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Short and Intermediate Range Structure at High Pressure: the QHP-PDF

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One advantage of the pressure variable in studying crystalline, nano-, glassy materials

- pressure varies short, intermediate and long range order (usually) without changing chemistry

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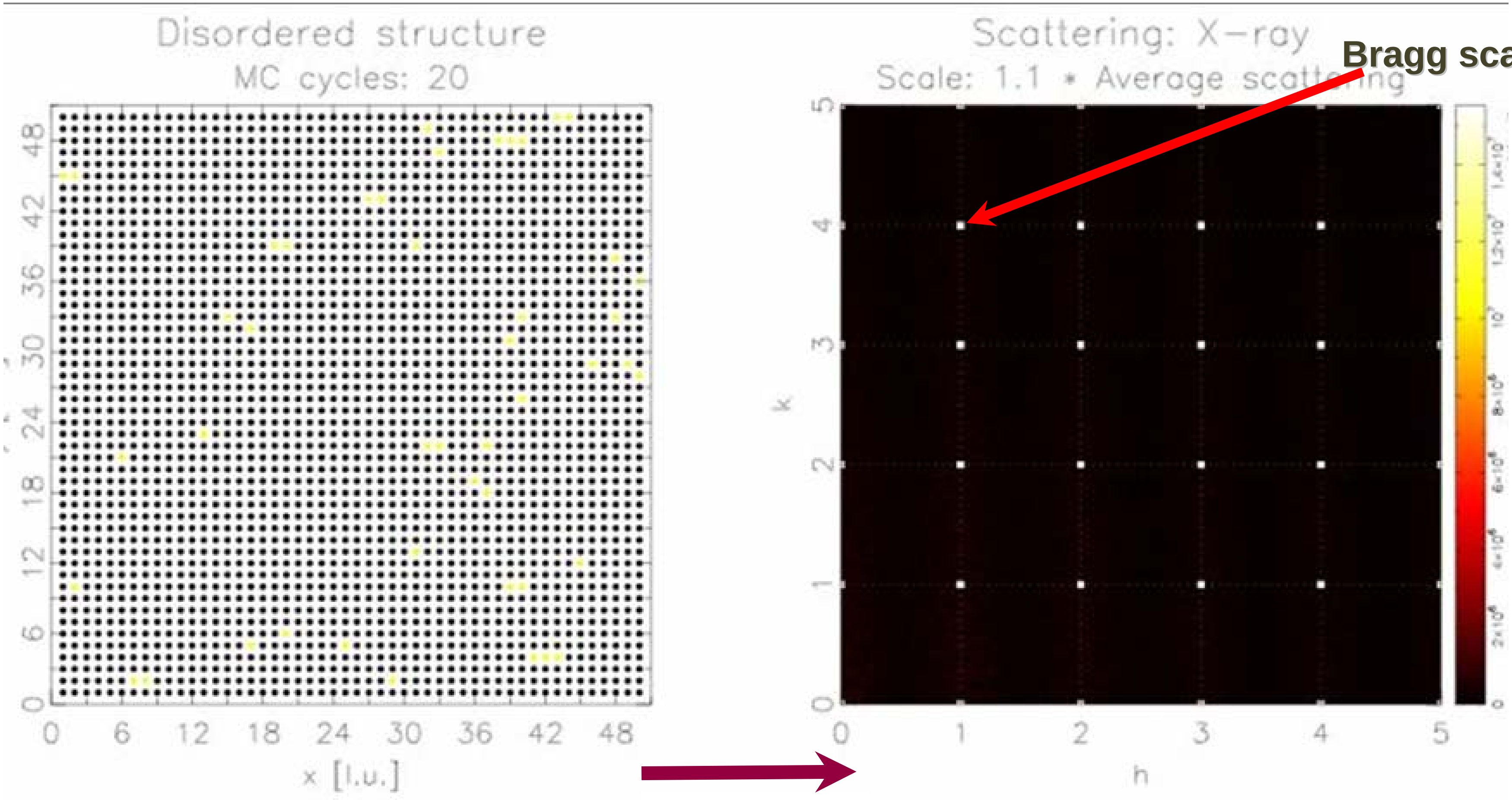
THE UNIVERSITY OF CHICAGO

Office of Science
U.S. DEPARTMENT OF ENERGY

Bragg scattering: our main structure probe

Perfect crystals (or random, uncorrelated disorder)

1% vacancies, No correlation only Bragg scattering



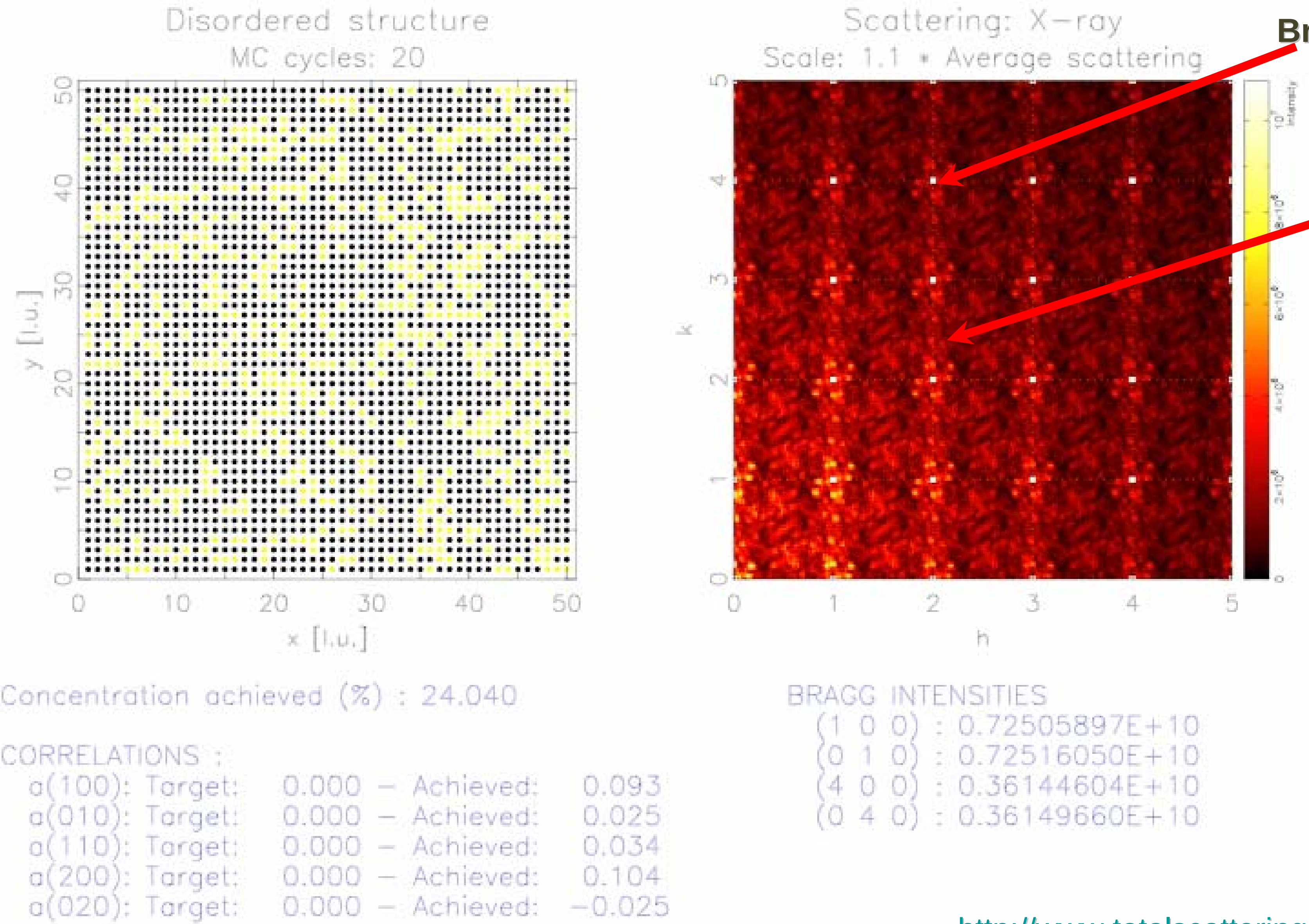
Bragg scattering

$\mathcal{F}_x[f(x)](k)$

http://www.totalscattering.org/teaching/

Bragg scattering: our main structure probe

24% vacancies: correlation unavoidable



```
Concentration achieved (%) : 24.040

CORRELATIONS :
  a(100): Target:   0.000 – Achieved:   0.093
  a(010): Target:   0.000 – Achieved:   0.025
  a(110): Target:   0.000 – Achieved:   0.034
  a(200): Target:   0.000 – Achieved:   0.104
  a(020): Target:   0.000 – Achieved:  -0.025
```

```
BRAGG INTENSITIES
  (1 0 0) : 0.72505897E+10
  (0 1 0) : 0.72516050E+10
  (4 0 0) : 0.36144604E+10
  (0 4 0) : 0.36149660E+10
```

