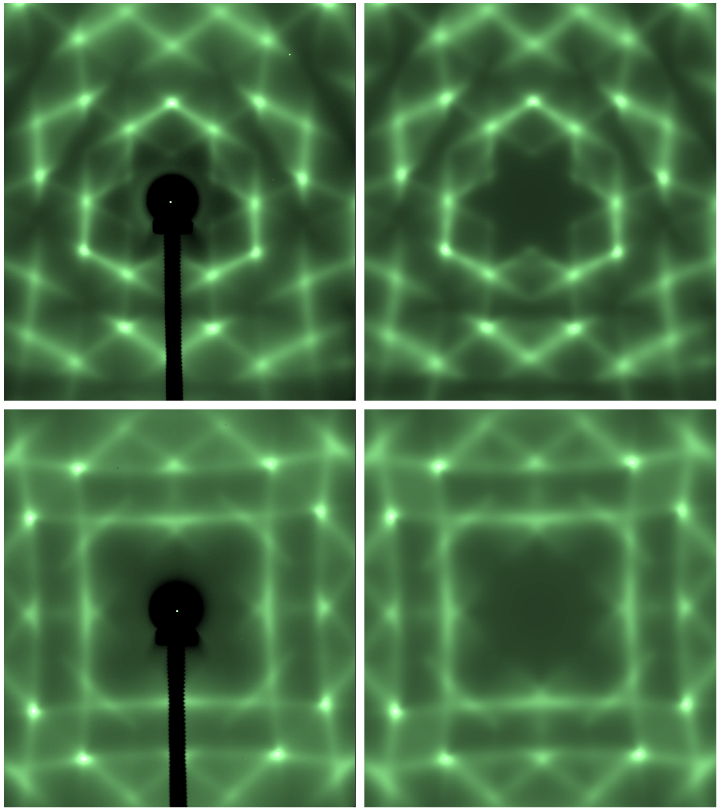
***Important for recognizing origins of diffuse scattering!***

# 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

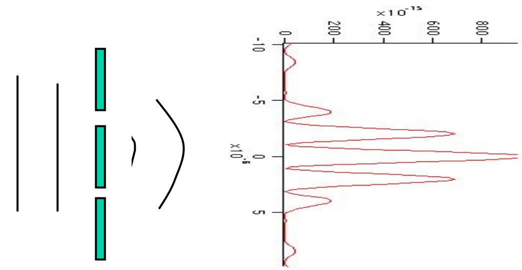
- New theories provide direct link between experiments and first-principles calculations



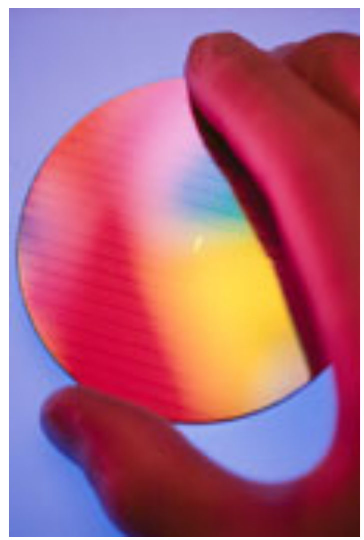
**Experiment** **Theory**

# What you already know- arrangement of atoms redistributes scattering

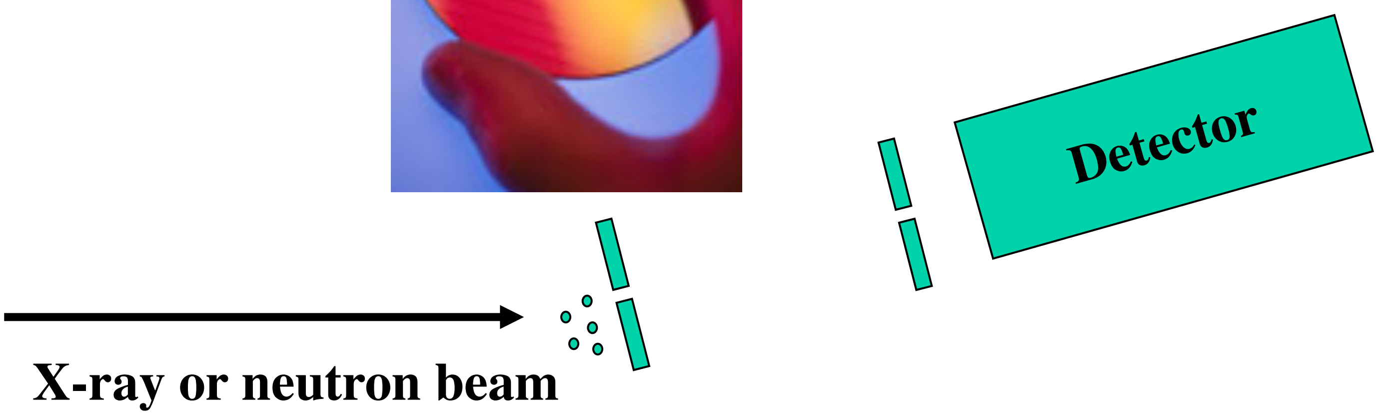
- Familiar light example



- Practical applications- zero background plates for powder diffraction

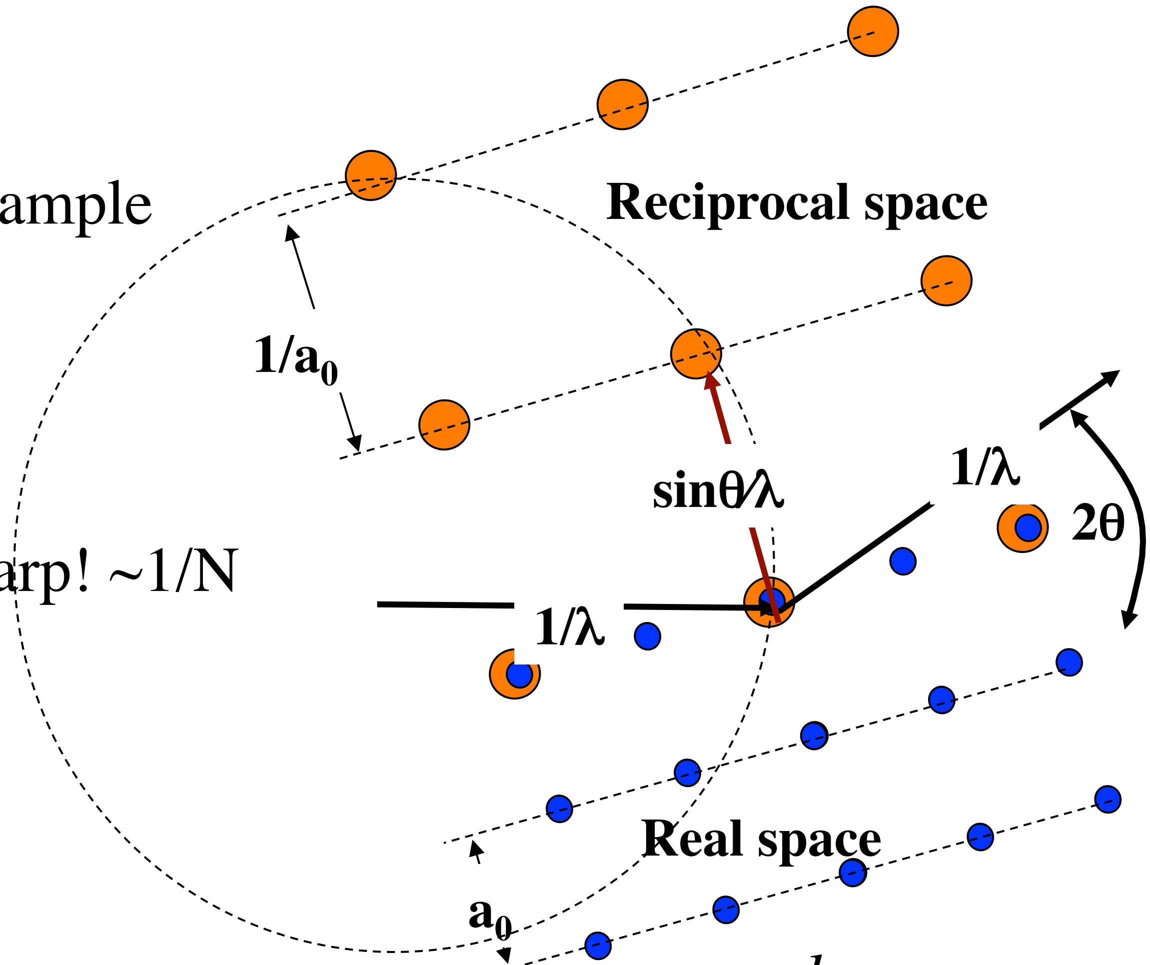


- Wave→diffraction



# You already know that Bragg reflections occur when scattering amplitudes add *constructively*

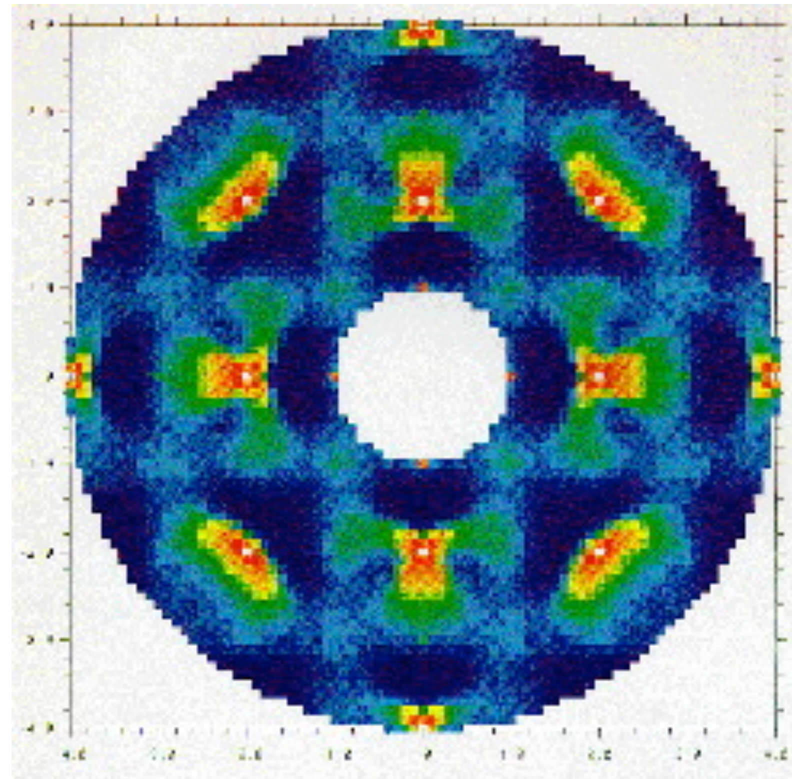
- Orientation of sample
- Wavelength
- Bragg Peaks sharp! ~1/N (arc seconds)




**Think in terms of *momentum transfer*** $\overline{p}_0 = \frac{h}{\lambda}\hat{d}_0$

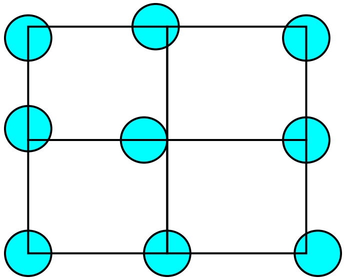
# If repeat crystal lattice of atoms leads to Bragg peaks- what happens when an atom is out of place/missing?

- Weakens Bragg peaks
- Redistributes scattering intensity in reciprocal space

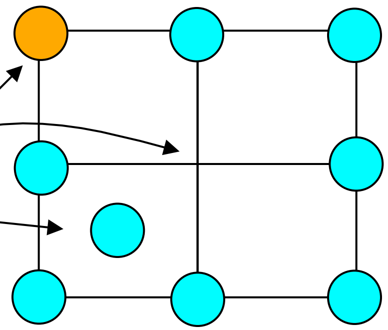


# Diffuse scattering due to *local* (short ranged) correlations/ fluctuations

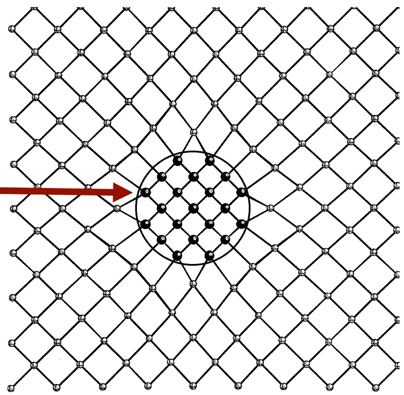
- Thermal diffuse scattering (TDS)



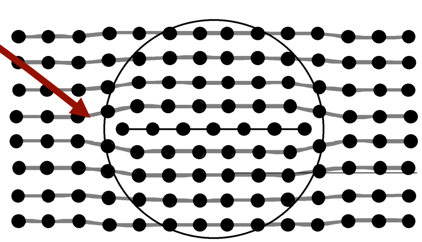
- Point defect
  - Site substitution
  - Vacancy
  - Interstitial