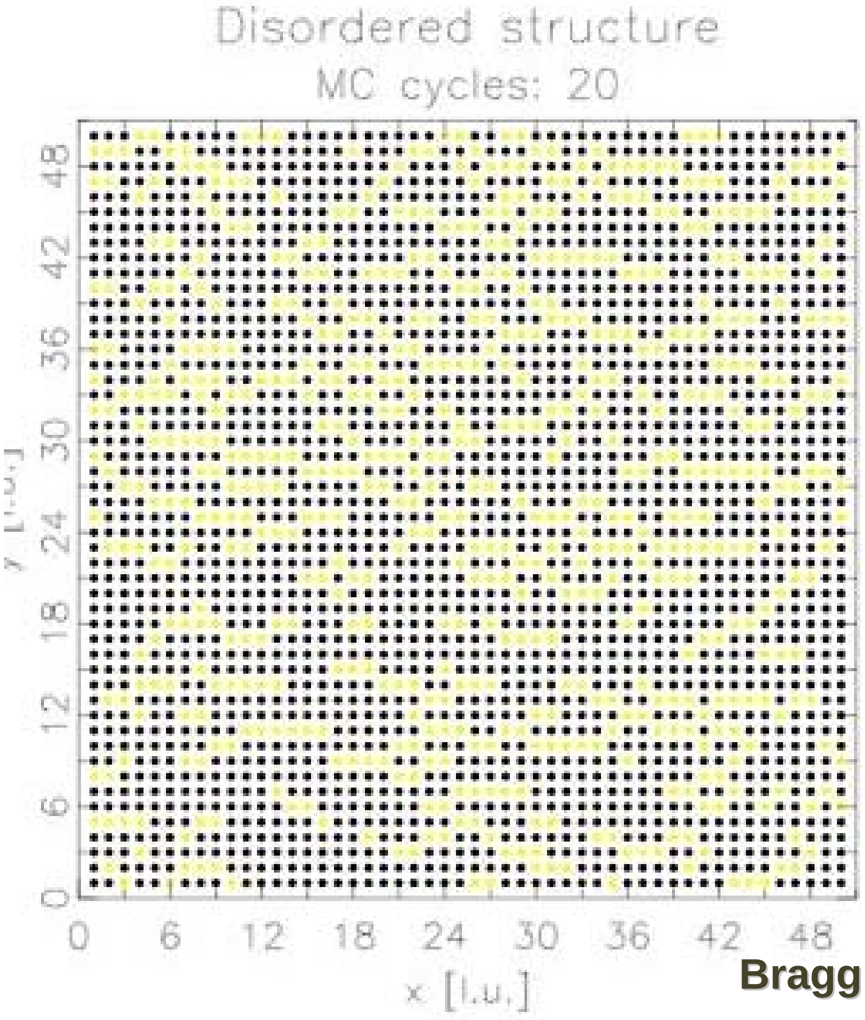
Bragg scattering

Diffuse Scattering

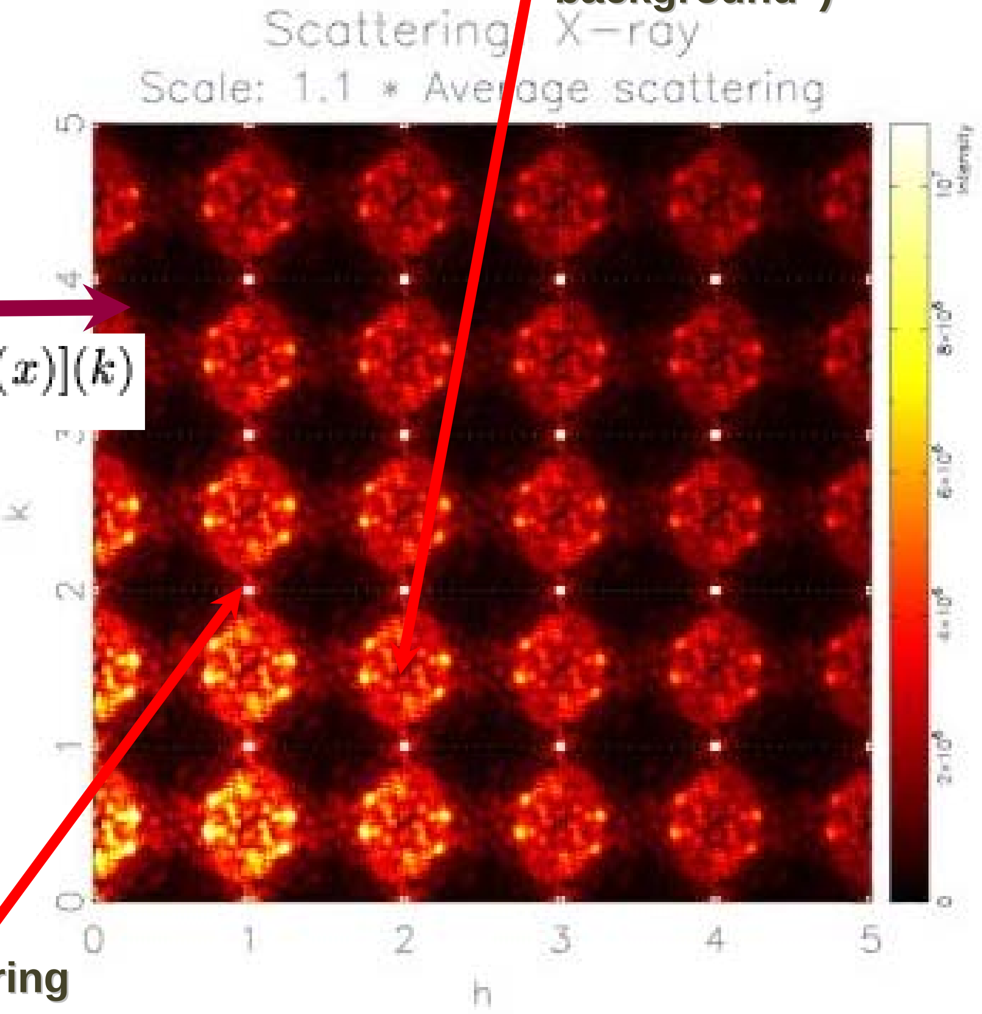
http://www.totalscattering.org/teaching/

Random and correlated disorder in scattering space

24% vacancies, 0.4 correlation in [100] (clustering along *x*)



$\mathcal{F}_x[f(x)](k)$

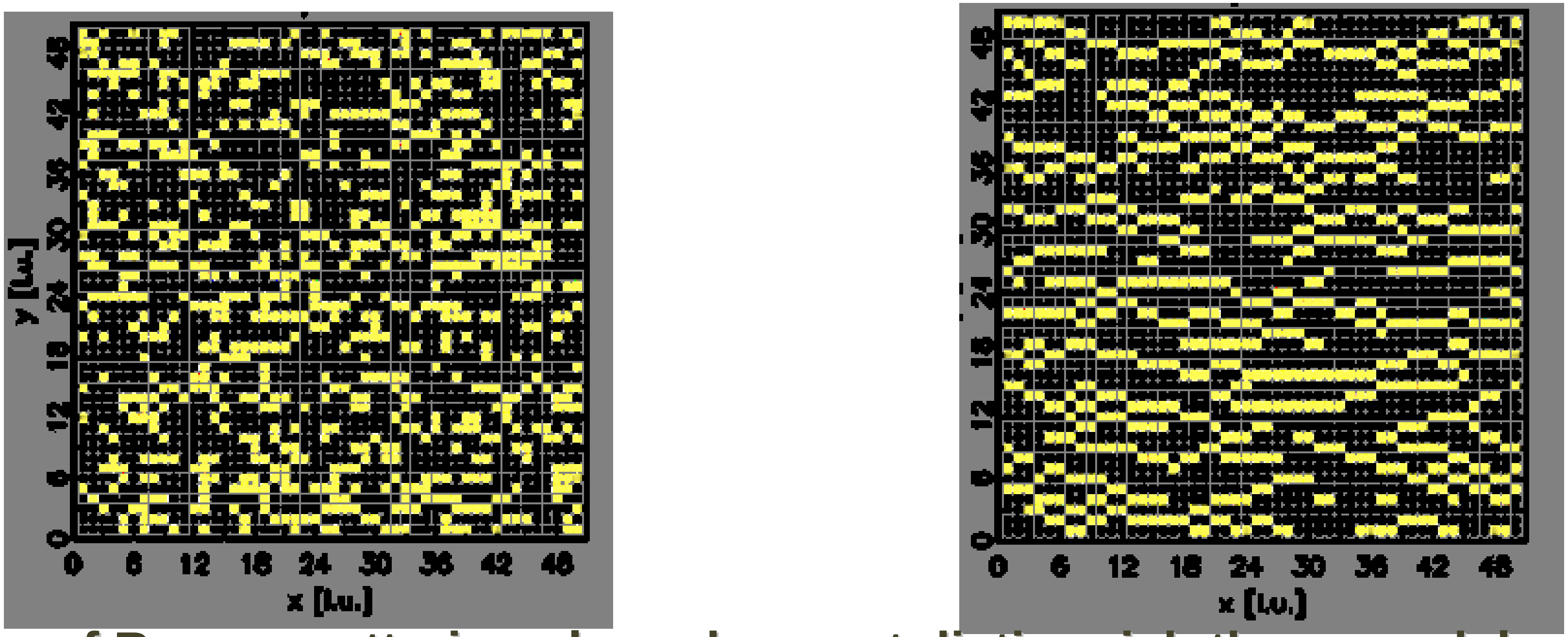


Diffuse between and under Bragg peaks (usually treated as "background")

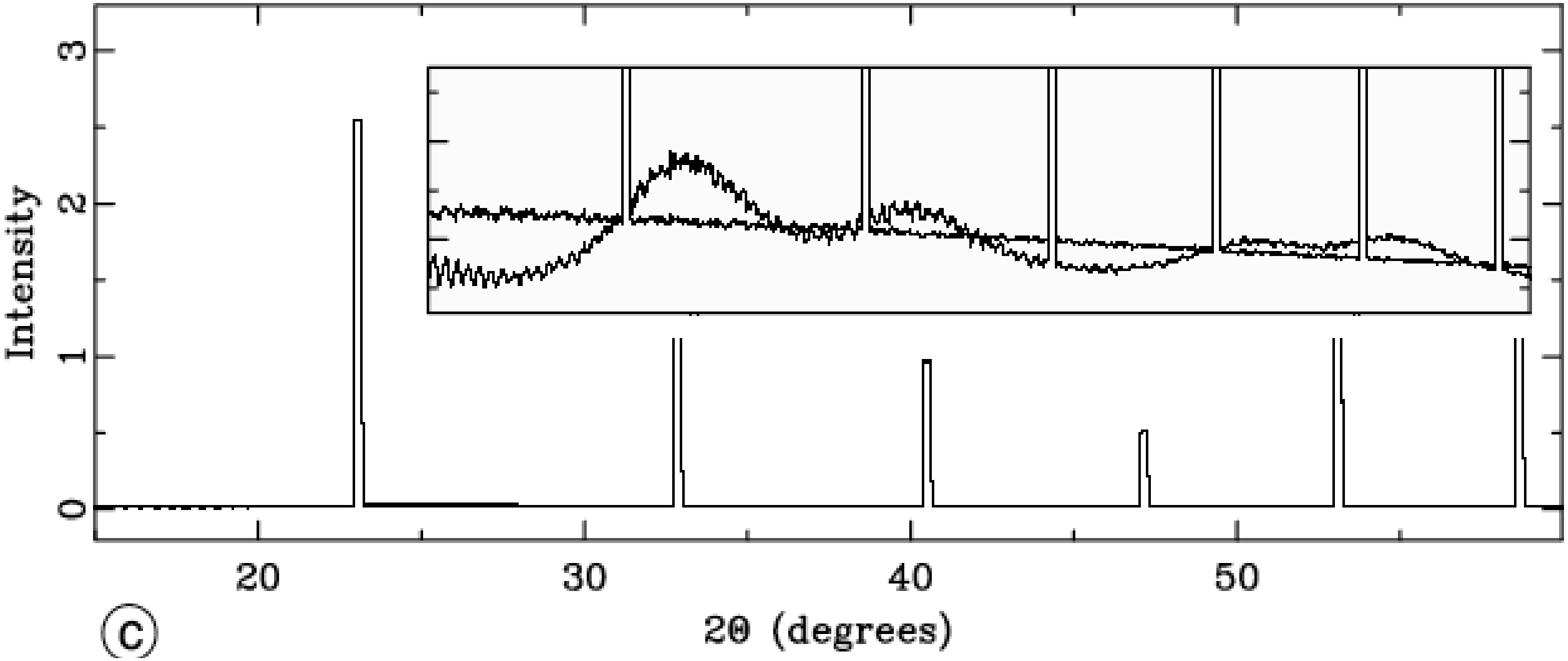
Bragg scattering

http://www.totalscattering.org/teaching/

"Random" and correlated vacancies



observation of Bragg scattering alone does not distinguish these models: lie atop one another. Structured "background" = diffuse scattering from correlation



Cornell, Jun

What is lost in going from a “good” to a “nano” powder?

Loss of information

- Increase in diffuse scattering (deviations from “average” structure) merging of Bragg peaks

Loss of Rietveld-like refinement strategies

- Too many parameters to define the scattering system
- Too few data (peaks in reciprocal space are now broadened and merged)

Some of the information is still there (just not as obvious)

- Fourier transform TOTAL scattering (Diffuse + Bragg) and work in real space
- Develop real space models (based on perfectly periodic models, guess, Monte Carlo....) and Fourier transform to produce to reproduce diffraction pattern

Obtaining the Pair Distribution Function for Powders:

An Experimentally Accessible Quantity from FT of Total Scattering (Bragg + Diffuse)

$Q=4\pi\sin\theta/\lambda$

$$I(Q) \rightarrow\rightarrow S(Q) \xrightarrow{\text{Fourier Transform}} G(r)$$

Measured Intensity

Structure Factor

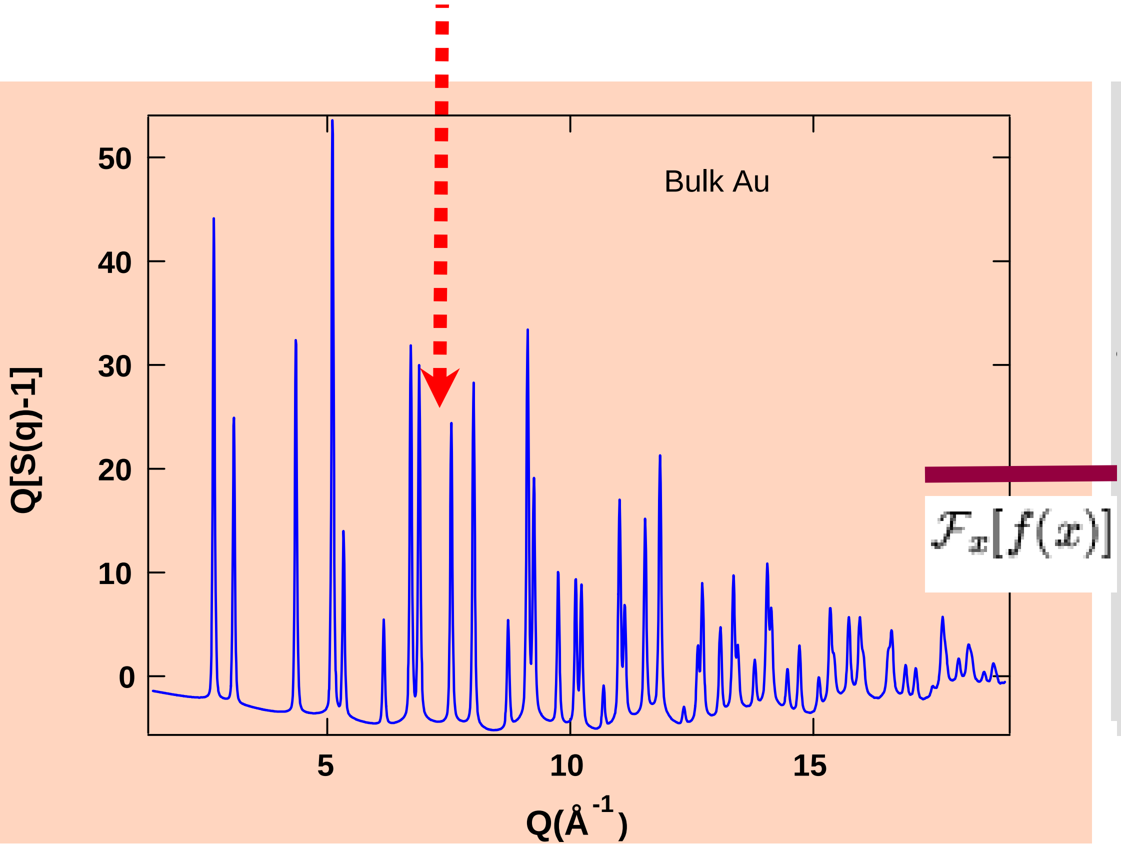
Pair Distribution Function

$$G(r) = (2/\pi) \int Q[S(Q) - 1]\sin(Qr)\,dQ$$

$$G(r) = 4\pi r[\rho(r) - \rho_0]$$

nano-crystalline/bulk materials in real and reciprocal space

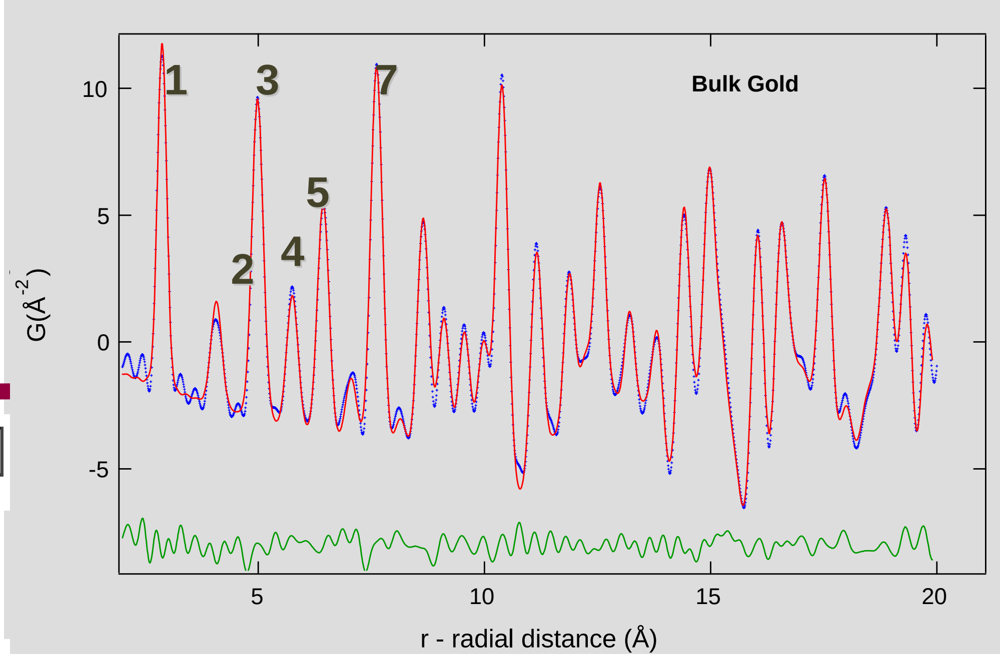
Limit of lab observations

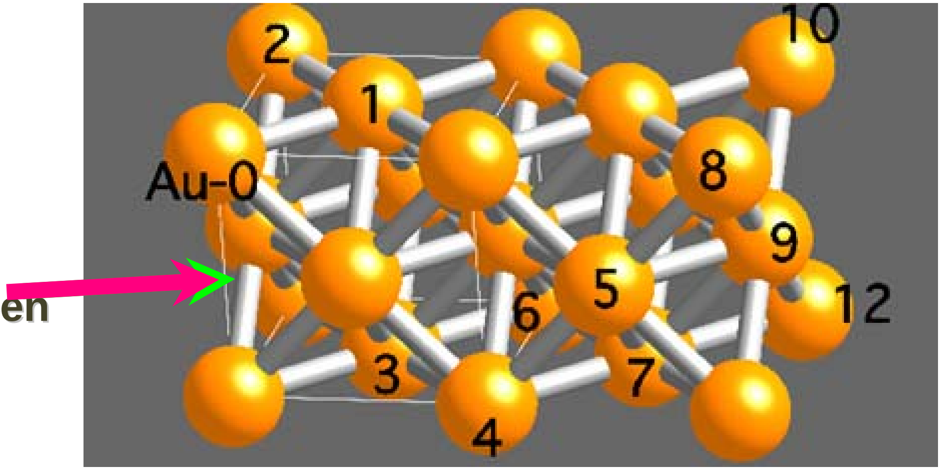


scattering (S(Q) - what we observe)

$\mathcal{F}_x[f(x)]$

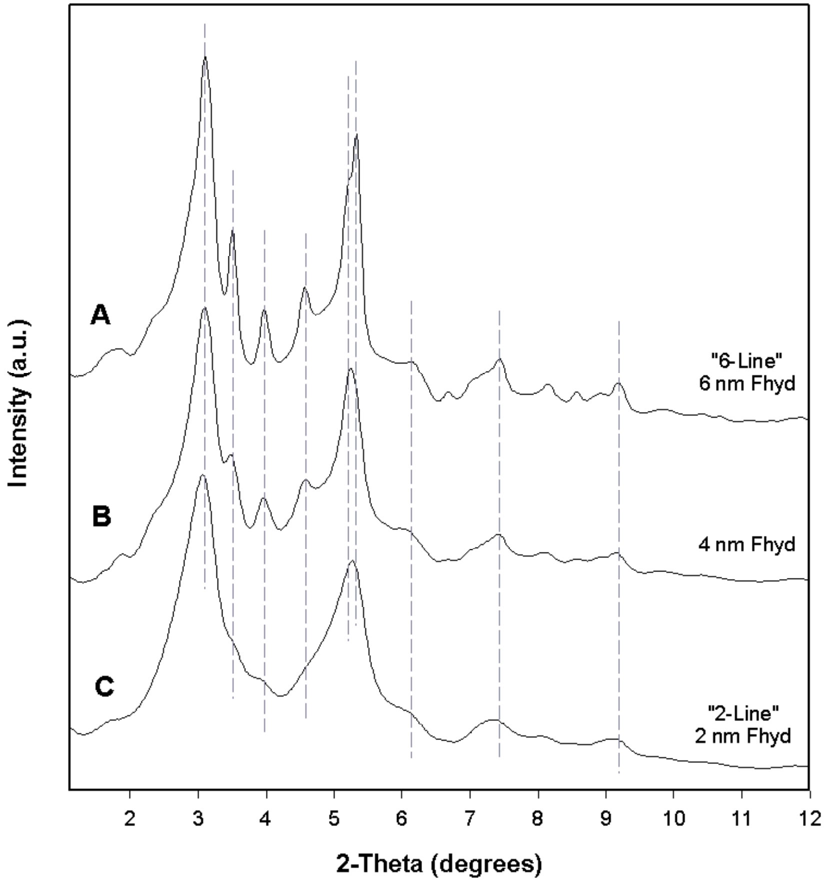
(G(r) + fit)

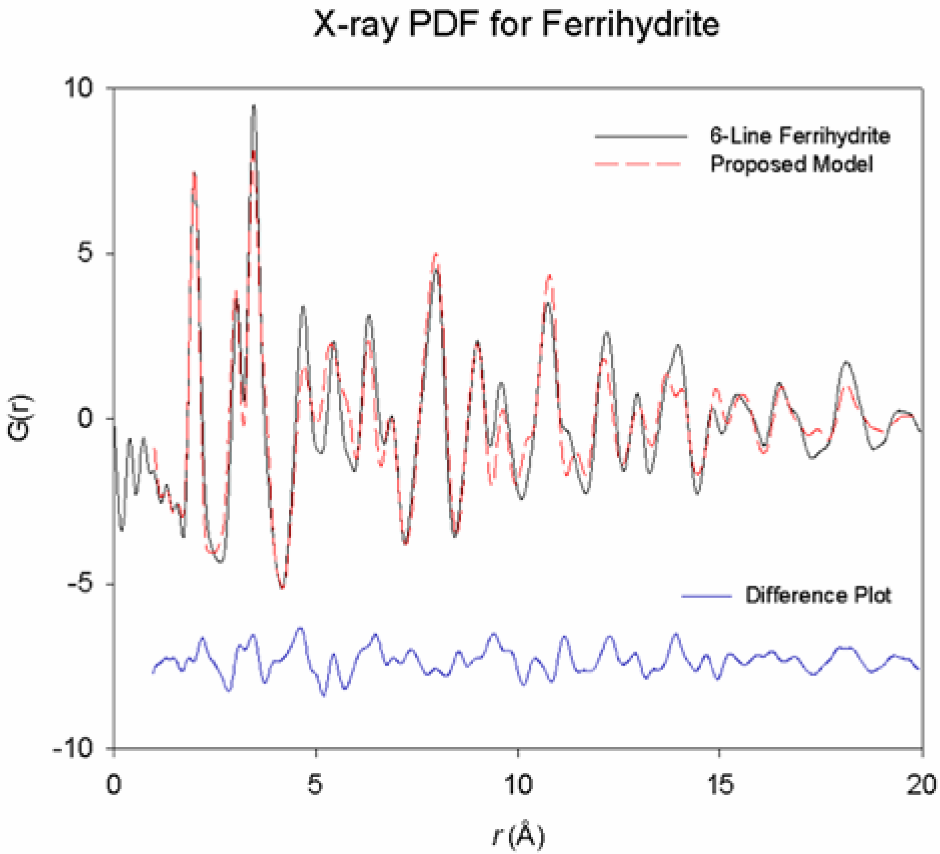




Adjust this model, calculate the red curve to minimize difference with "observed" G(r) - the green curve

Comparing possible models - multiphase + disordered phase proposed for "structure" of ferrihydrite