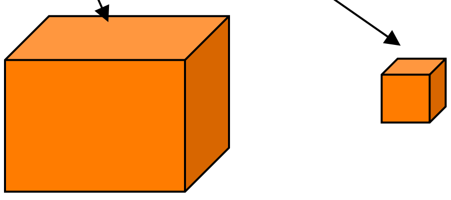
- Precipitate



- Dislocations



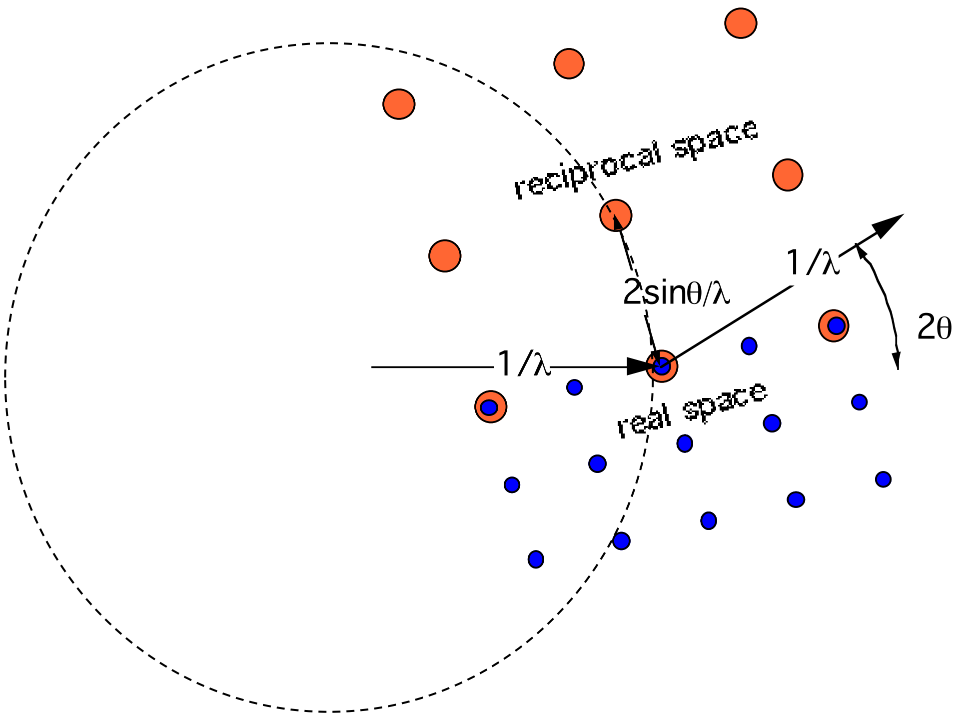
- Truncated surface- more



**All have in common reduced correlation length!**

# You already know length scales are inverted!

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

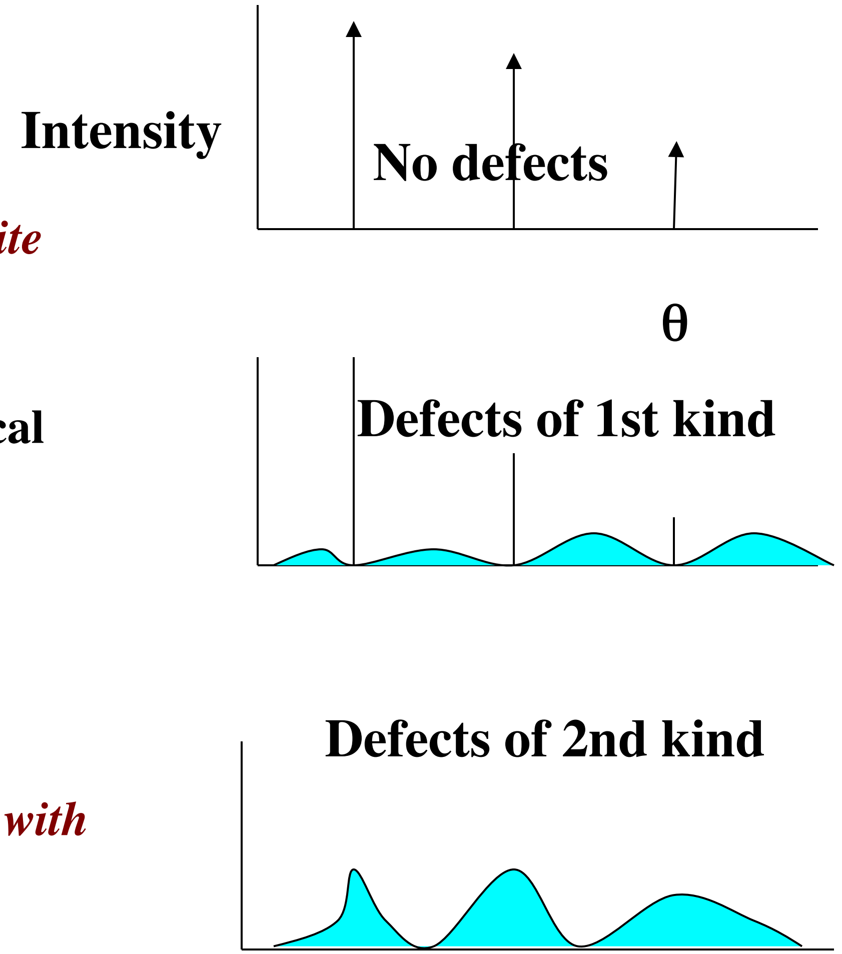



***If you remember nothing else!***

# 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**

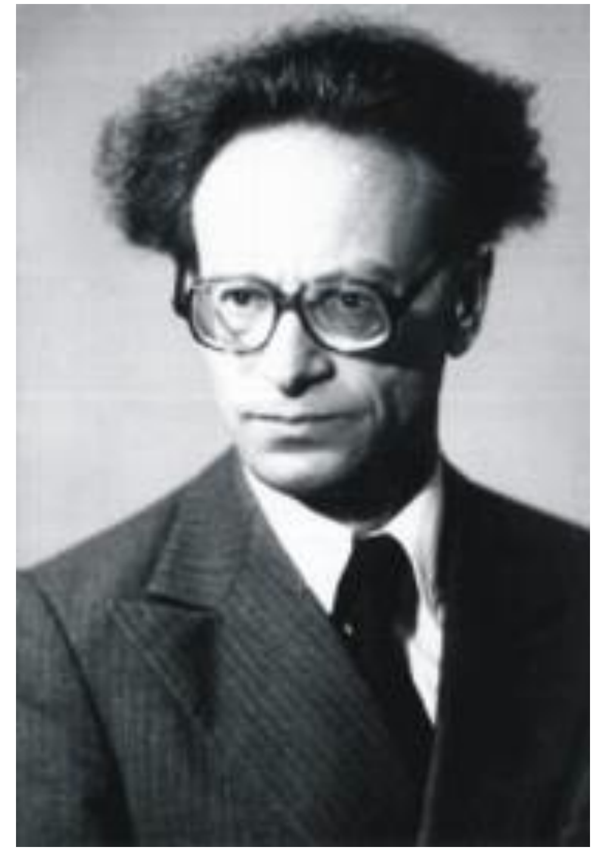
- **Defects of 2nd kind**
  - **No longer distinct Bragg peaks**
  - *Displacements continue to grow with crystal size*



# Who the heck was Krivoglaz?

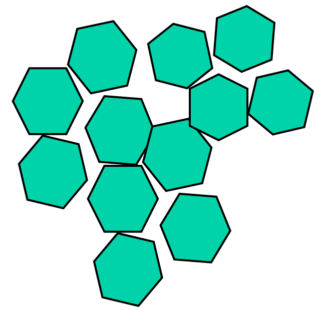
- Brilliant Ukrainian scientist
- Dissertation –predated Mossbauer’s work

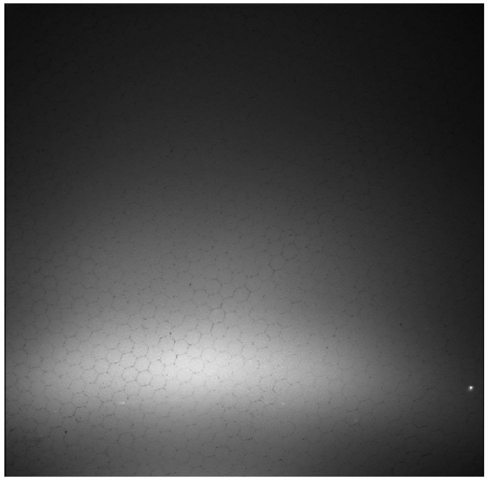
- Pioneered a general way of categorizing and studying defects using x-rays/neutrons



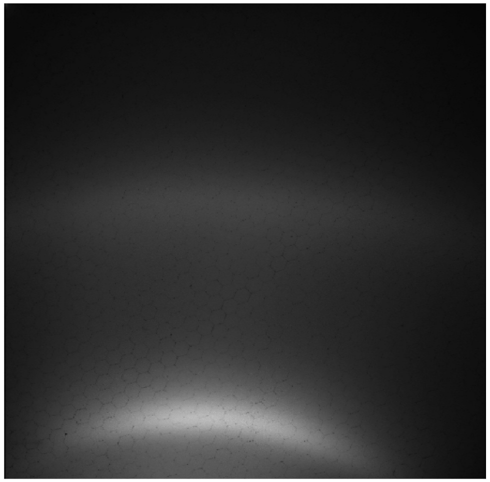
# Dimensionality Krivoglaz defect of second kind- influences diffraction

- **Small size→broad diffraction**
- **Polycrystalline**

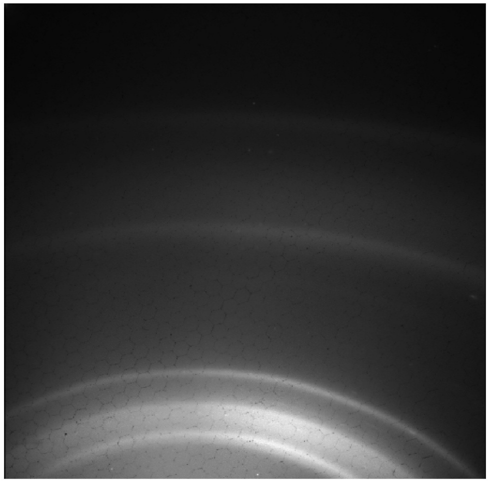




a. Amorphous

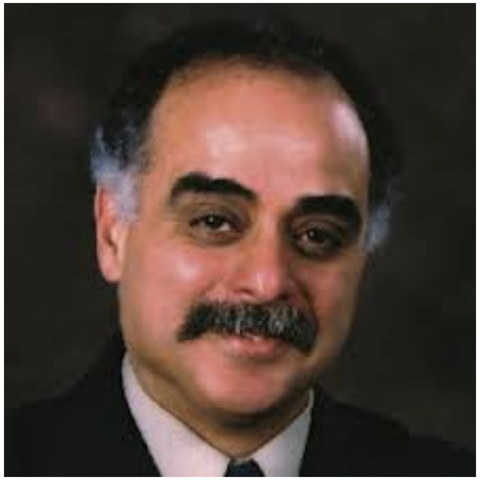


b. nanocrystalline



c. crystalline

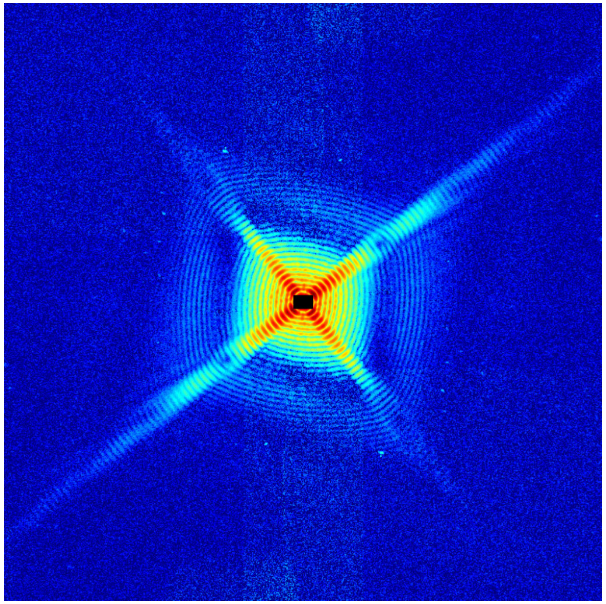
# Cev Noyan and Coworkers Studying Particle Statistics/Using Modern Tools



- **Numerical tests of long-time powder diffraction averages**

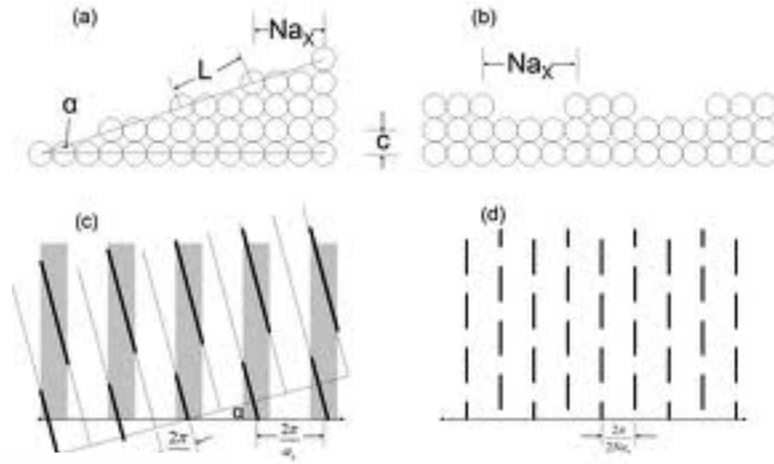
- **When are enough particles contributing to satisfy statistical averages**

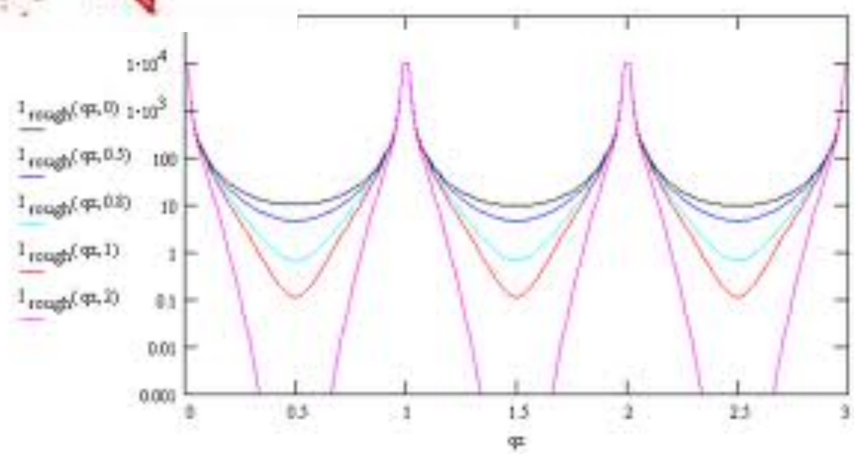
$$\frac{\sin^2 Nx}{\sin^2 x}$$



# Single crystals and surfaces -truncation rods

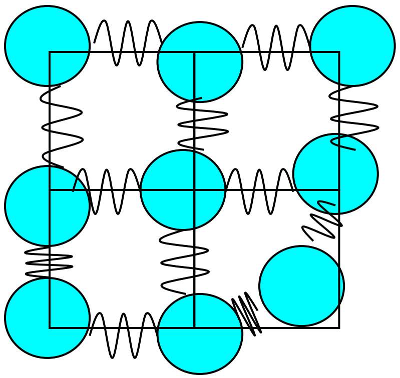
- Diffuse scattering perpendicular to surface
- Connect to Bragg Peaks
- Intensity falloff indicates roughness
  - Slow (smooth or abrupt)
  - Fast (rough)



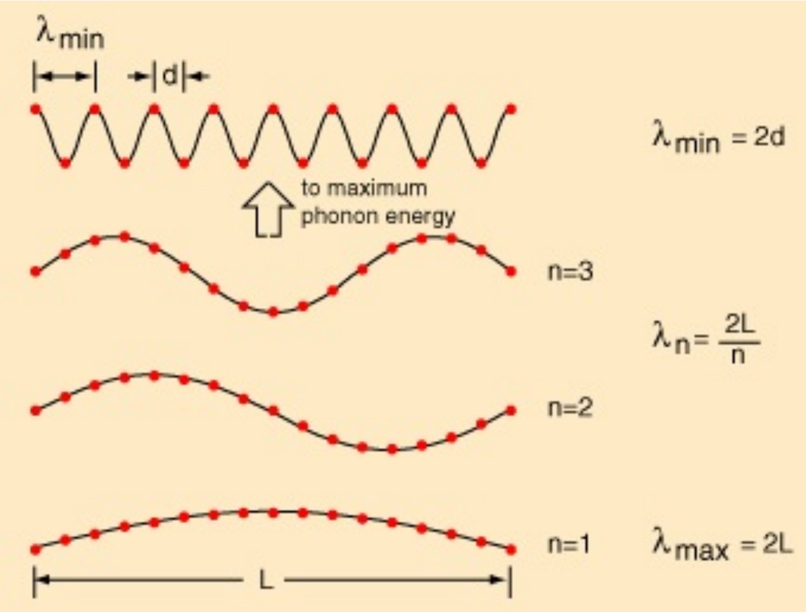
# Thermal motion-Temperature Diffuse Scattering-(TDS) -defect of 1st kind

- 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**

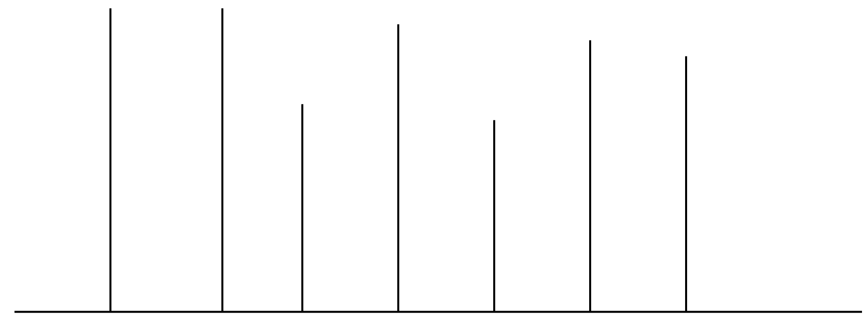
# A little math helps for party conversation

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

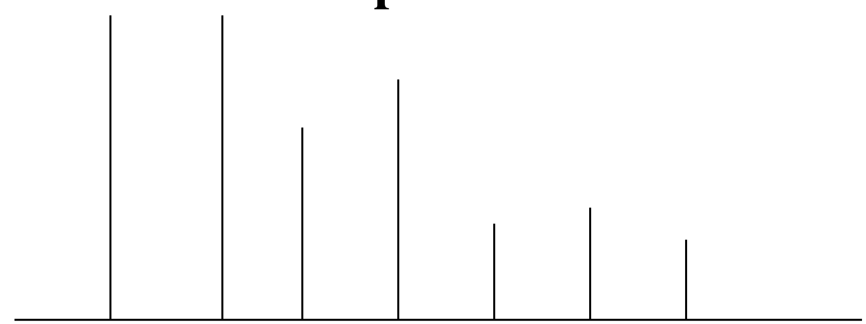
$$2M = 16\pi^2 \langle u_s^2 \rangle \frac{\sin^2\theta}{\lambda^2}$$

- ***Small*** θ →***Big*** reflections

- $e^{-2M}$ shrinks (***bigger*** effect) with θ (q)



**Low Temperature**



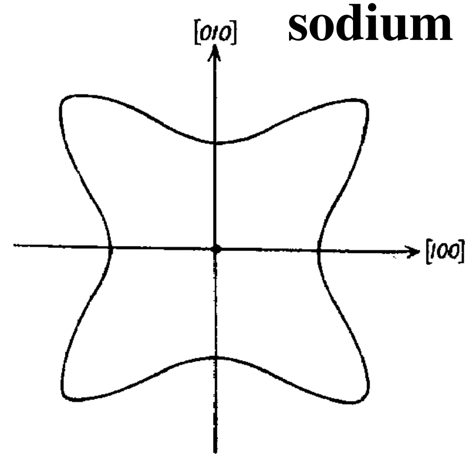
**High temperature**

Displacements, $u_s$ depend on ***Debye Temperature $\theta_D$* - *Bigger $\theta_D$*** →***smaller*** displacements !