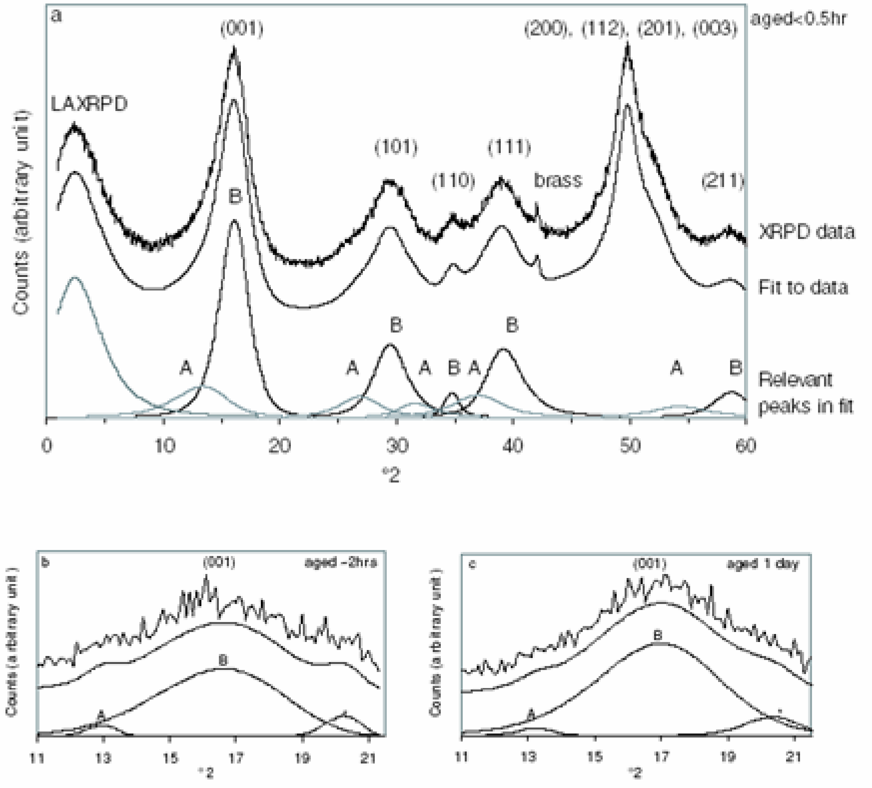
***** 2- and 6-line ferrihydrite (11-IDB, APS λ = 0.13724 Å) are they different? We obtain these patterns from a large number of preparation routes (ferritin, precipitation, aging...) Need to probe possible heterogeneities with nm - μm beams***

We obtain a credible fit with a single phase

Comparing/contrasting models

Debunking models: is nano-crystalline FeS Single phase - or two phase?

- Research dates back to early 1900's
- Berner, 1967
- Rickard, 1975; 1997
- Benning, 2000
- Widler & Seward, 2002
- Wolthers, 2003
- Multi-phase structure models
- Particle size ranging from 2 – 400 nm!
- Estimated using various techniques:
- BET
- TEM/SEM
- XRD (low-energy)



Wolthers, 2003
Geochemistry and environmental mineralogy of the iron-sulphur-arsenic system

Two phases:
MkA = 2.2 x 1.7 nm
a = b = 4.02 Å, c = 6.60 ± 0.1 Å
MkB = 7.4 x 2.9 nm
a = b =3.65 Å, c = 5.48 ± 0.2Å
30 % MkA and 70% MkB

- Opportunity to resolve controversy
- Application of PDF technique
- Fully characterize fundamental properties
- Provide the foundation for more complex studies

Comparing/contrasting models

Structure of Mackinawite - FeS

FeS_4 tetrahedral coordination

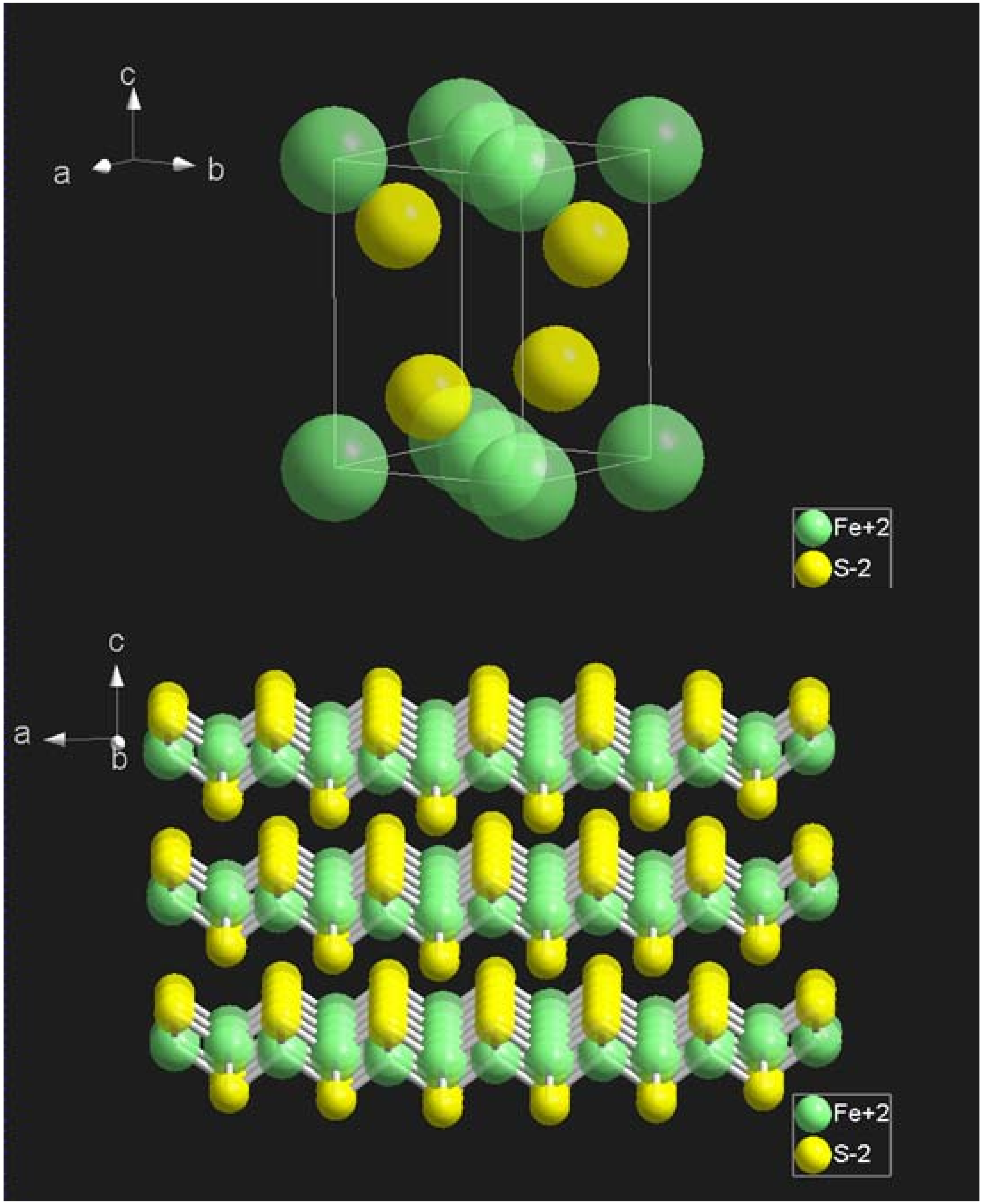
Crystalline FeS:

(P4/nmm)