# TDS makes beautiful patterns reciprocal space

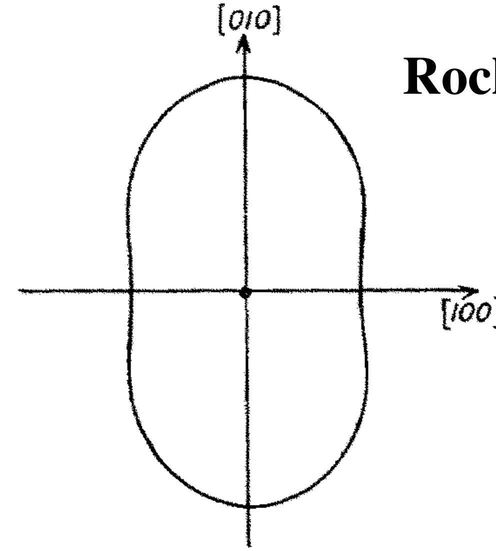
- Iso- intensity contours
  - Butterfly
  - Ovoid
  - Star
- Transmission images reflect symmetry of reciprocal space and TDS patterns

**sodium**



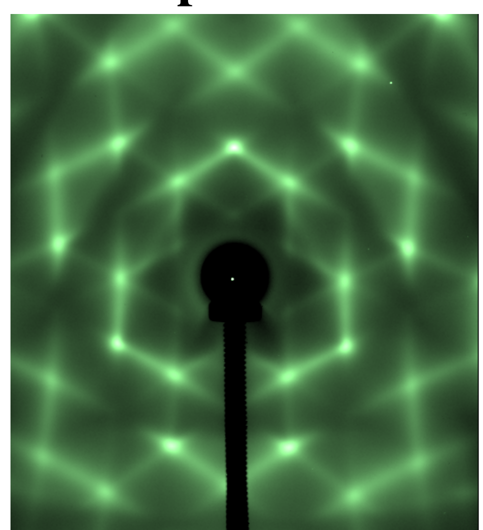

(a) 200 spectrum

**Rock salt**

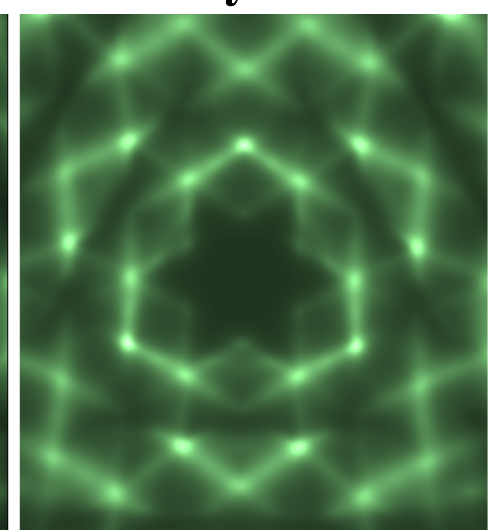



(a) 200 spectrum

**Experiment**



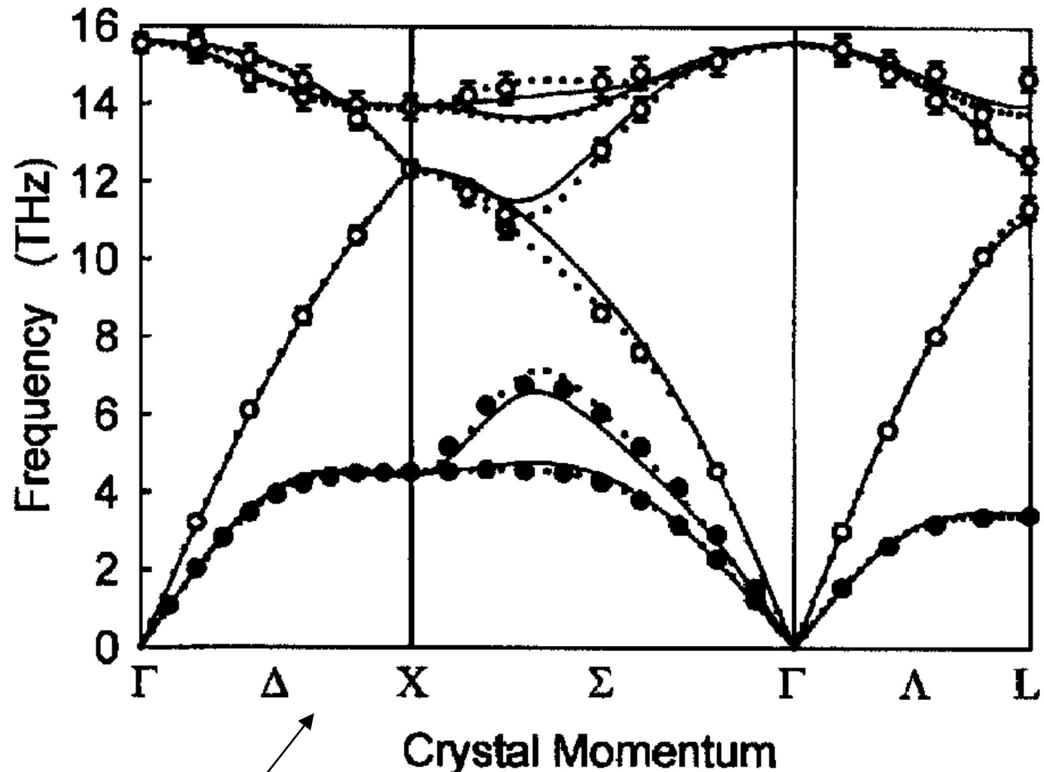
**Theory**



**Chiang et al. Phys. Rev. Lett. 83 3317 (1999)**

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

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

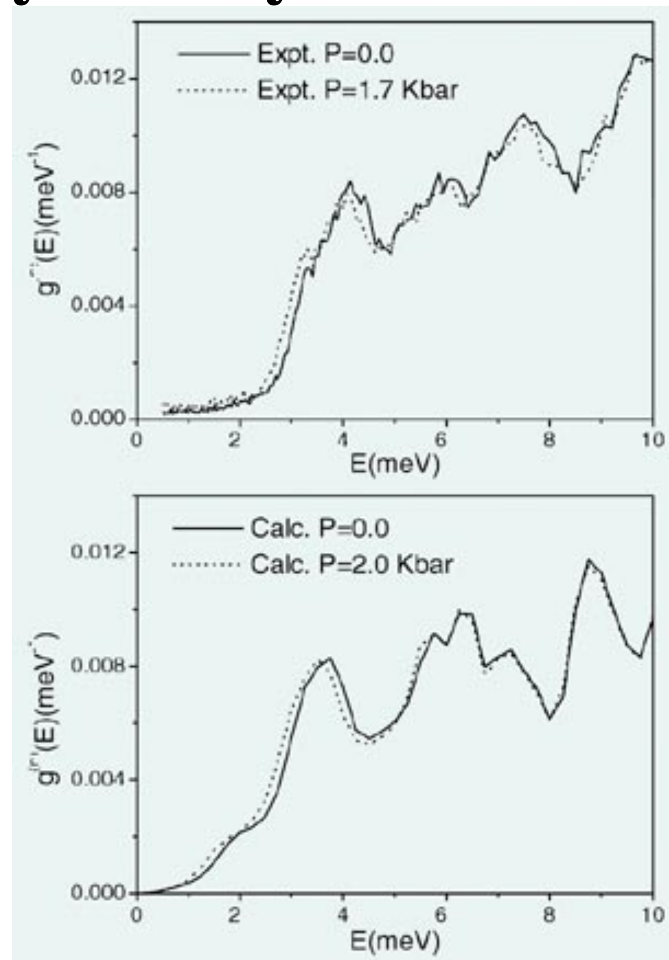



**Phonon spectrum gives natural vibration frequencies in different crystal directions!**

# Inelastic neutron/x-ray scattering directly measures phonon spectra in symmetry directions

- **Inelastic neutron scattering confirms origins of negative Grüneisen coefficient in cubic $ZrW_2O_8$ (negative thermal expansion)-disordering phase transition.**

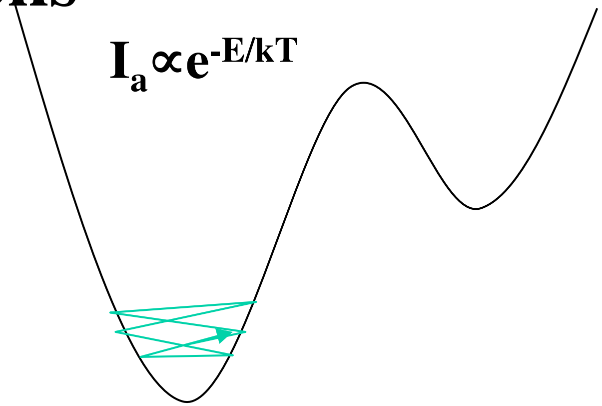
- **Unusual thermal displacements *often associated with phase transitions*.**

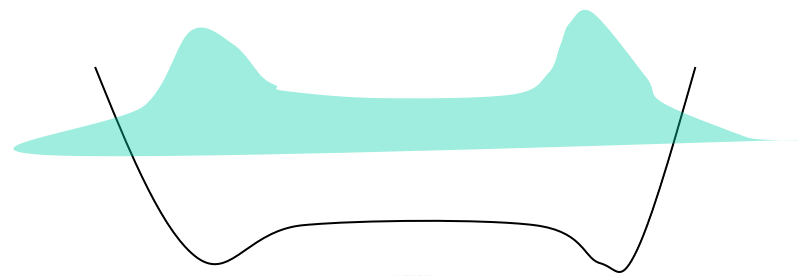


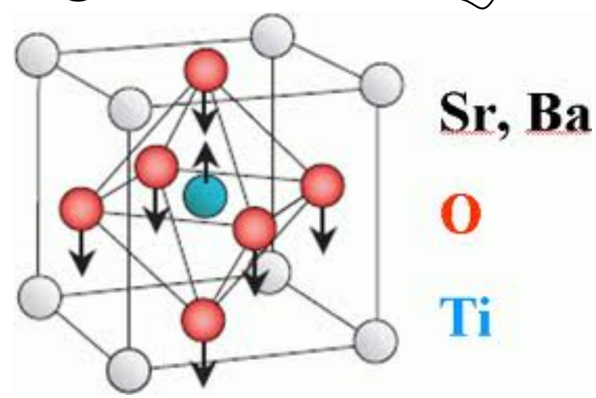

***Phonon energies similar to meV neutron energies.***

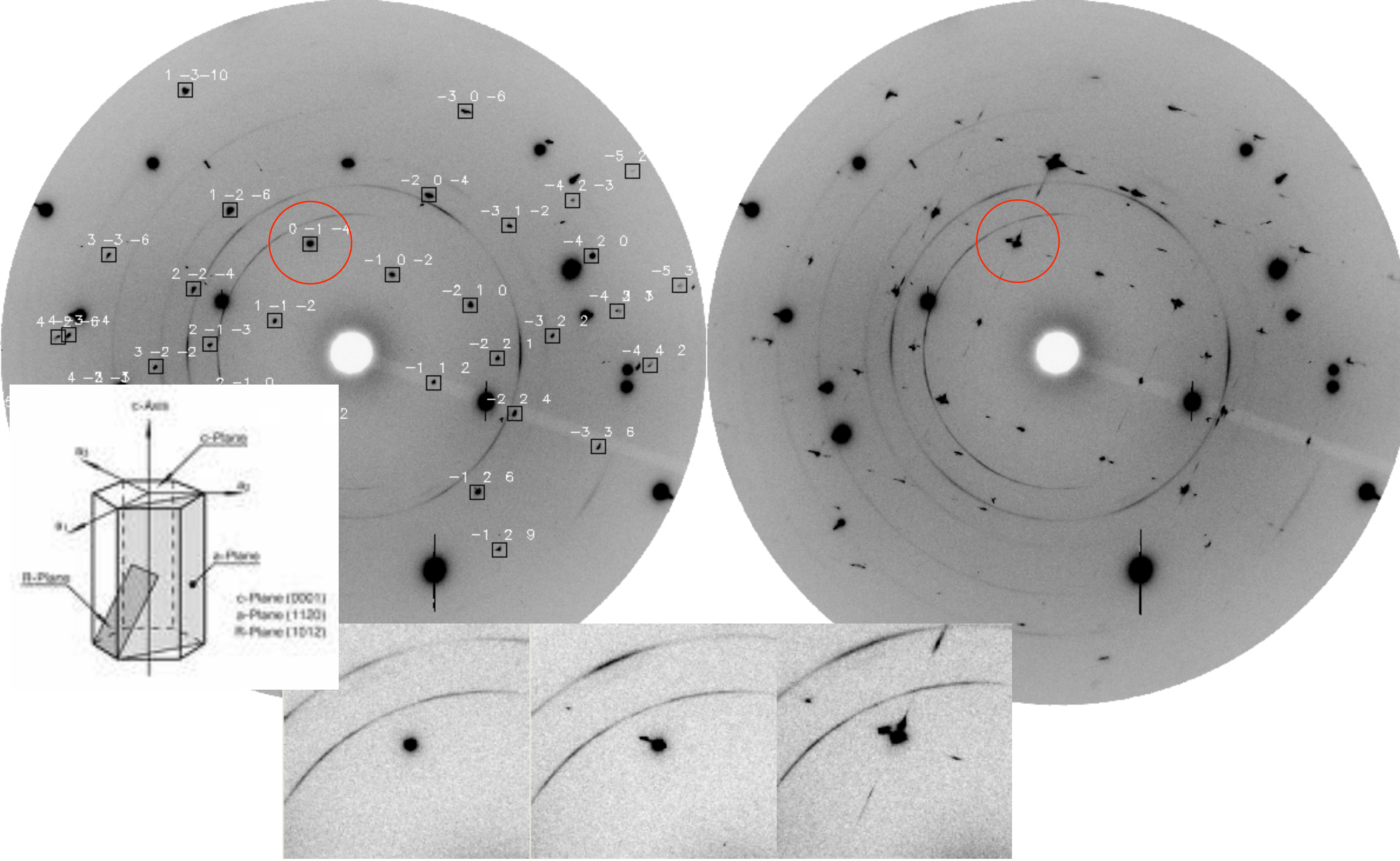
# Extra diffuse scattering often observed from materials near phase transitions

- **Distribution of configurations at finite temperature**
  - Mixed phases (1st order)
- **Extended displacements**
- **High-pressure**
  - higher-co-ordination
  - Longer NN bond distance
  - Smaller volume/atom