a = 3.676 Å, c = 5.032 Å

Lennie et al., 1995

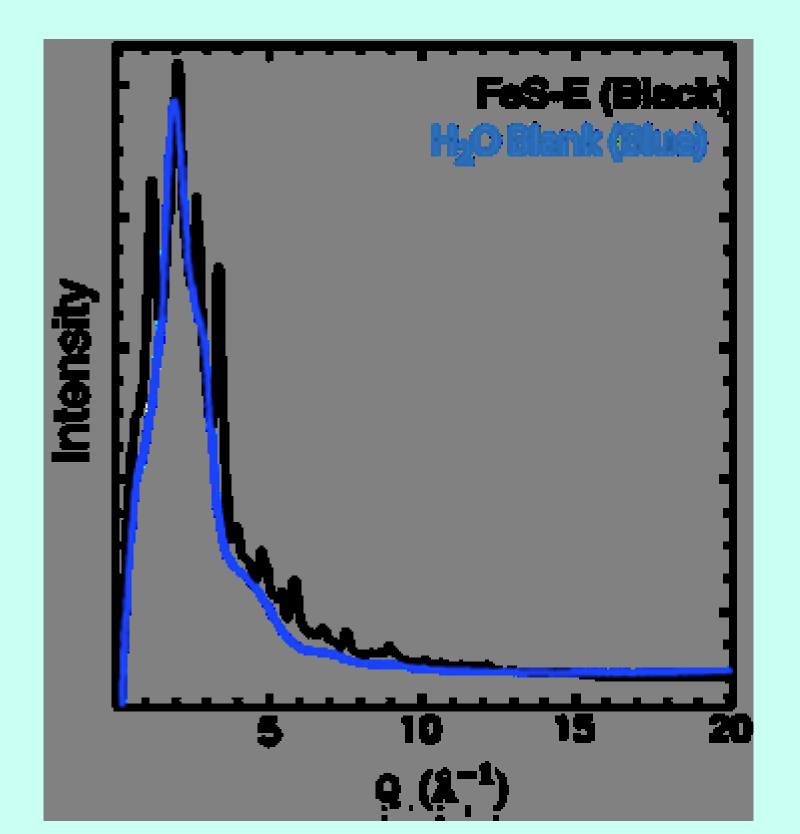
Highly susceptible to oxidation



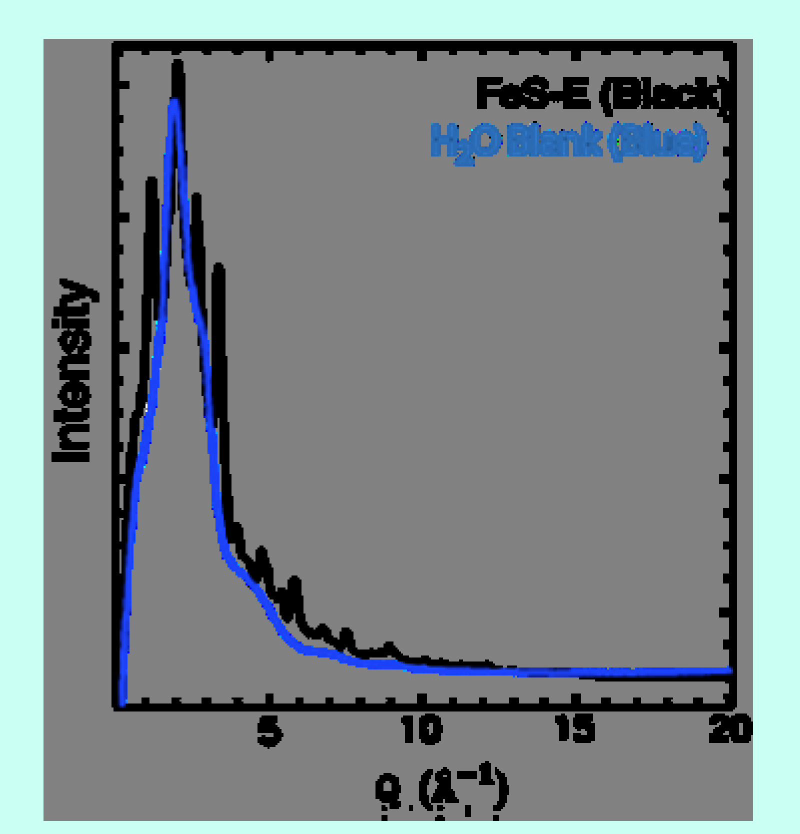
Comparing/contrasting models

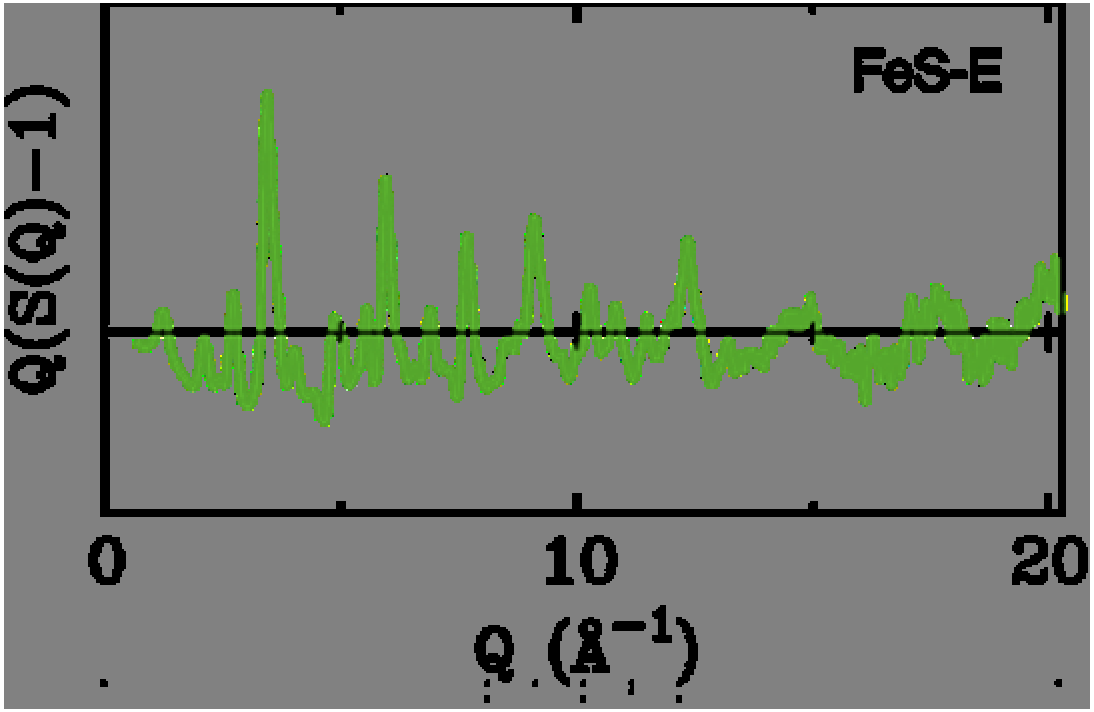
PDF: Normalization of S(Q) - Total Scattering Structure Function

Normalization
Use background spectrum (sample holder, medium, hutch…)
Scaling of background
Contribution of Bragg and diffuse scatter from SAMPLE ONLY



PDF: Normalization of S(Q) - Total Scattering Structure Function





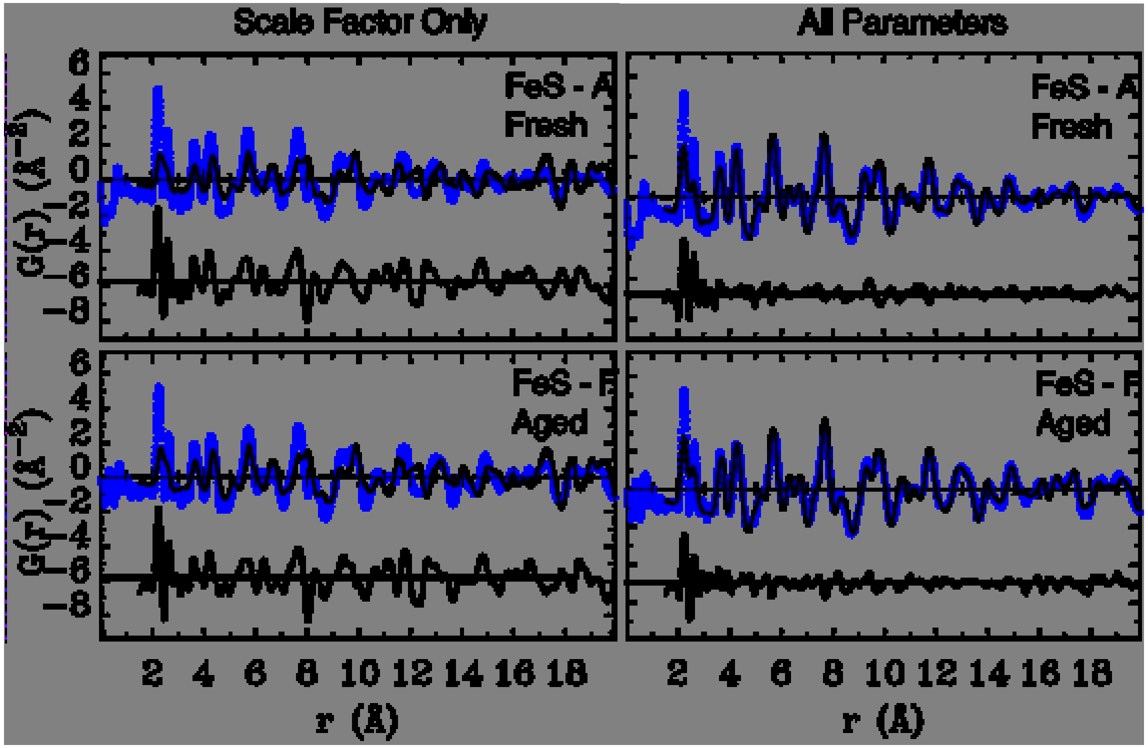
PDF: Test Modeling G(r) – Wolthers, 2003

- Two phase:
- MkA: Mackinawite
  [a = 4Å, c = 6.6Å]
- MkB: Mackinawite
  [a = 3.65Å, c = 5.5Å]

- Phase Mixture:
  - 30% MkA
  - 70% MkB

- Aging Effects:
- Decrease % MkA

*** Two-phase model does not fit ***



FeS – A (Fresh)	MkA	MkB
Scale Factor	**0 %**	**60 %**
***a* – parameter (Å)**	**--**	**3.67**
***c* - parameter (Å)**	**--**	**5.11**
Rw	**77.7% / 35.4%**	
FeS – F (Aged)	MkA	MkB
Scale Factor	**0 %**	**61 %**
***a* – parameter (Å)**	**--**	**3.69**
***c* - parameter (Å)**	**--**	**5.07**
Rw	**72.7% / 32.4%**	
Rw	**72.7%**	

Comparing/contrasting models

PDF: Range of Structural Coherence

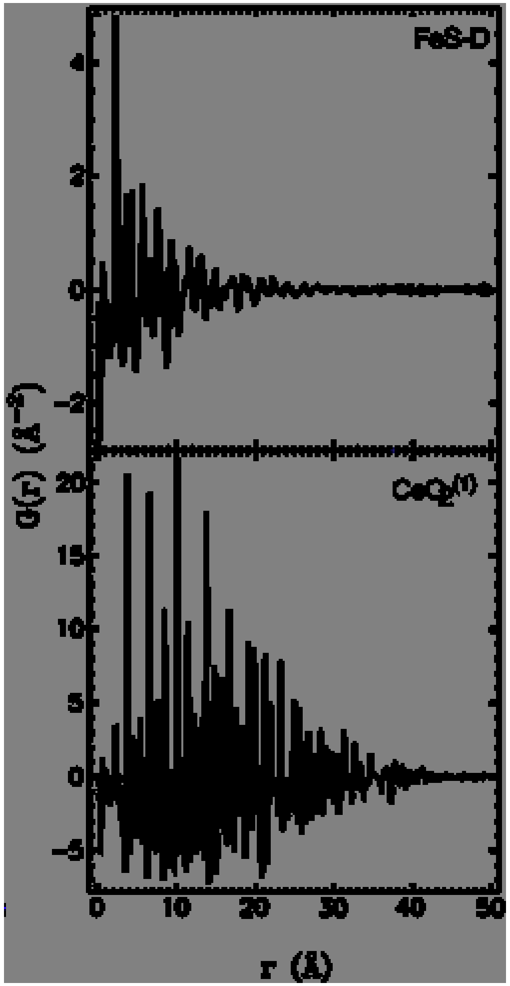
- Fundamental particle size Range of structural coherence

Volume-weighted average maximum dimension of individual particles

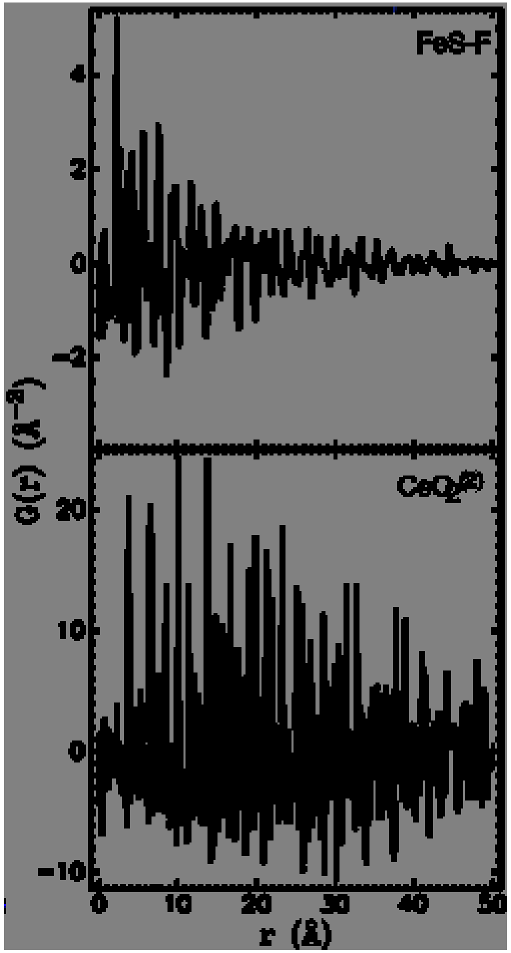
Assumes:
Single phase
Monodisperse
Within resolution envelope of instrument

Fundamental particle sizes:
Fresh FeS ~ 2 nm
Aged FeS ~ 4- 4.5 nm

Fresh PPT (11-IDC)