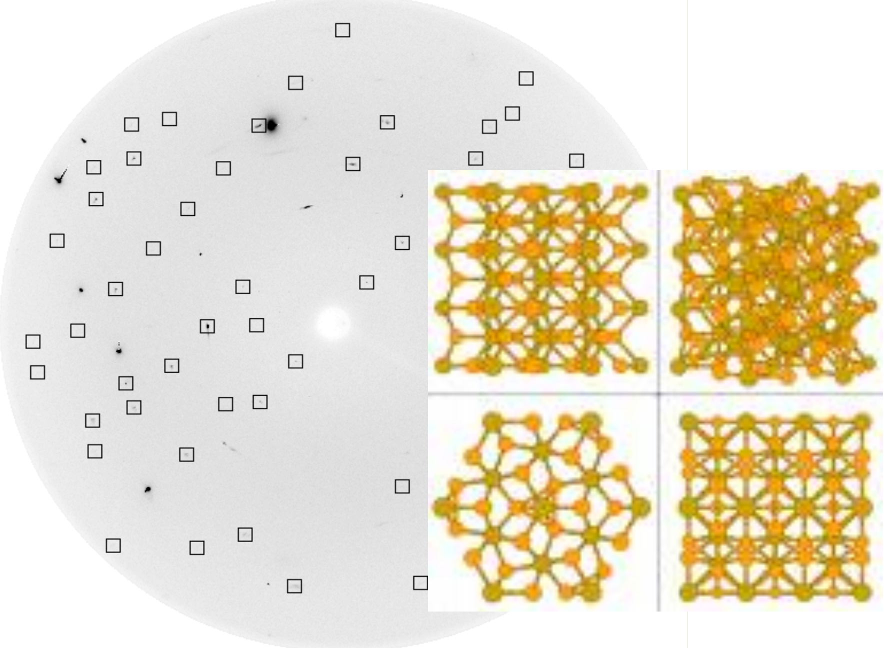


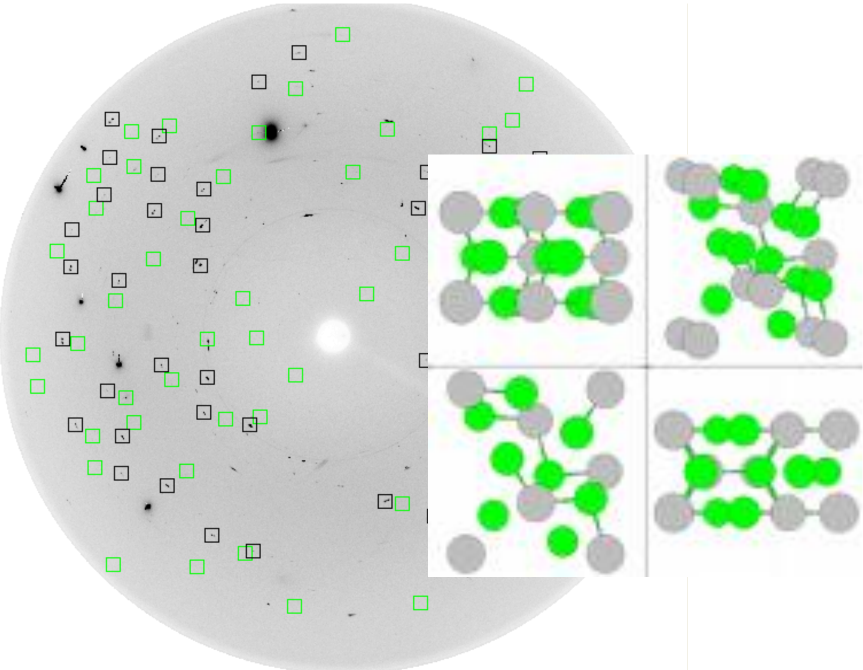





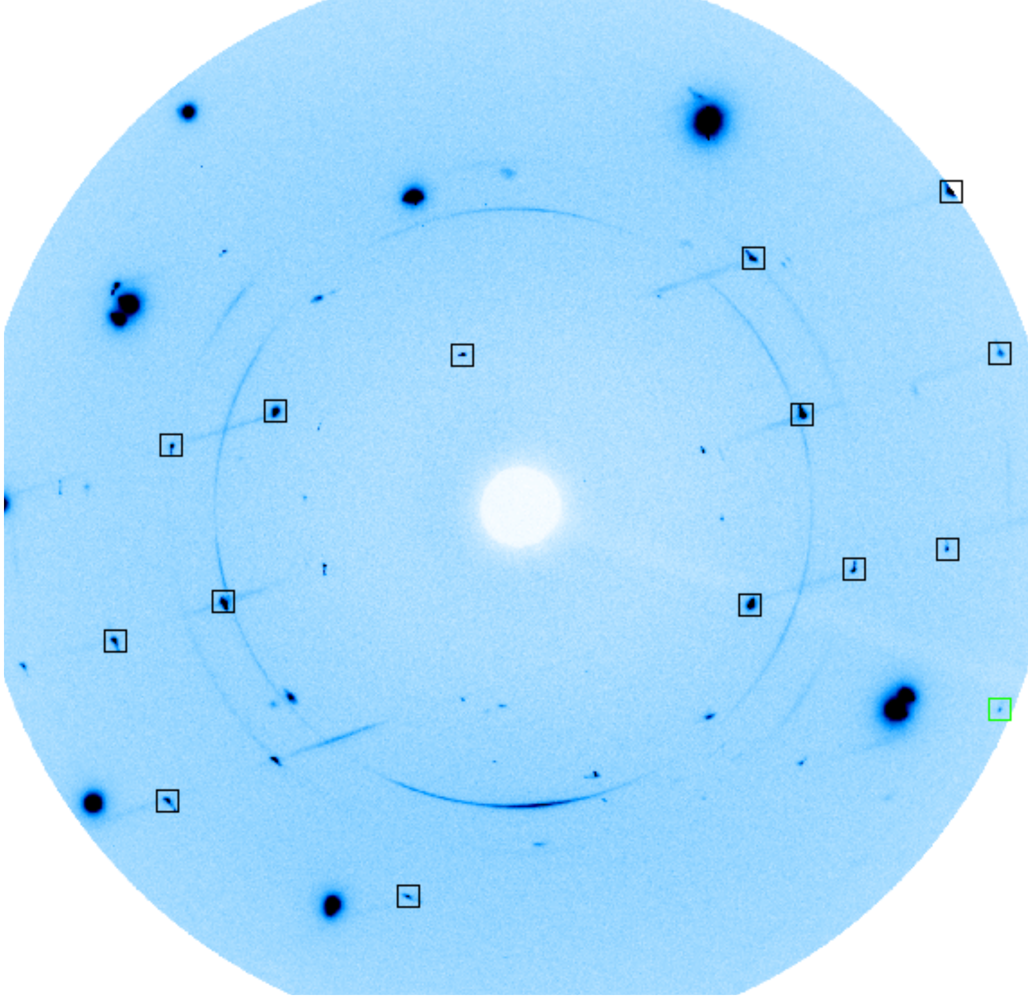



R-3c→I2/a displacive transition observed in a single crystal of $Cr_2O_3$ at 80 GPA





Complete transformation induced by heating the sample to 2000 K



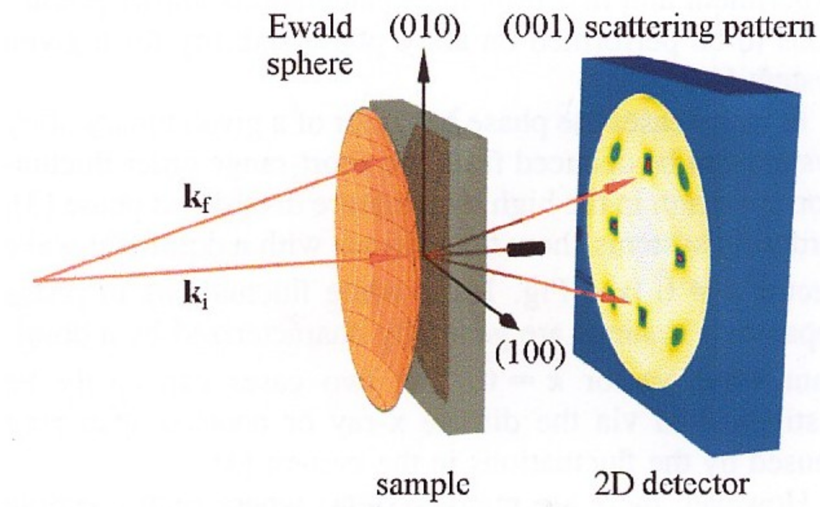
Diffuse scattering before the transformation occurs, heating at~1000 K

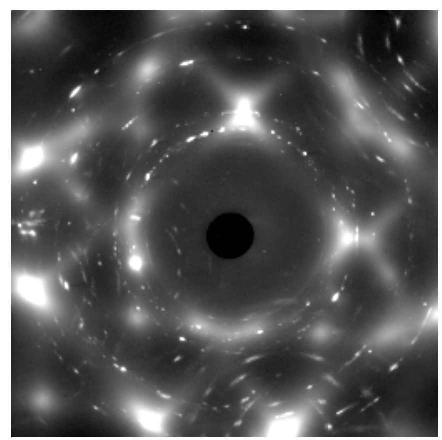
# C22→C23 transition in $Fe_2P$ at 10 GPa

Dera et al. (2008) *Gophys. Res. Lett.*, **35**, L10301

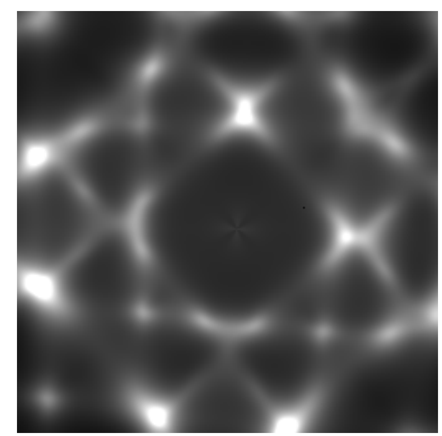
# High-energy Synchrotron X-rays are revolutionizing TDS measurements

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



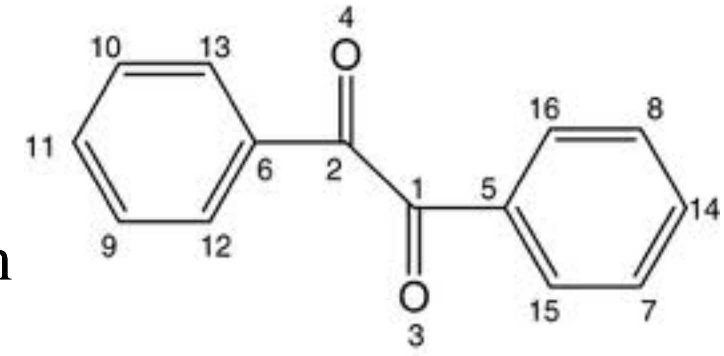
**Pu experiment**



**Pu theory**

# Neutrons uniquely sensitive to low Z

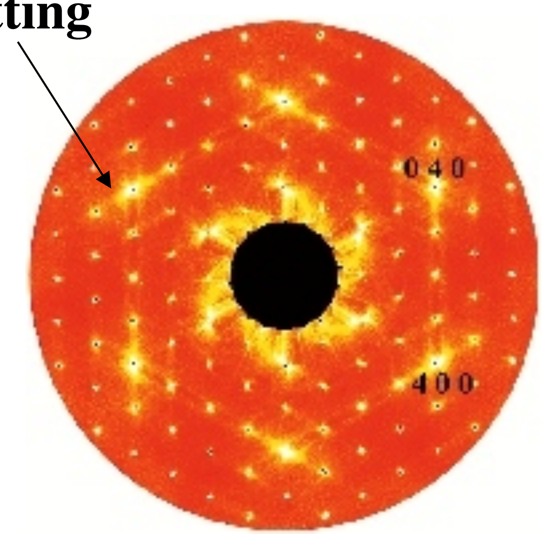
- Deuterium cross section large
- Phonon energy comparable to neutron energy
- New insights into dynamics of "molecular crystals"



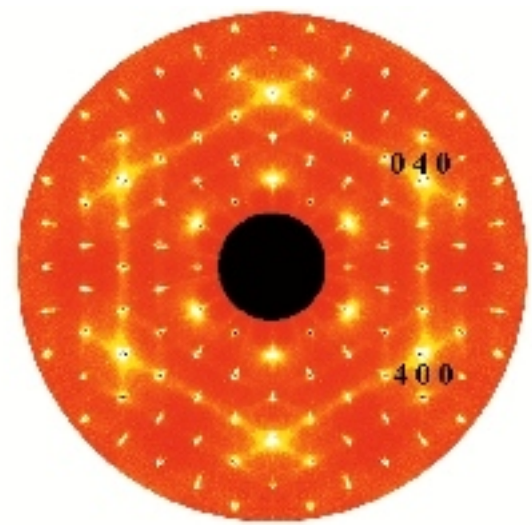

(I)

Welberry et al. ISIS

**splitting**



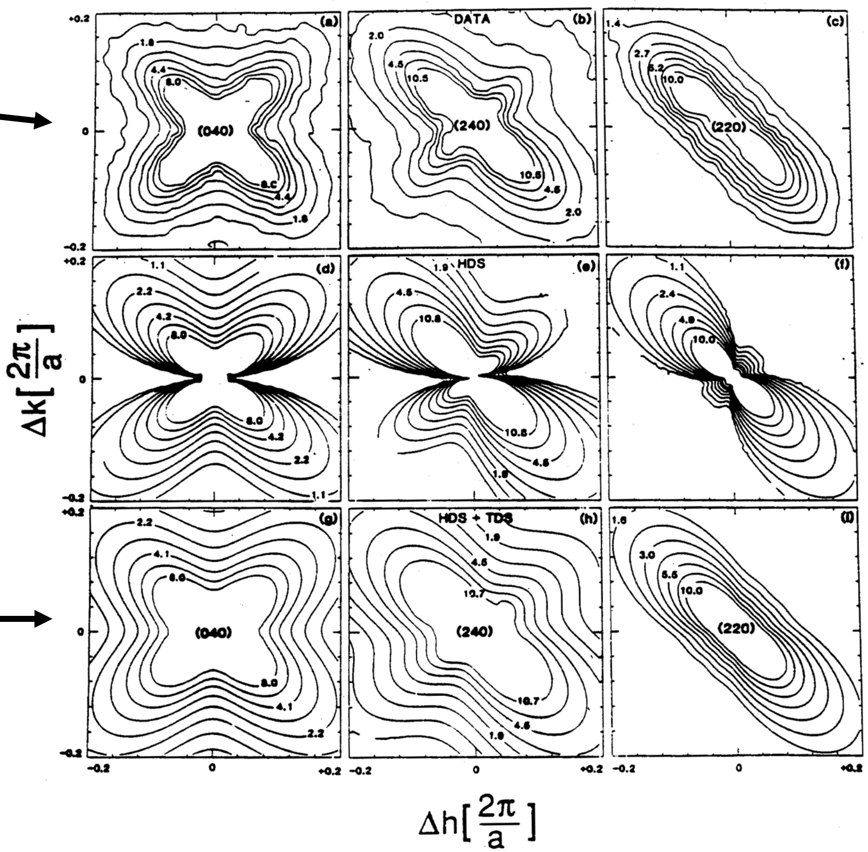

**Experiment**




**Theory**

# Often TDS mixed with additional diffuse scattering

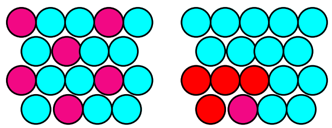
- Experiment
- Strain contribution
- Combined theoretical TDS and strain diffuse scattering




**TDS must often be removed to reveal other diffuse scattering**

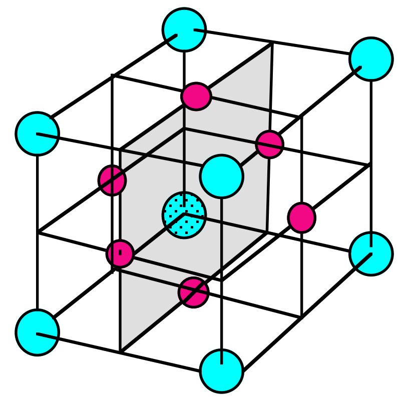
# Alloys can have another ***type 1*** defect-***site substitution***

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

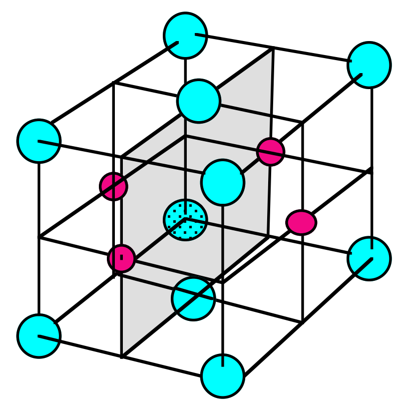


- Short ranged
  - Ordering
  - Clustering (like neighbors)

Each Au has 8 Cu near-neighbors



$Cu_3Au$
$L1_2$



CuAu
$L1_0$

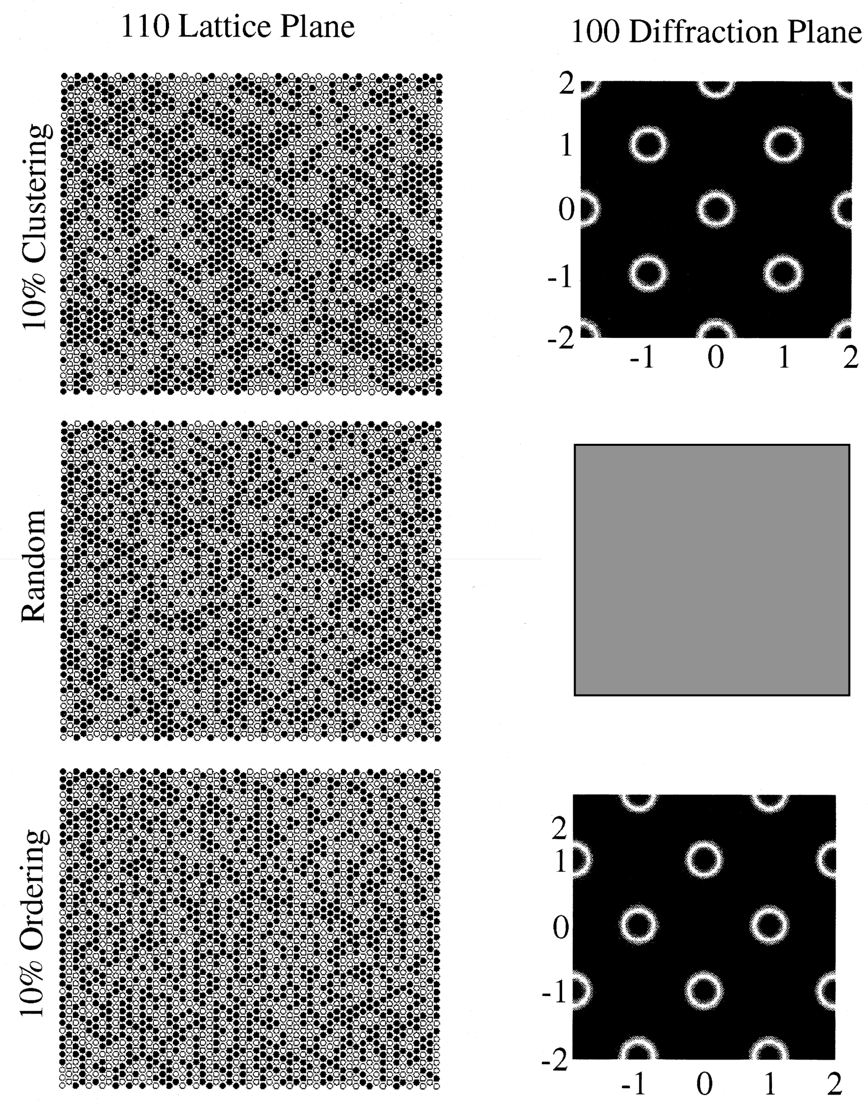
Alternating planes of Au and Cu

# Redistribution depends on kind of correlation

Clustering intensity
→ fundamental sites

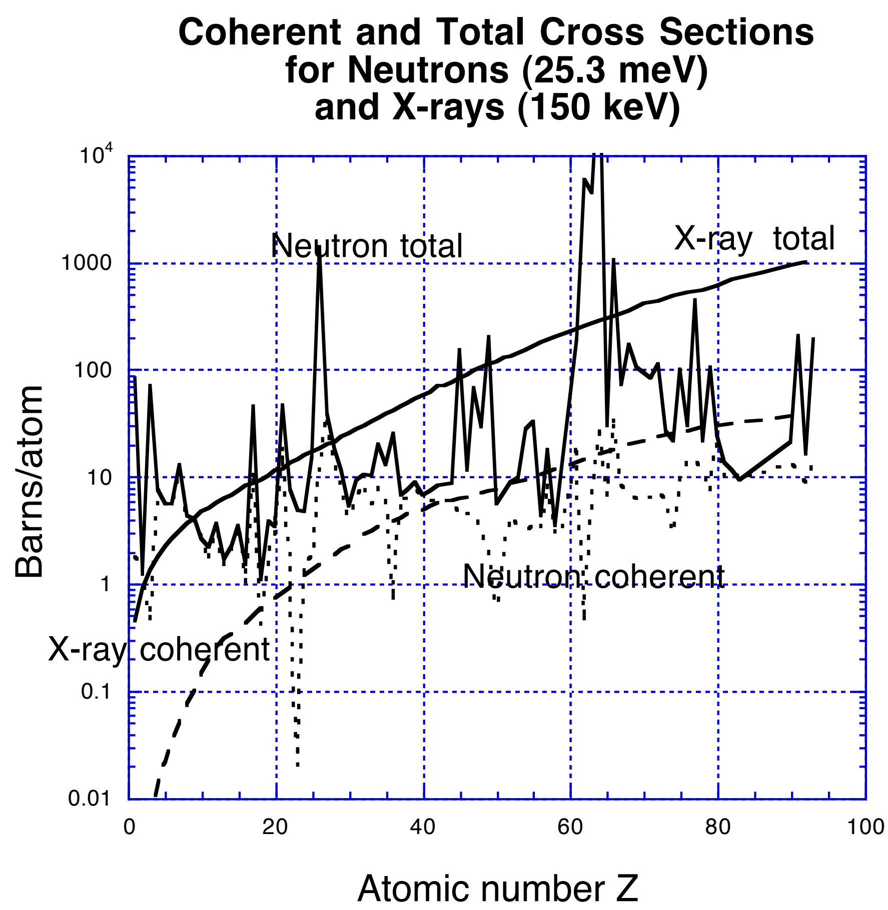
Random causes
*Laue monotonic*

Short-range ordering
→ superstructure sites



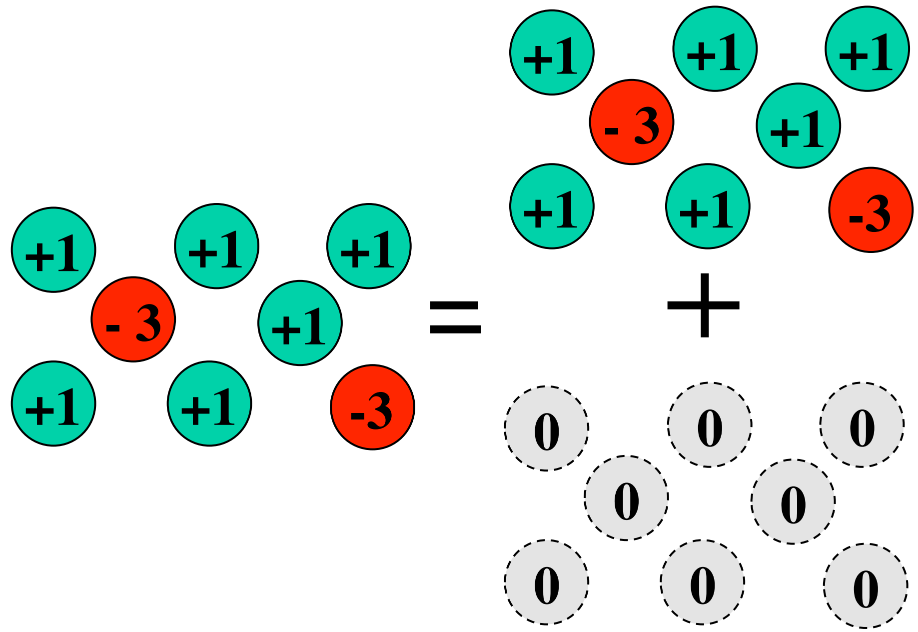
# Neutron/ X-rays Complimentary For Short-range Order Measurements

- Chemical order diffuse scattering **proportional to contrast $(f_A\text{-}f_B)^2$**
- 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



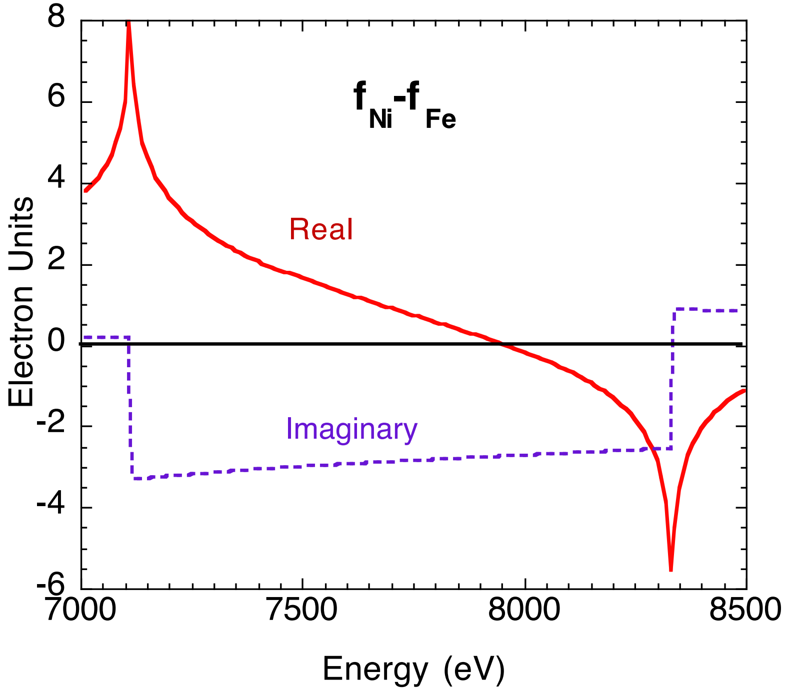
# Neutrons can select isotope to ***eliminate*** Bragg scattering

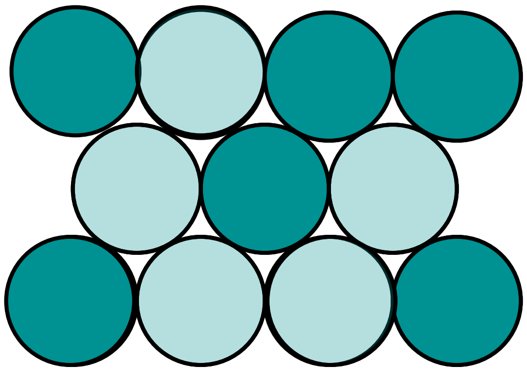
- **Total scattering $c_a f_a^2 + c_b f_b^2 = 3$**
- **Bragg scattering $(c_a f_a + c_b f_b)^2 = 0$**
- **Laue (diffuse) scattering**
  **$c_a c_b (f_a - f_b)^2 = 3$**



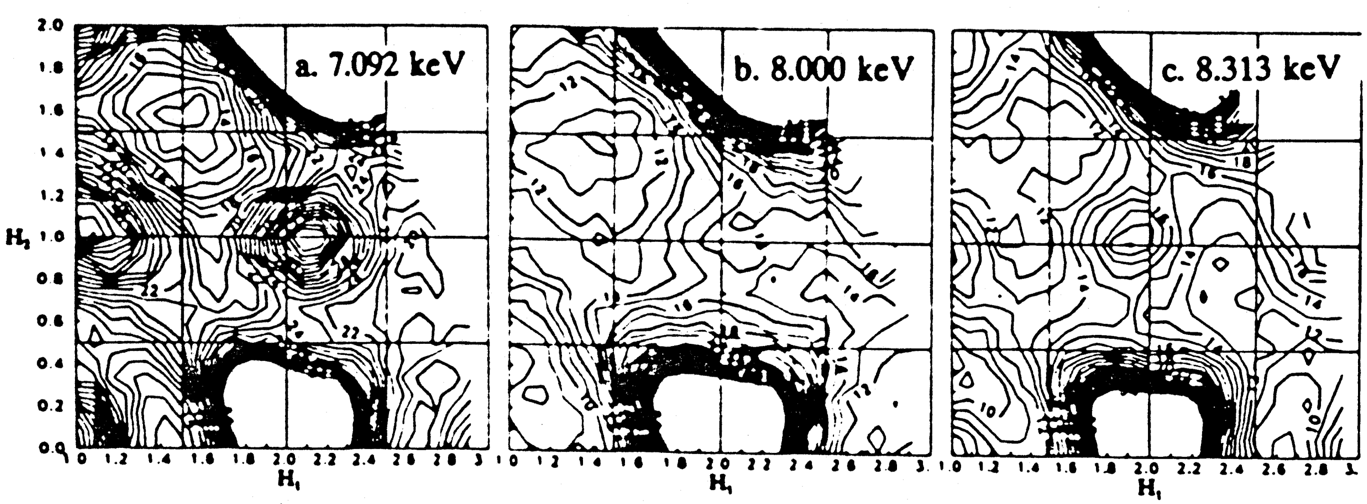

***Isotopic purity important as different isotopes have distinct scattering cross sections- only one experiment ever done!***

# X-ray anomalous scattering can change x-ray contrast



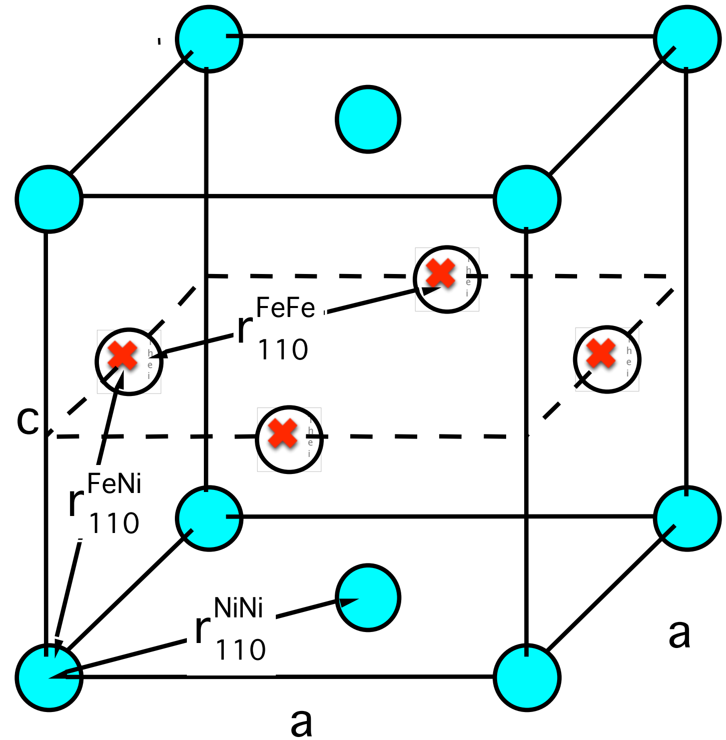
- Chemical SRO scattering scales like $(f_a-f_b)^2$
- Static displacements scale like $(f_a-f_b)$
- TDS scales like $\sim f_{average}^2$



# Atomic size (static displacements) affect phase stability/ properties

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

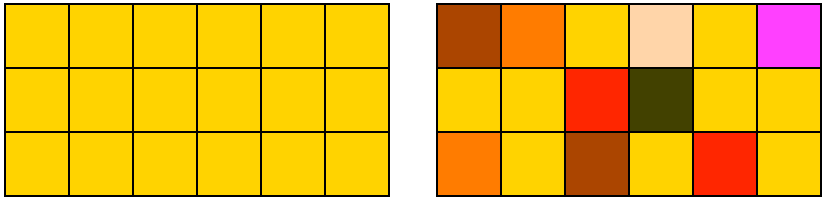
- *Metals and alloy phases (hume-Rothery)*
  - Ratio of radii
  - Valence electron concentration
  - Electrochemical factor



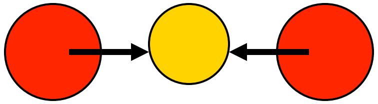

***Grand challenge -include deviations from lattice in modeling of alloys***

# Measurement *and* theory of atomic size are hard!

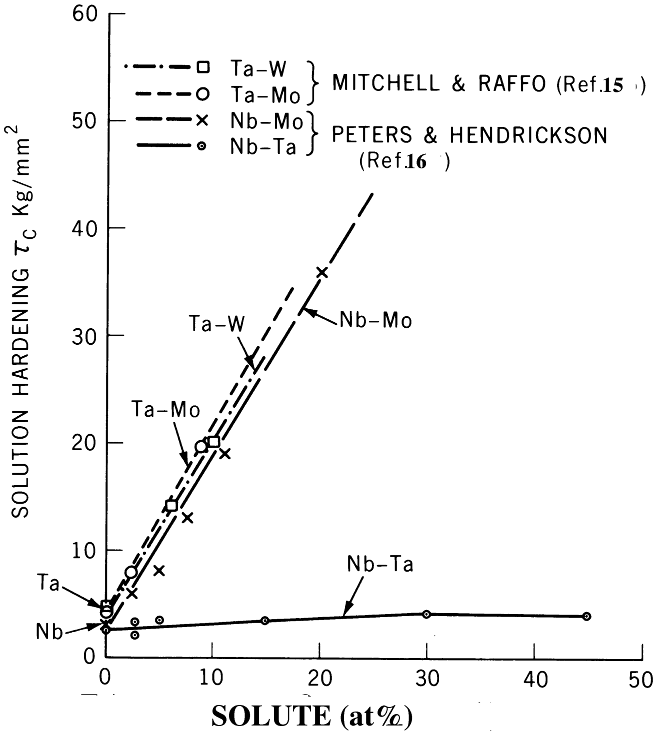
- Theory- violates repeat lattice approximation- every unit cell different!