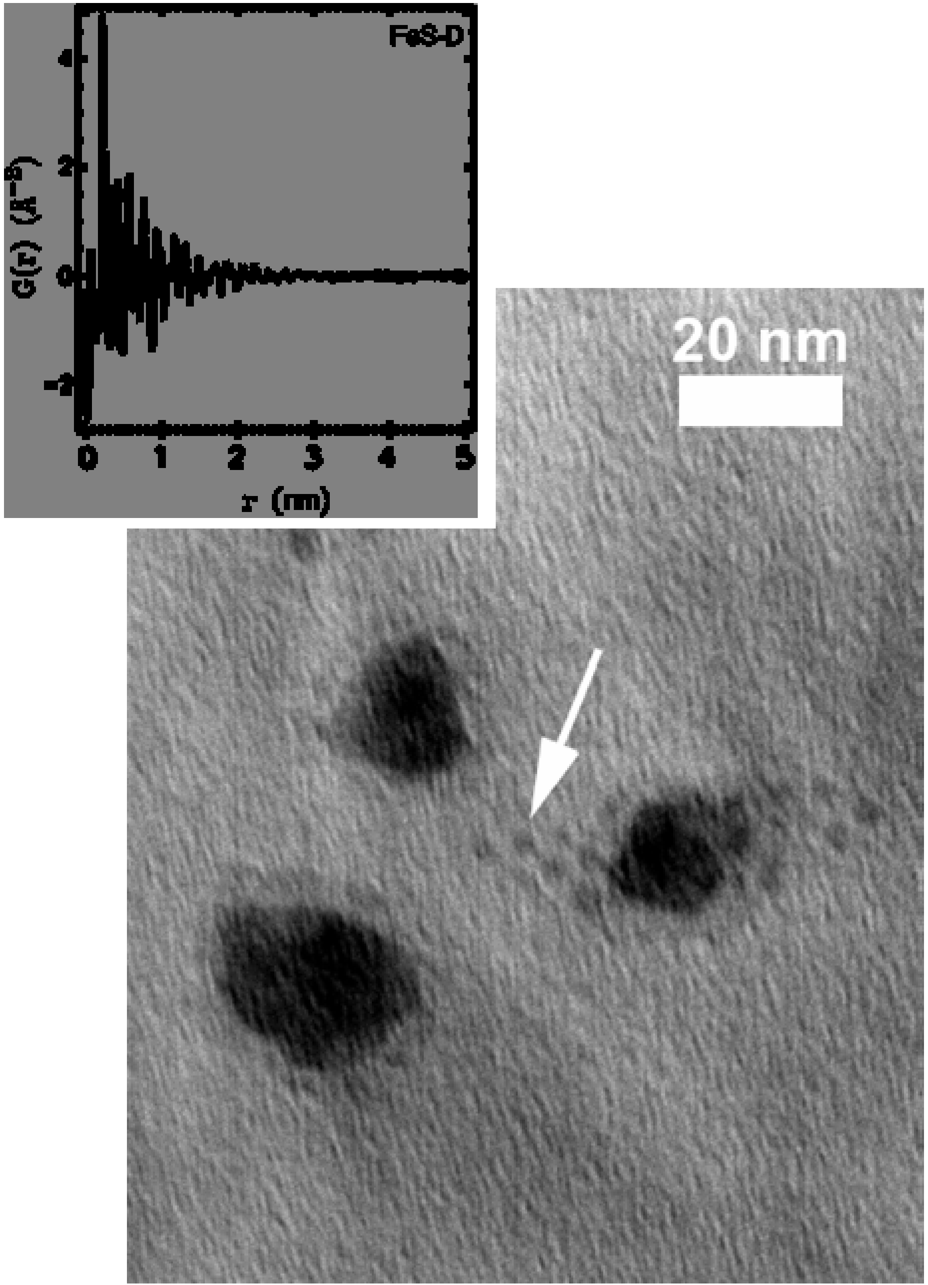


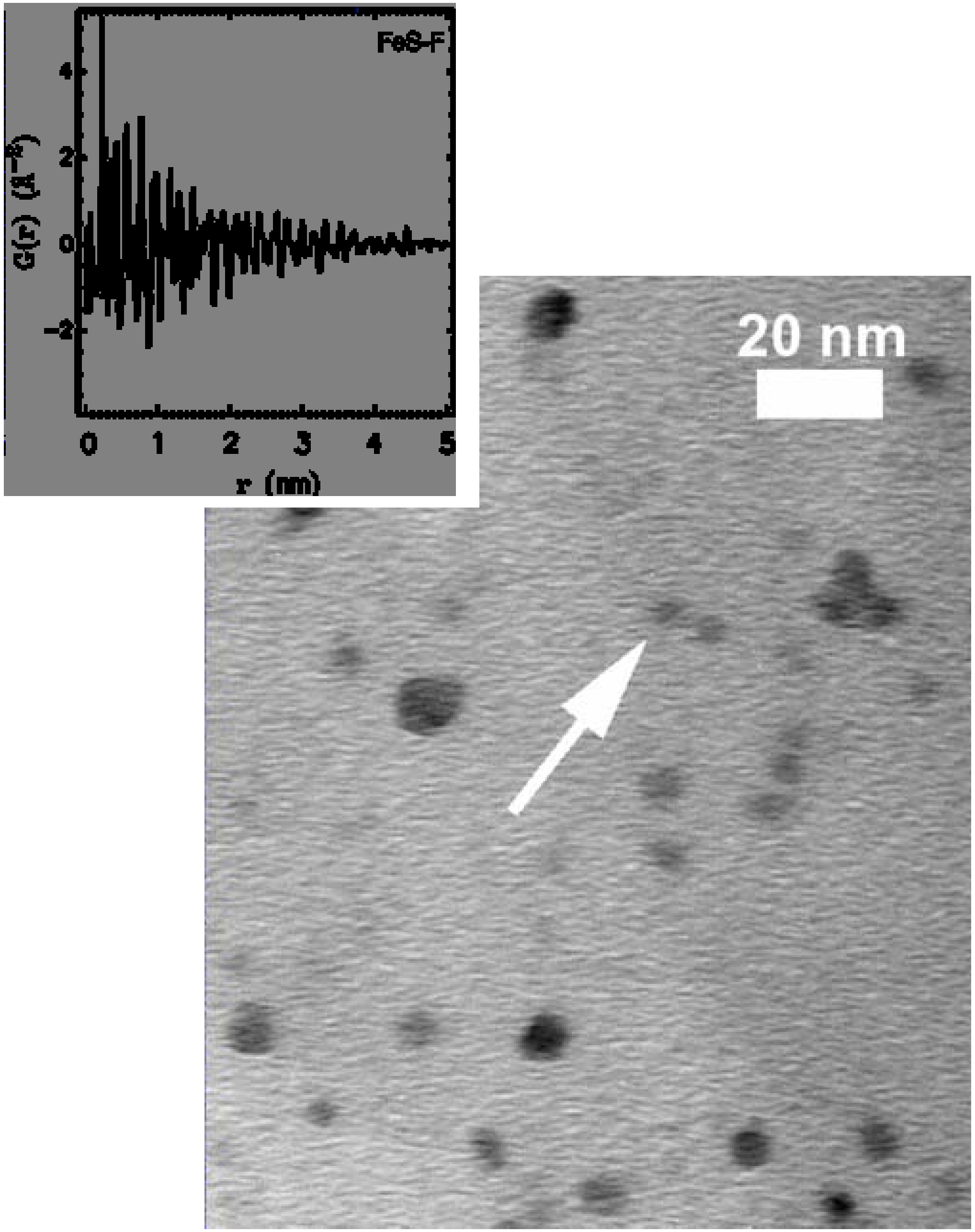
Aged PPT (1wk 70°C)



Comparing/contrasting models

TEM: Fresh vs. Aged FeS

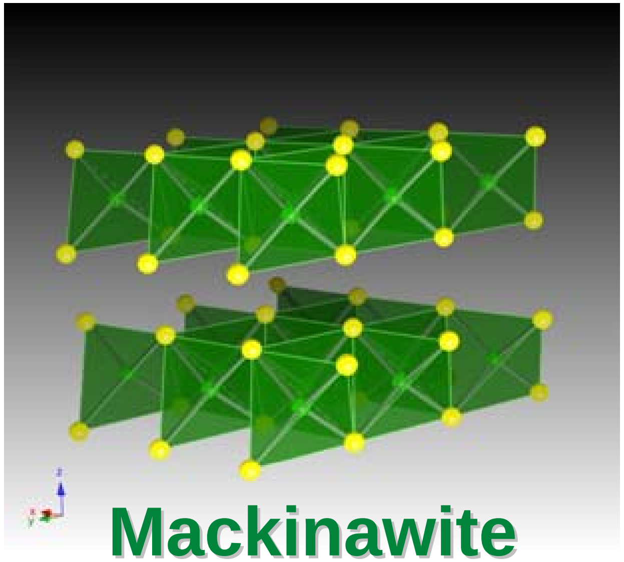


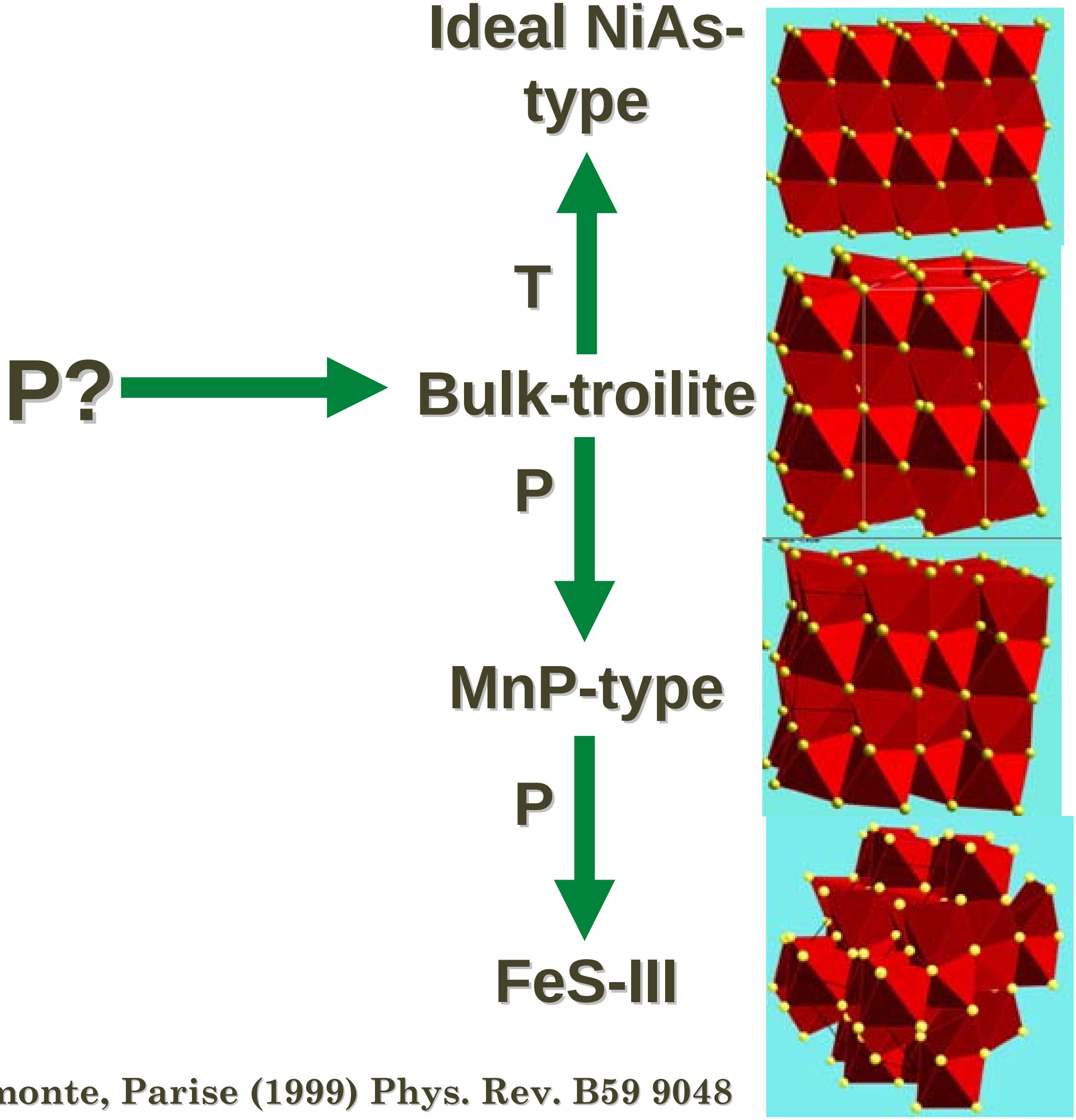


High Pressure studies - *n*-FeS (Mackinawite)

nano-crystalline FeS (mackinawite)

Same transformation pathways at high P as bulk FeS (troilite)?





P? → Bulk-troilite

Bulk-troilite —T→ Ideal NiAs-type

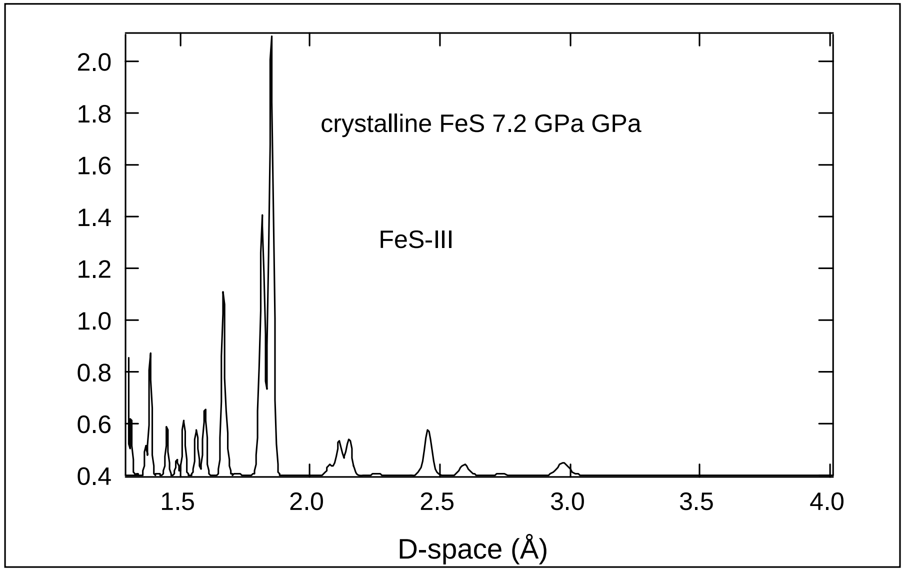
Bulk-troilite —P→ MnP-type —P→ FeS-III

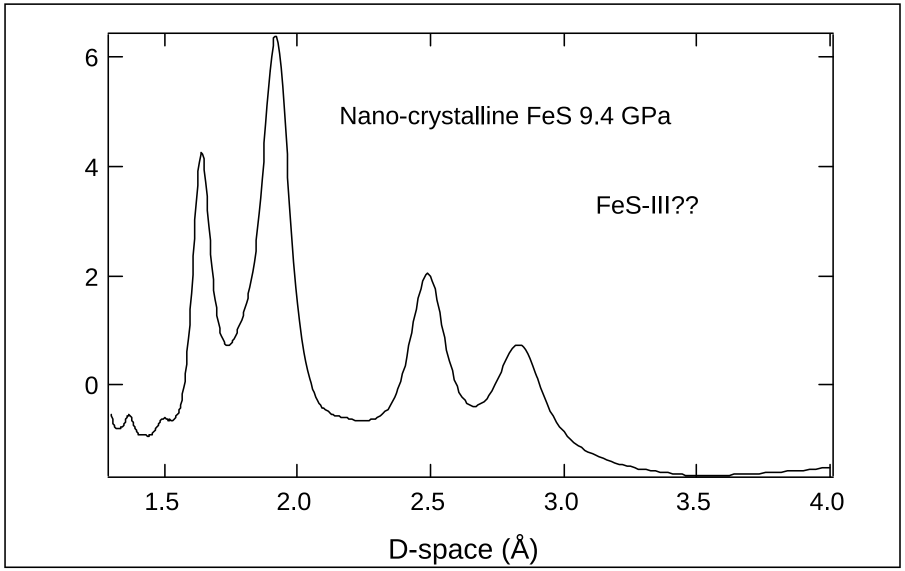
Subtle changes in Fe-position (<0.5Å)

Nelmes, McMahon, Belmonte, Parise (1999) Phys. Rev. B59 9048

The balancing act - QUANTITATIVE HP-PDF in DAC

FeS-III, stable above 7 Gpa - structure refinement from these data was challenging (~24 structural parameters) Nelmes et al PRB (1999)





Is this FeS-III? How do we expect to test this?

The balancing act - QUANTITATIVE HP-PDF in DAC

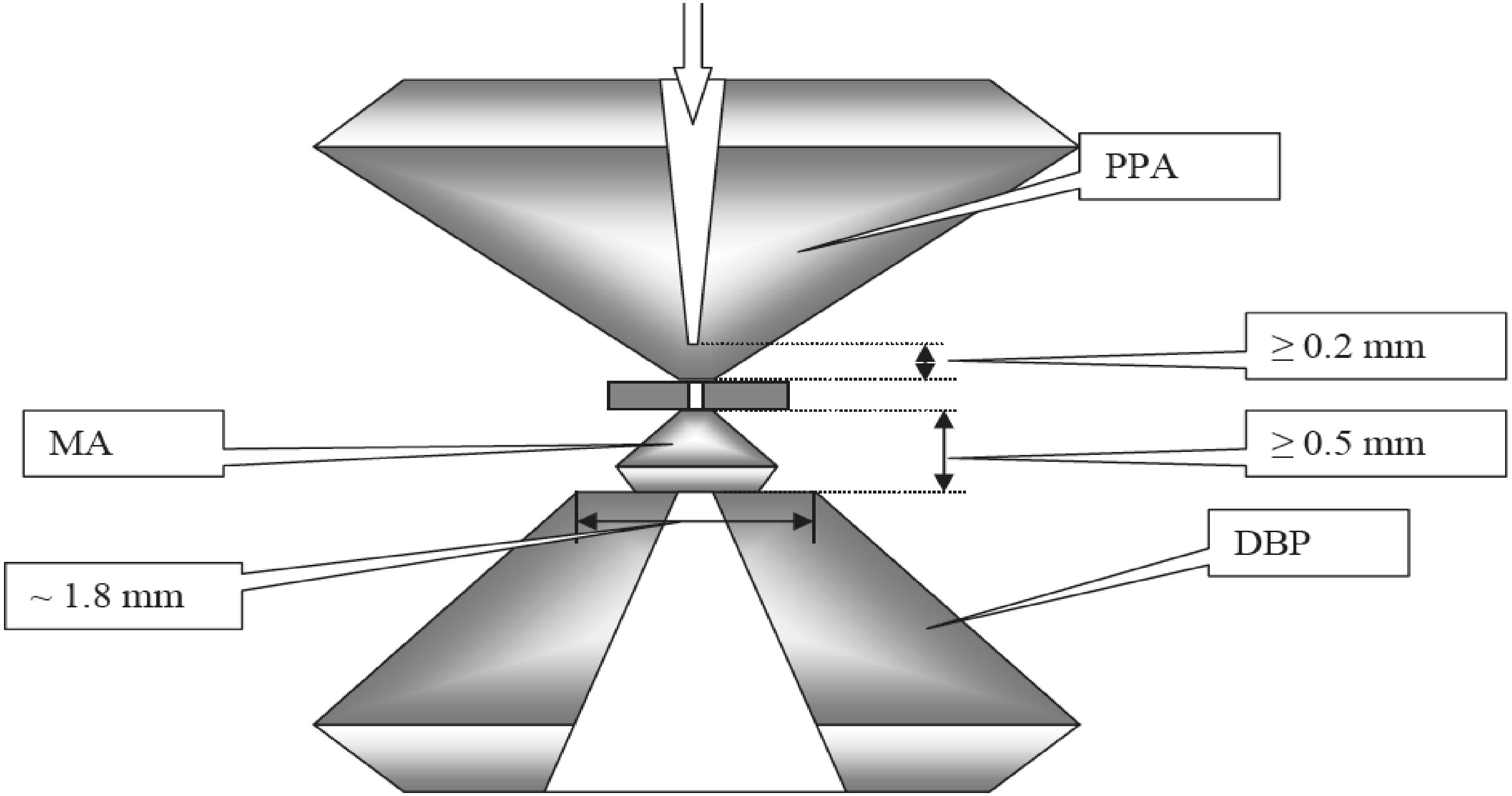
Energy
- max Thompson (E < 30 keV),
- min Chompton - practically independent of energy
- Q-space resolution
  - choose E, IP-sample distance for $Q_{max} > 15$ Å^{-1}

Interference from DAC
- heavy scatterers (Au, Ag) not a problem (see Martin et al J Appl Phys, 2005; Parise et al., J Synch Rad. 2005)

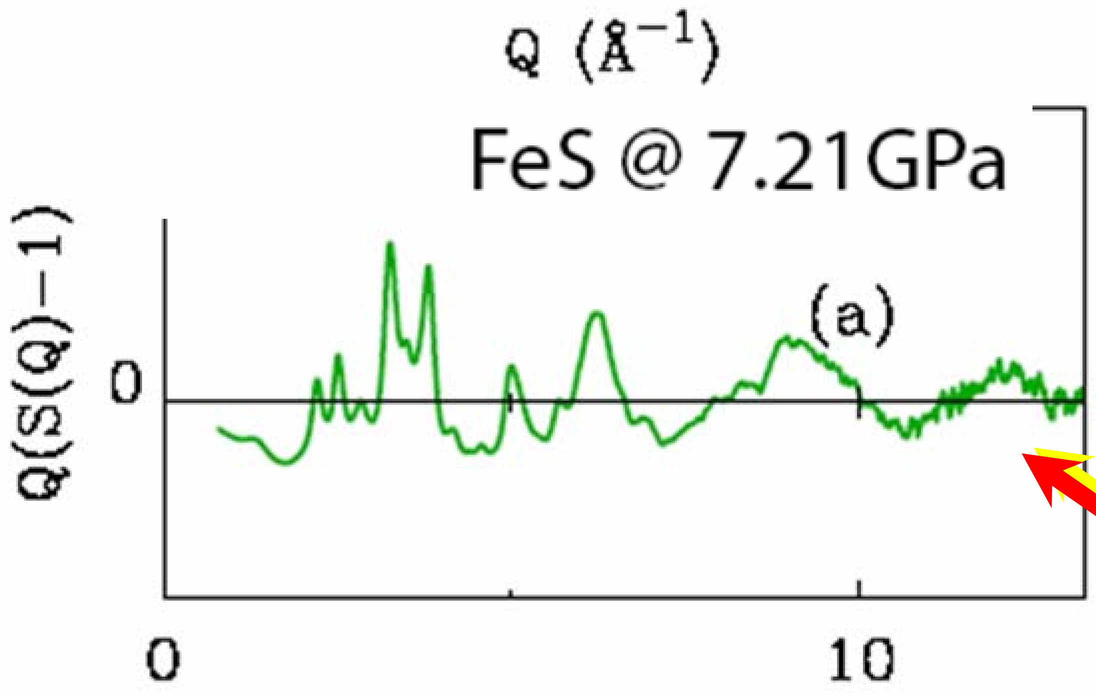
- light scatterers - minimize diamond in beam
  - perforated diamond

- Use large sample volume

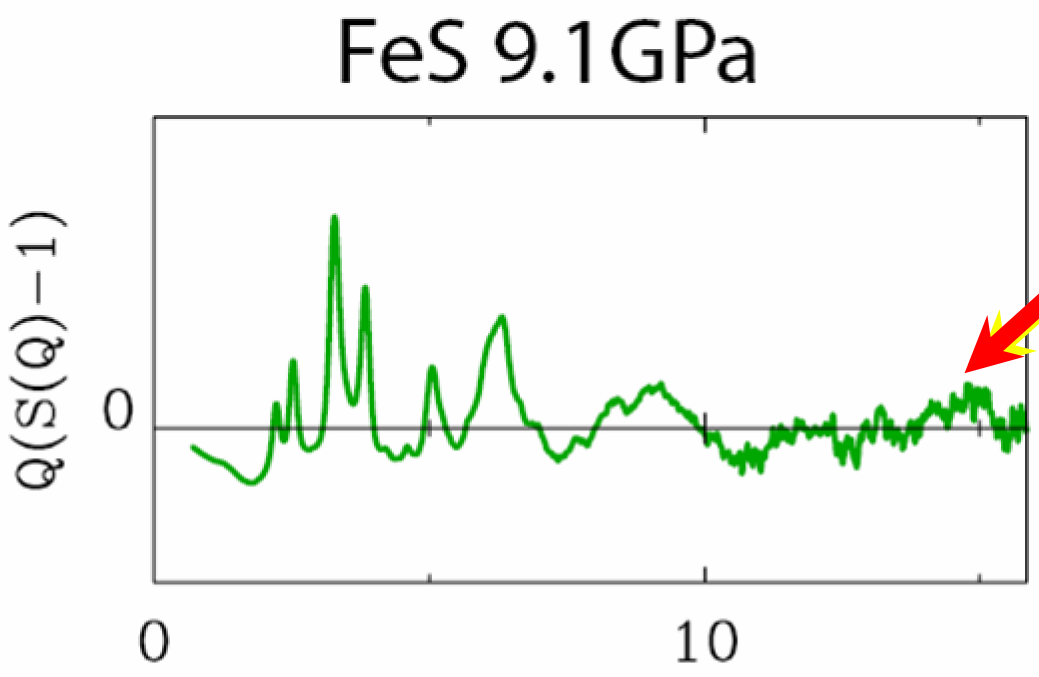
Reduction of radiation interference from diamond (D'Anvils)