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



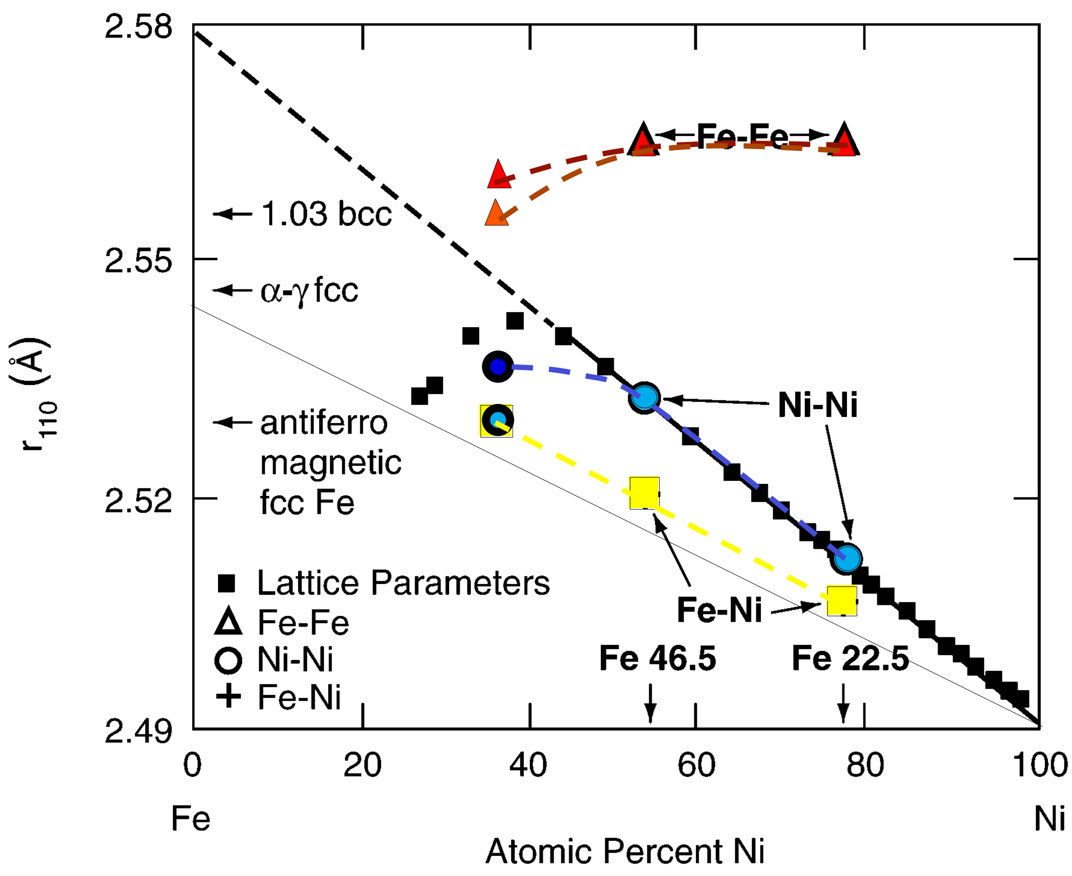
**Important!**



# Systematic study of bond distances in Fe-Ni alloys raises interesting questions

ORNL 98-7348A/rra

- 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?

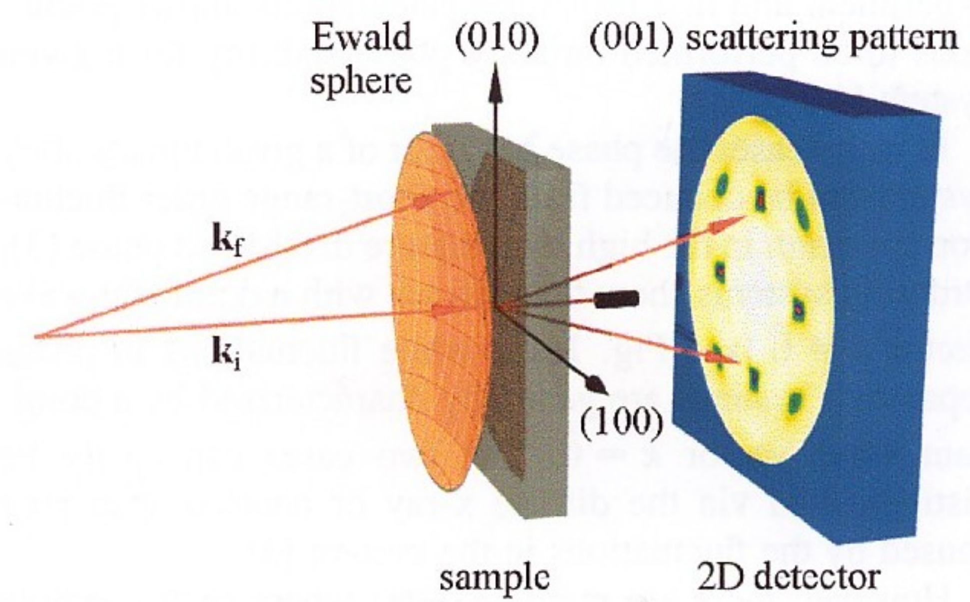


# High-energy x-ray measurements revolutionize studies of phase stability

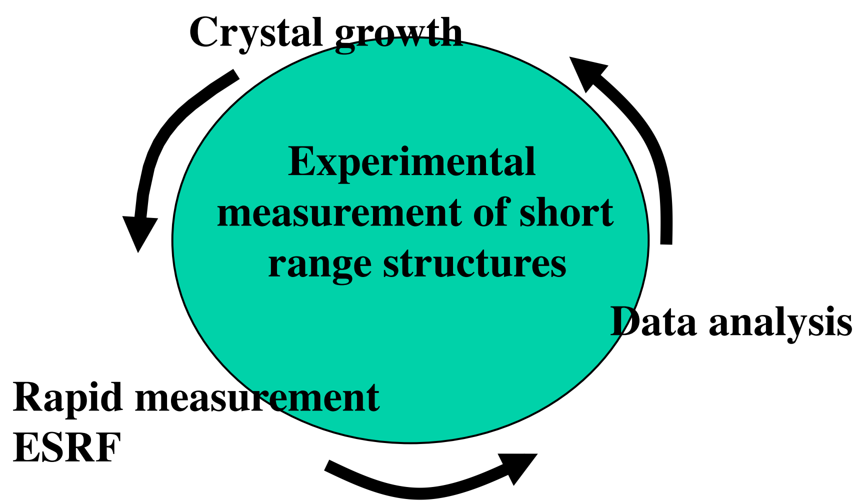
- Data in ***seconds*** instead of ***days***

- Minimum absorption and stability corrections

- New analysis provides direct link to first-principle

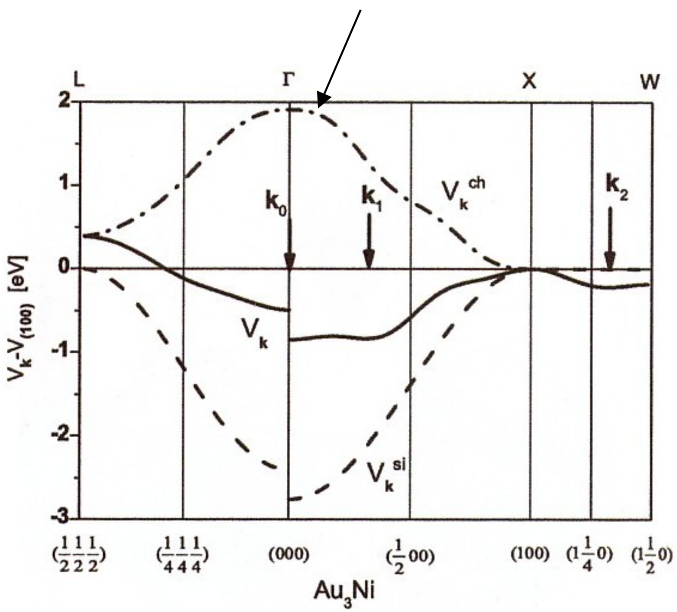



***Max Planck integrates diffuse x-ray scattering elements!***

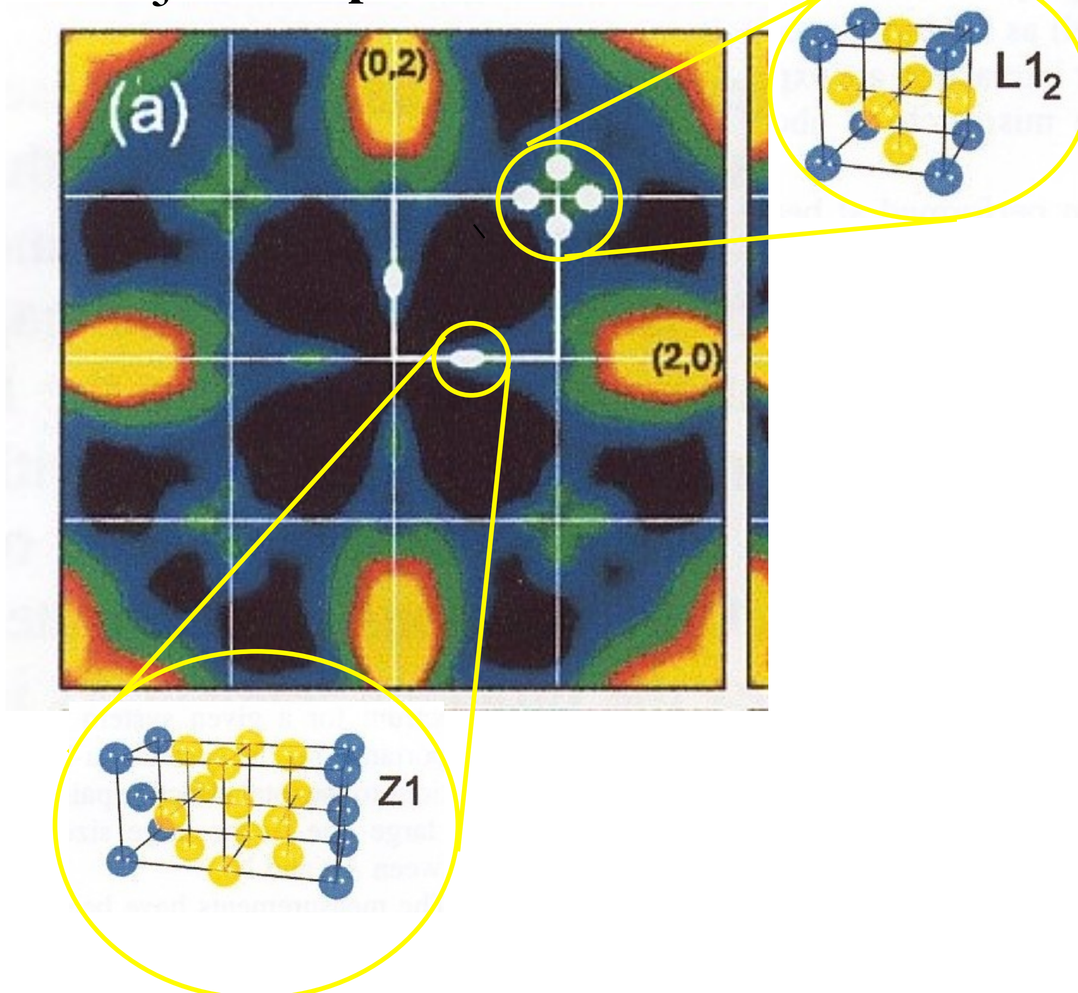


# Measurements show competing tendencies to order

- Both $L1_2$ and $Z_1$ present
- Compare with first principles calculations




**$Au_3Ni$ -001 plane**

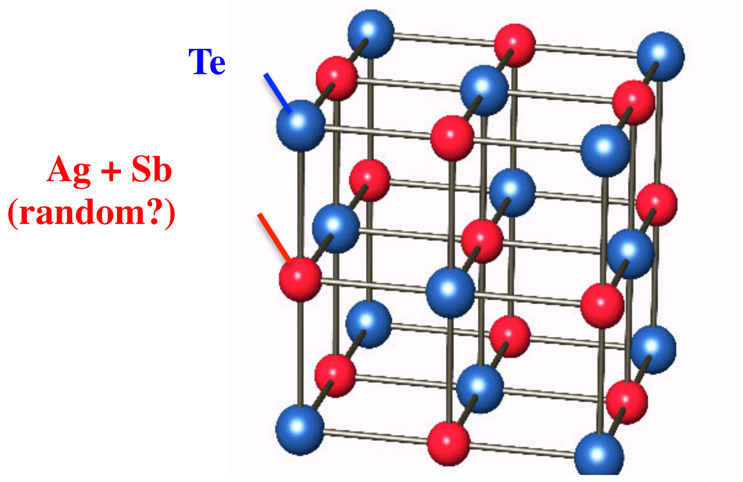



Reichert et al. Phys. Rev. Lett. **95** 235703 (2005)

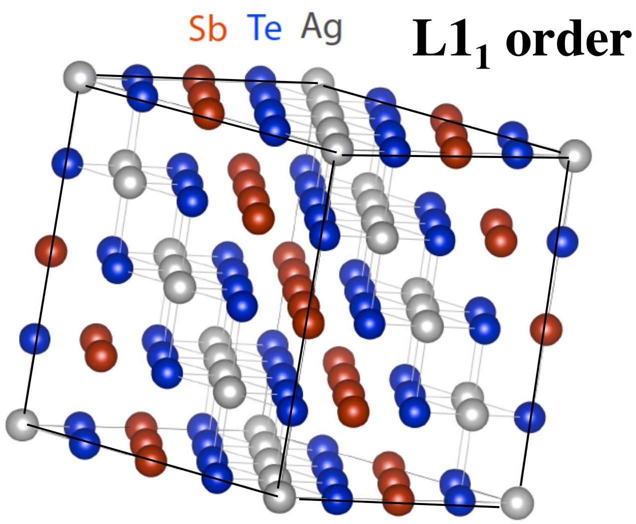
# Short-range and long-range order can also impact functional materials

- Interest in $AgSbTe_2$ because of very low thermal conductivity in a nominal rock-salt system: $\kappa_{lat}$ = 0.7 W/m/K at 300K.

  [Morelli, Jovovic, Heremans, PRL 2008].




- Strong Ag, Sb ordering predicted on sublattice by DFT

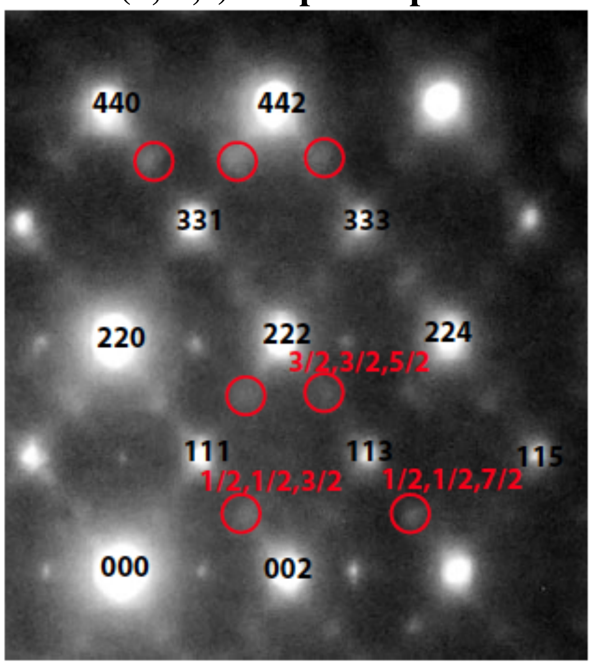


# Single-crystals reveal nano-scale ordering

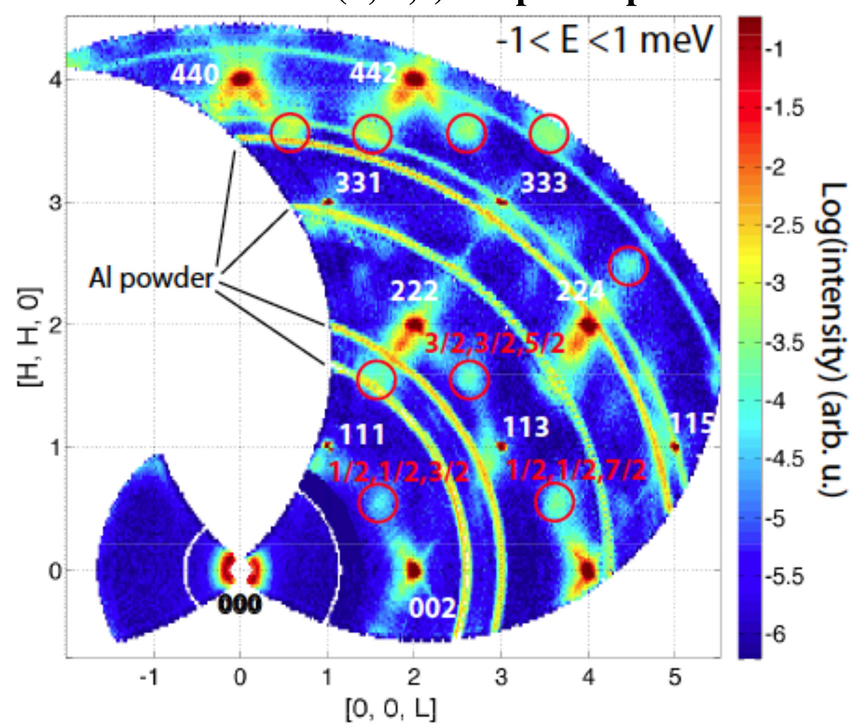
- **Superlattice peaks**, indicating **doubling of periodicity along <111>**, associated with cation ordering (compatible with DFT predictions).
- Superlattice peaks are broad, ordering **correlation length ξ~3nm**.
- Diffuse streaks along <111> from sharp interfaces (APBs).
- Agreement with XRD (Quarez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

**same results in $AgSbTe_2$ and $Ag_{0.8}Sb_{1.2}Te_{2.2}$.**

**TEM diffraction single-crystal ($Ag_{0.8}Sb_{1.2}Te_{2.2}$) in (1,-1,0) reciprocal plane.**

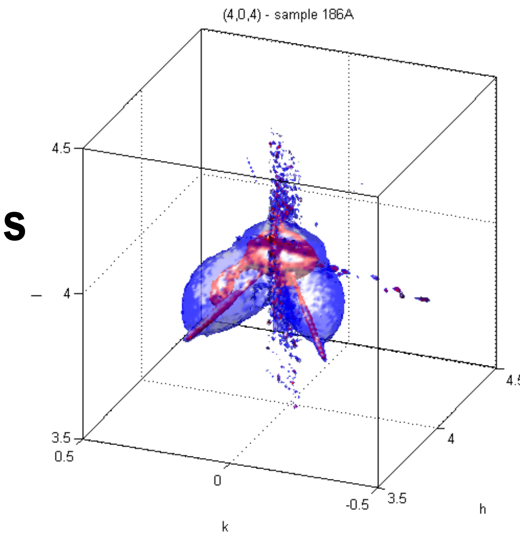


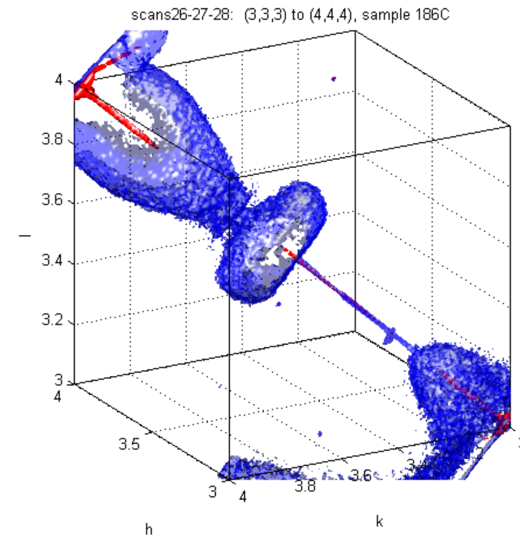

**Neutron scattering on single-crystal ($Ag_{0.8}Sb_{1.2}Te_{2.2}$) in (1,-1,0) reciprocal plane.**



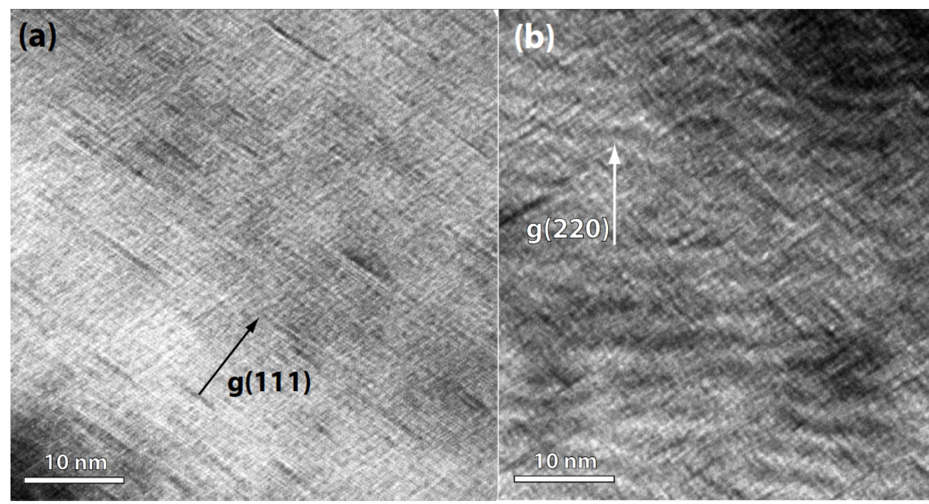
# TEM and synchrotron x-ray scattering

- **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.



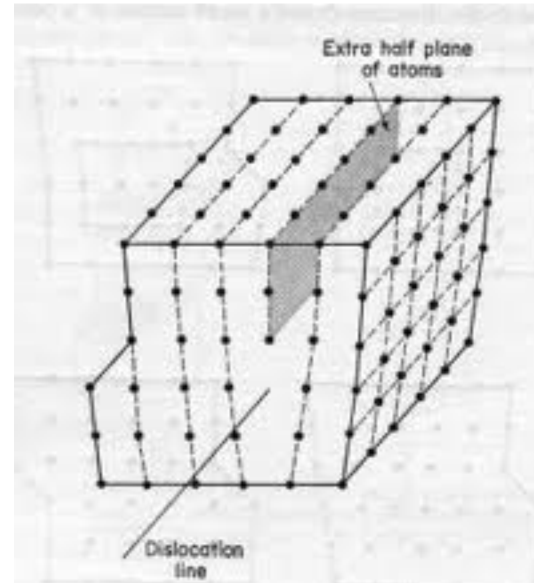

With E. Specht, J. Budai

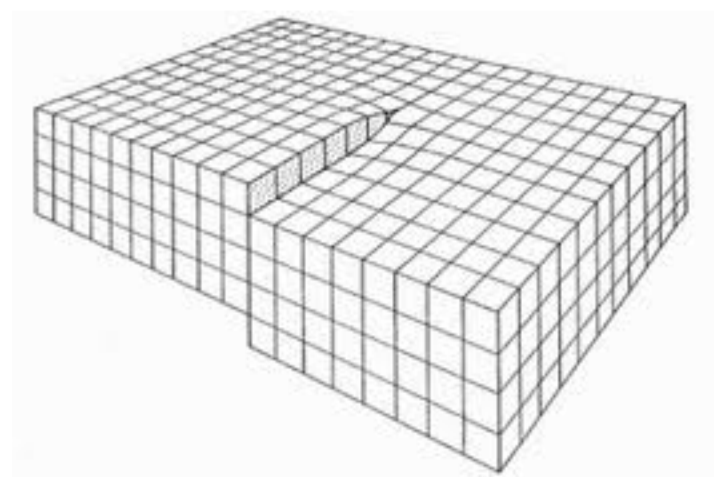



TEM: Carlton and Shao-Horn, MIT

# Dislocations -Krivoglaz defect of the second kind

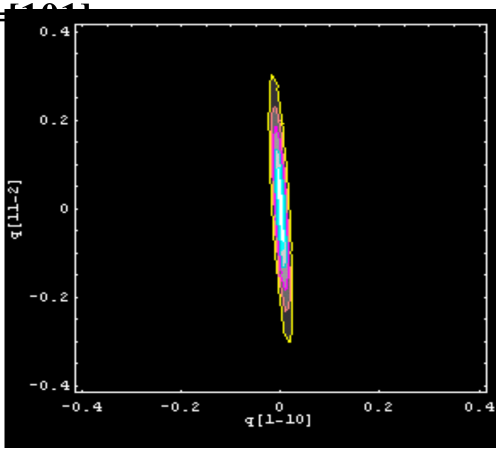
- Unbounded displacement with increased number
- Broaden Bragg peak
- Fundamental to plasticity



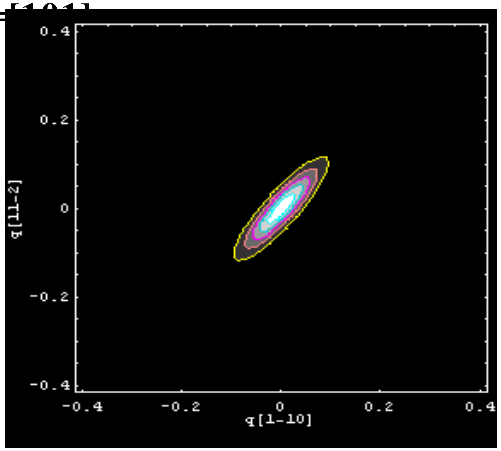



# Influence of number and orientation of dislocations can be quantified

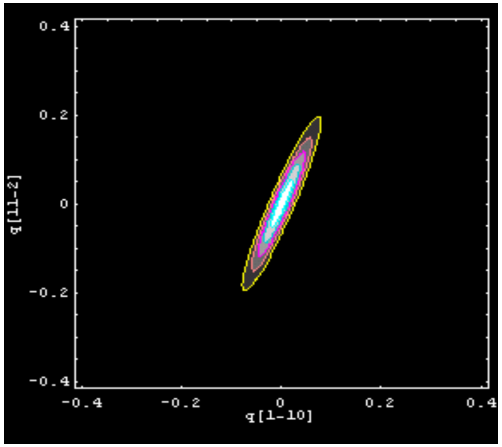
=[1-2-1], n=[-1-11], b=[101]



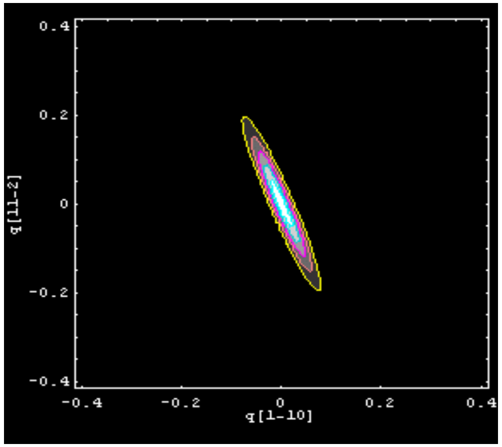

=[-1-21], n=[-111], b=[101]




=[-11-2], n=[1-1-1], b=[110]



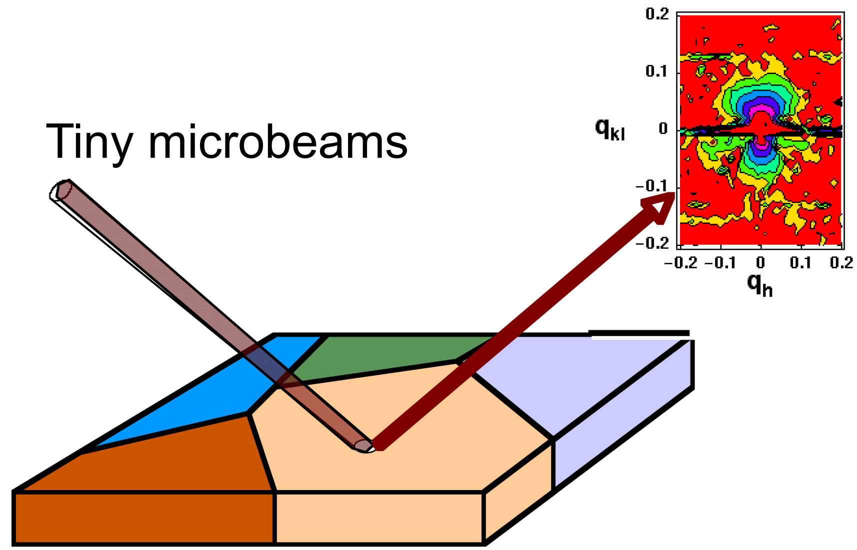

=[1-1-2], n=[1-11], b=[110]



# Intense microbeams/area detectors provide new direction in diffuse scattering

- Tiny crysals (20 μm)
  - Natural polycrystals
  - No special sample prep
- Combinatorial
- Dangerous samples

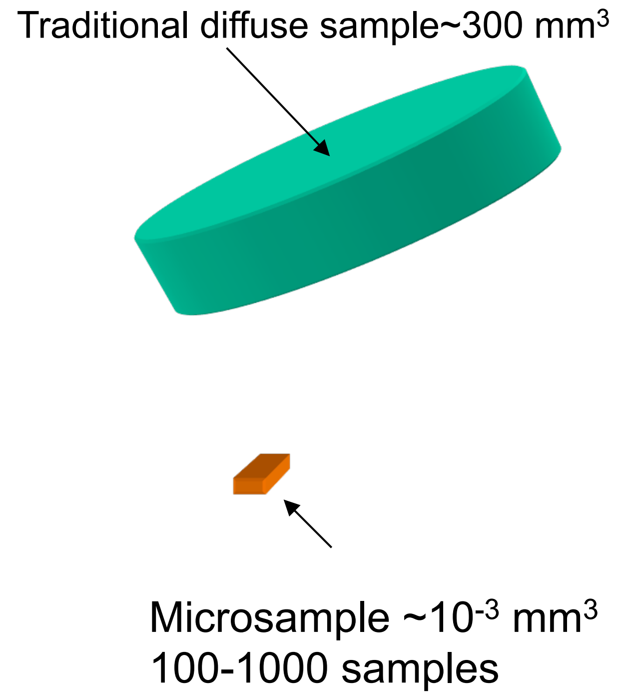
Single-crystal-quality defect characterization




Hazardous ***polycrystal*** samples

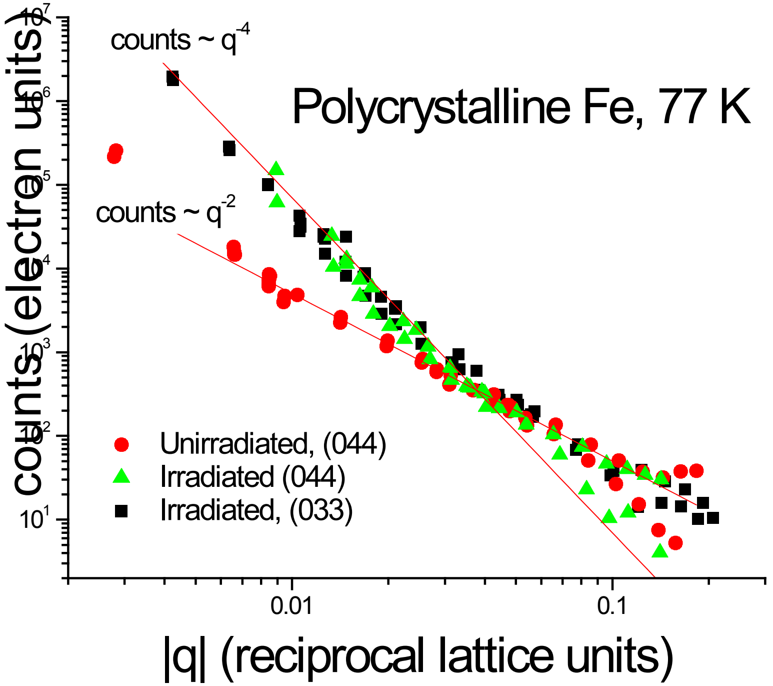
# Small irradiated volumes simplify handling/preparation

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



# *Diffuse* microdiffraction holds promise for irradiated materials

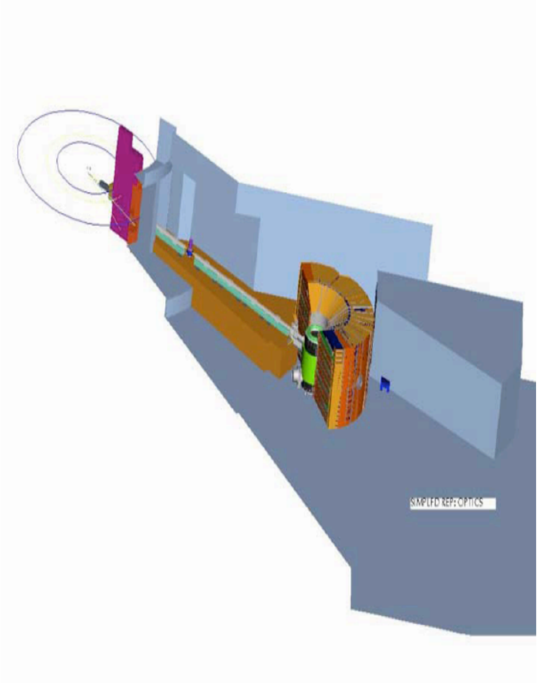
- Powerful single crystal techniques applied to polycrystals
- ~4-6 Orders of magnitude lower activity
  - Safer/lower backgrounds
- Cryocooled samples to study initial defects
- New information about point/line/mesoscale defect interactions

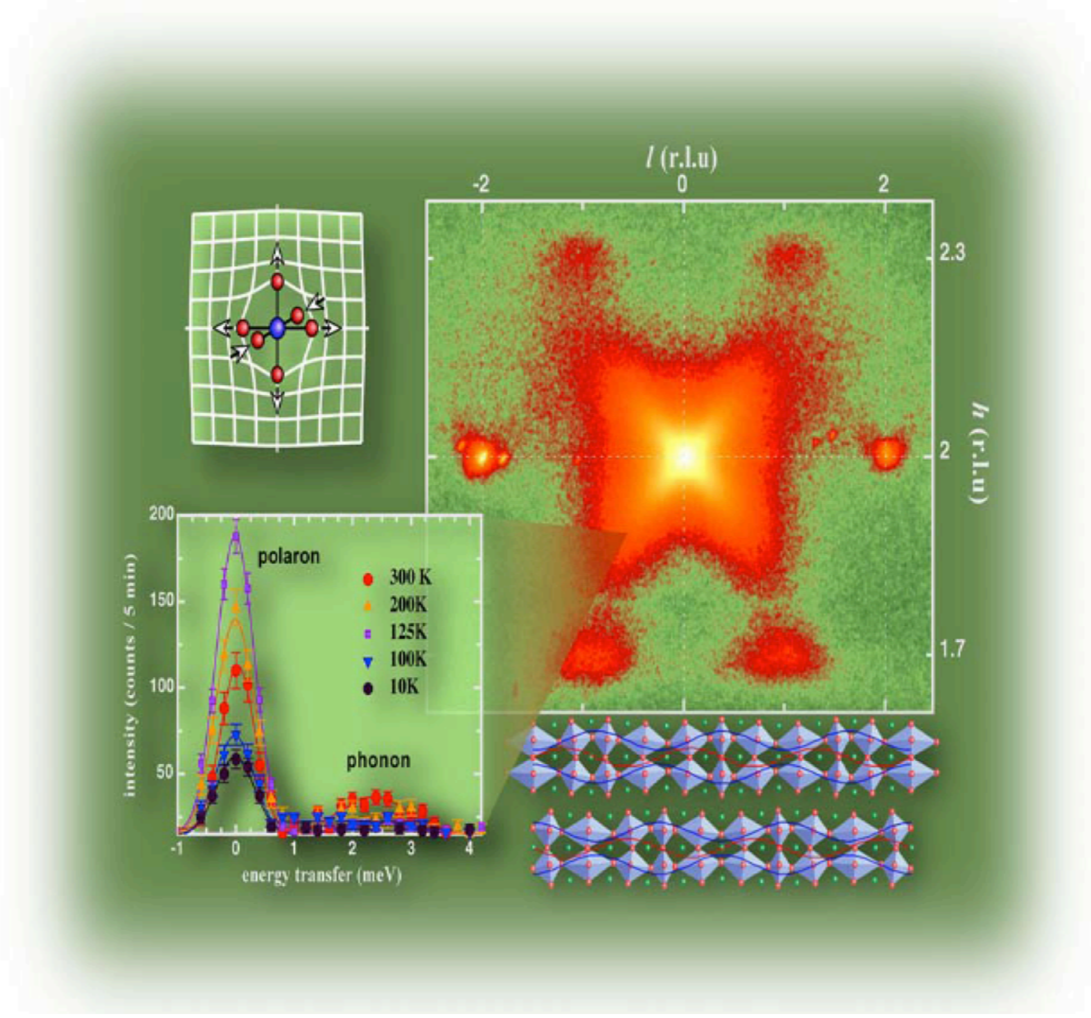



***Successful demonstration experiments!***

# Corelli SNS beamline specialized for diffuse scattering with elastic Discrimination

- Complex disorder and short-range correlations





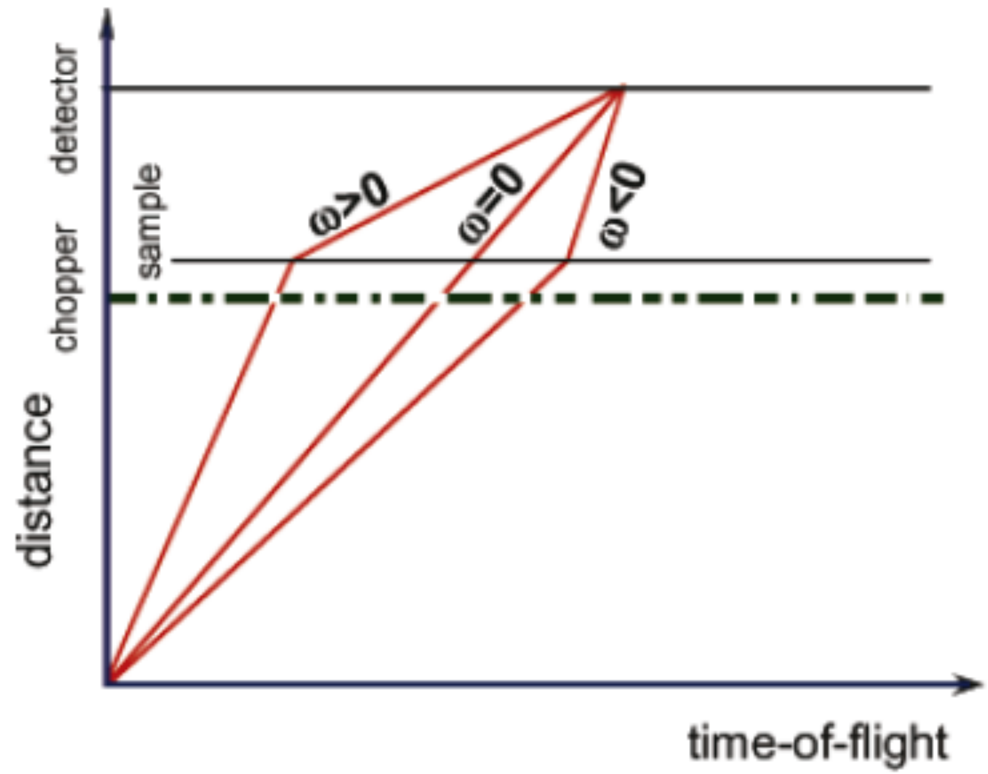
# Correlation Chopper efficiently determines incident/final neutron wavelengths

- **Probability that beam can pass ~50%**

- **Probability independent of wavelength**

# Time to detector depends on speed/distance traveled for incident *and* scattered neutron

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

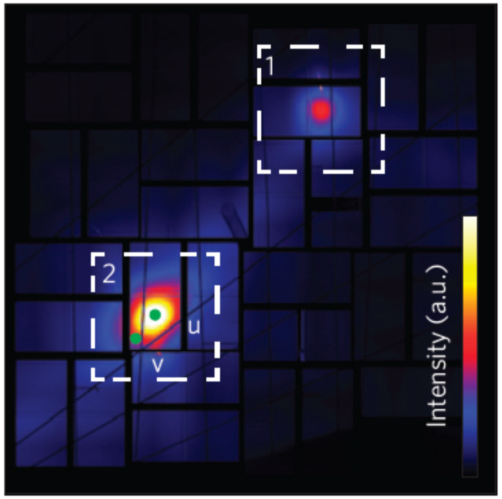


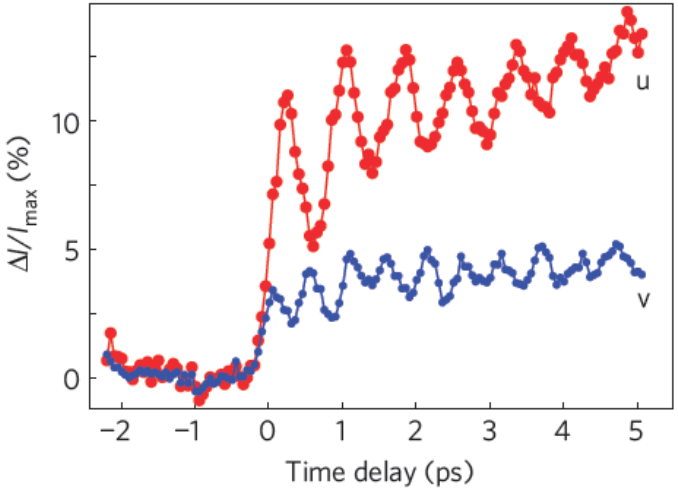

Up to 50 x gain! Distinguishes static/dynamic contributions.

# X-ray diffuse scattering at Femtosecond Resolution

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

Static diffuse



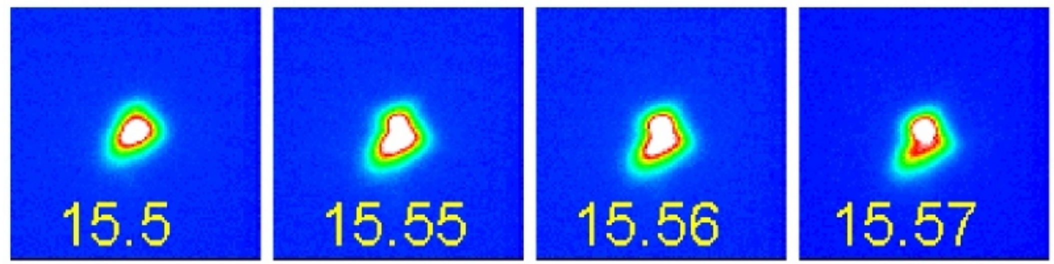




Time-dependent change in scattering for two different Q regions

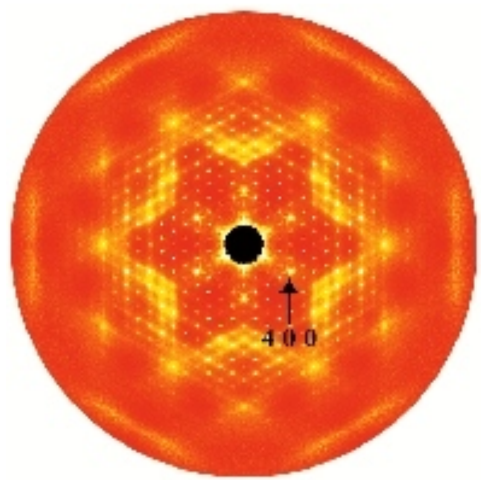
Trigo et al. *Nature Physics* **9** 790-794 (2013)

# New directions in diffuse scattering

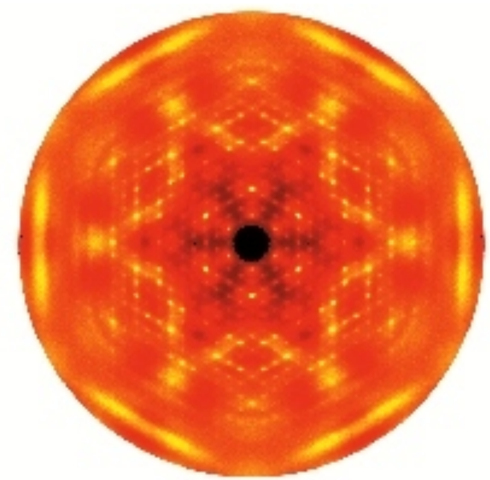
- High-energy x-ray
- Microdiffuse x-ray scattering
  - Combinatorial
  - Easy sample preparation




- Diffuse neutron data from every sample
- Time-evolution and diffuse scattering
- Interpretation more closely tied to theory
  - Modeling of scattering x-ray/neutron intensity



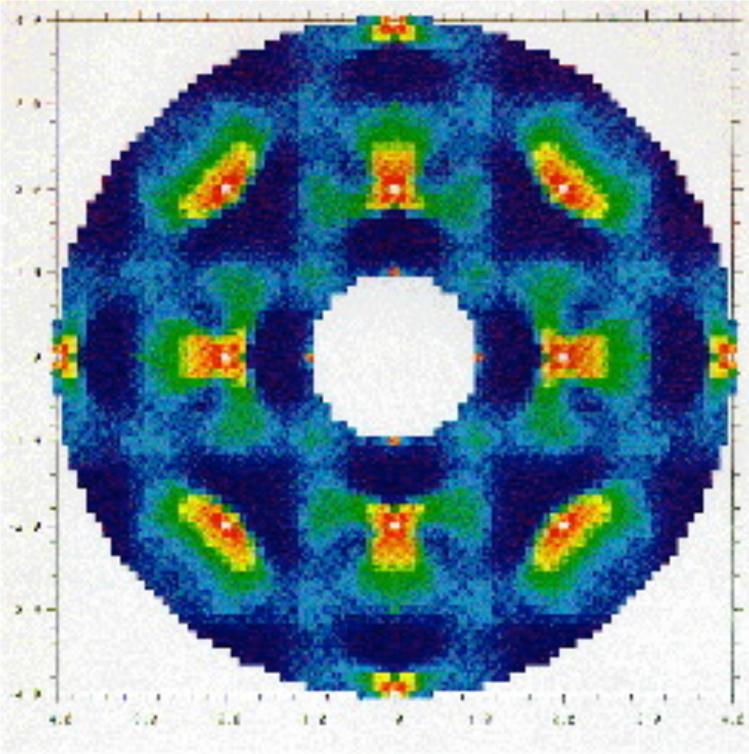

**Experiment**



**Model**

# 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)
- K. Huang *Proc. Roy. Soc.* **190A** 102 (1947)-*long ranged strain fields*
- J. M Cowley (1950) J. Appl. Phys.-*local atomic size*
- Warren, Averbach and Roberts *J. App. Phys* **22** 1493 (1954) -*SRO*
- Krivoglaz *JETP* **34** 139 1958 *chemical and spatial fluctuations*

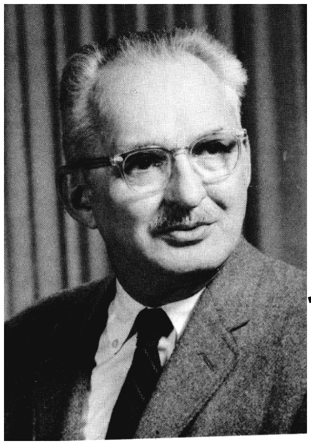


## Other references:

- X-ray Diffraction- B.E. Warren Dover Publications New York 1990.
- 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

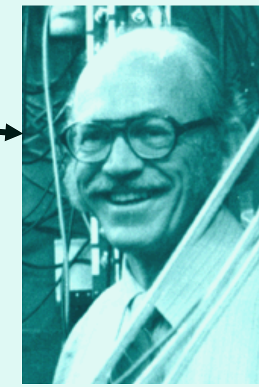


**S. Cowley**, *Arizona St.*

**Bernie Borie,** *ORNL*

**Jerry Cohen,** *Northwestern*

Cullie Sparks
***ORNL***



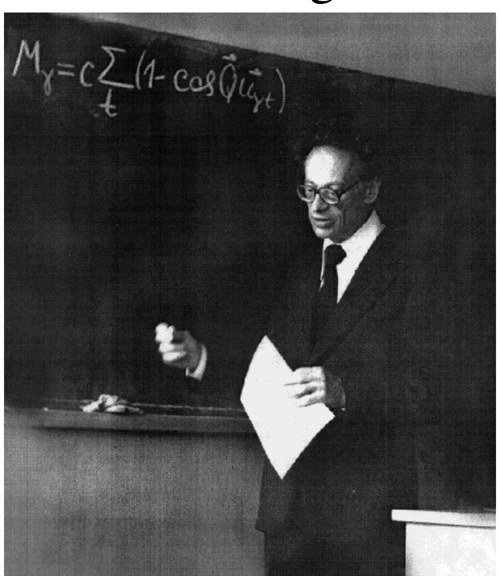
**B. Schoenfeld,** ETH Zurich

**W. Schweika,** KFA Jülich

**Simon Moss,** *U. Of Houston*

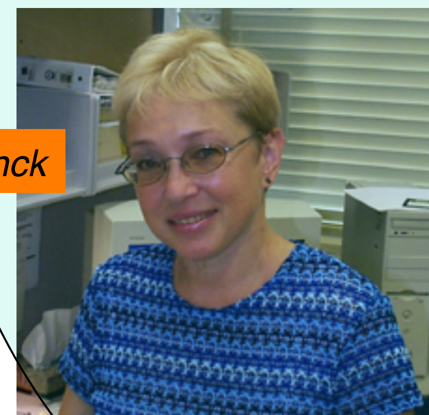
A. Gunier

- Krivoglaz school




**Peisl,** *U. München*

**H. Reichert,** *Max Planck*



Rosa Barabash
***ORNL***

**Gitgarts,** *Minsk*

**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