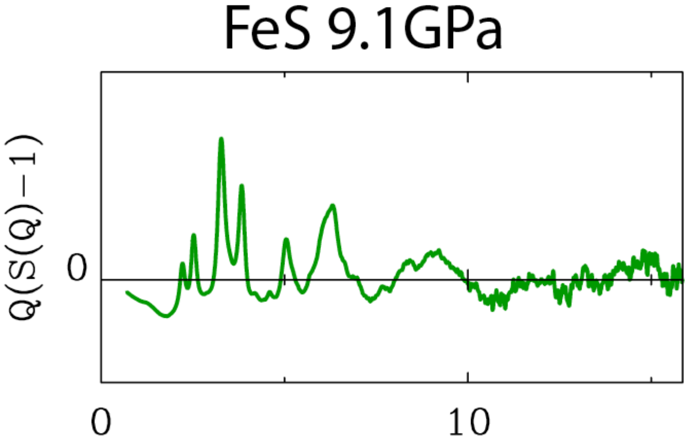


Why 1-ID?
The sample is small, we need high energy, we need to get a beam down an 80μm hole



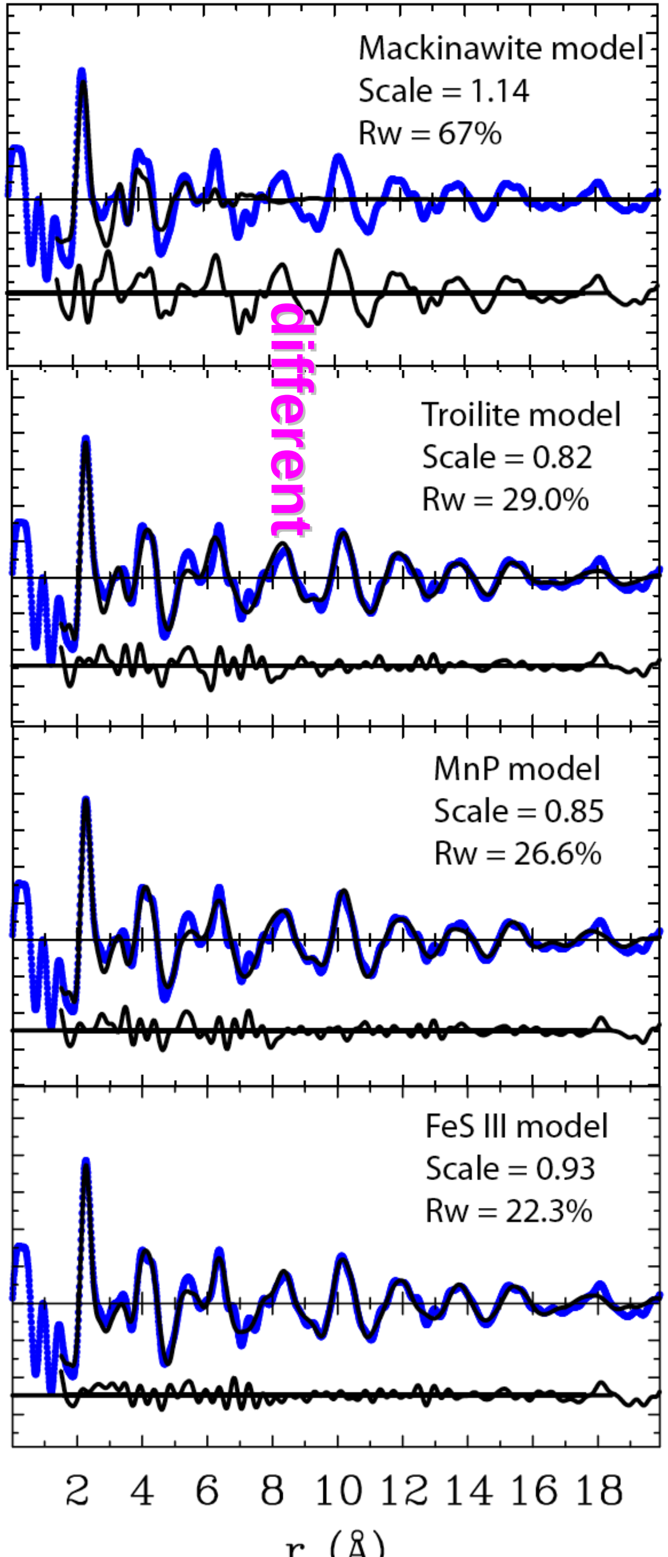
there is not enough signal out here

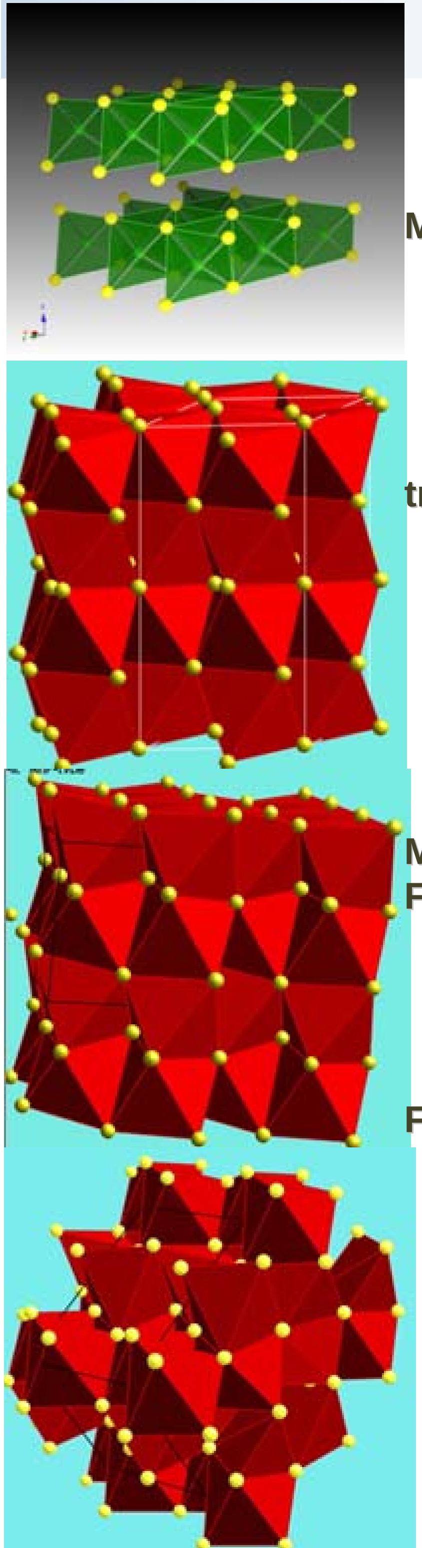




Relatively insensitive

different





Mackinawite

troilite

MnP-type FeS

FeS-III

Michel, Antao, Martin, Chupas, Lee, Schoonen, Parise April 2005

Conclusions: nanomaterials, HP & scattering

We know FeS! (no surface terminal groups....

Moving onto “real” systems: need information *in situ*

- scattering (still) a unique tool for in situ studies

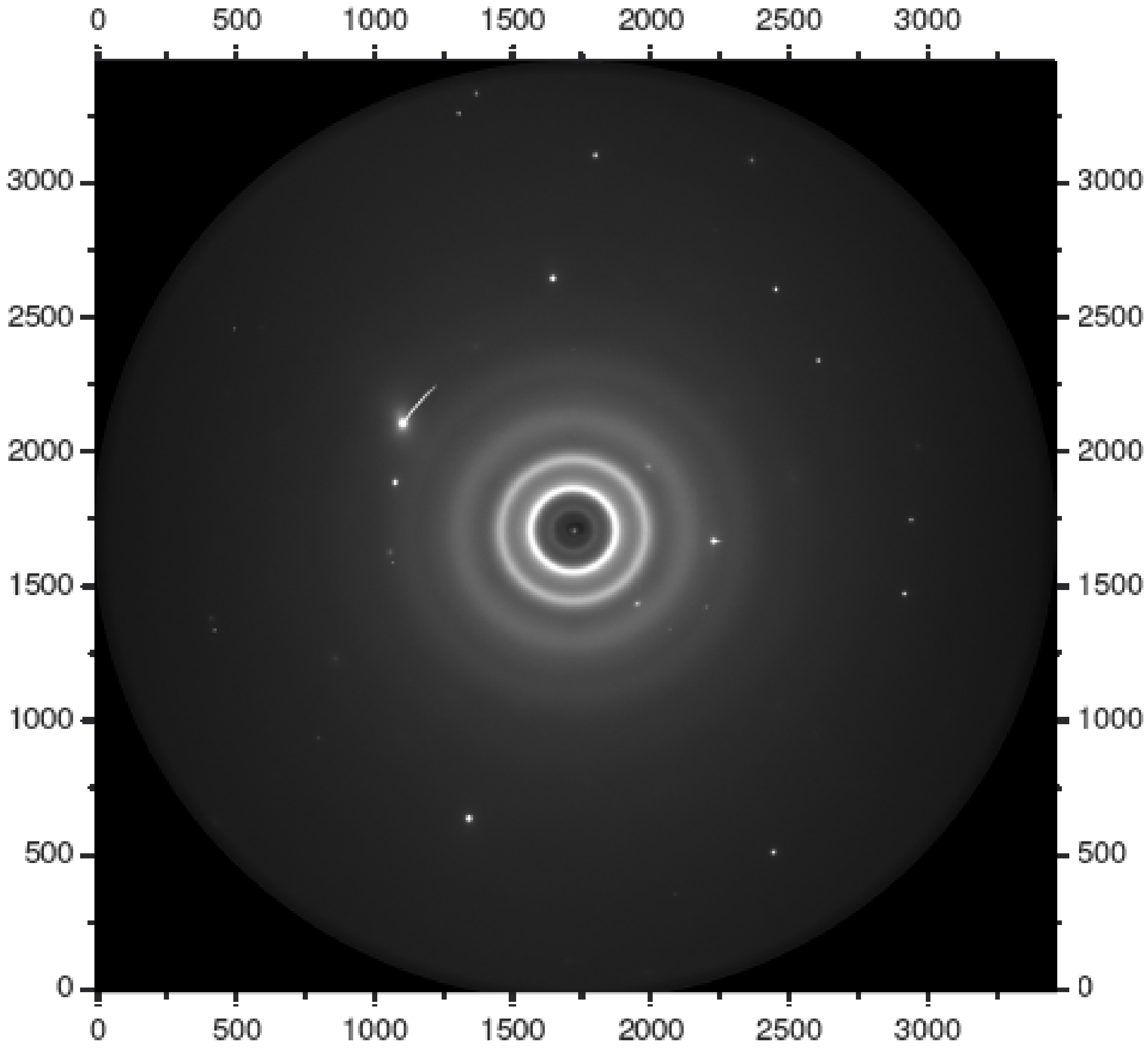
Relatively SENSITIVE when

- large structural changes

Relatively INSENSITIVE

- Very Subtle structural changes
- Mixtures of closely related phases
- Solution: differential PDF?
  - Neutrons: use +v/-ve isotope (Bréger, Grey, Parise JACS 2005)
  - X-rays: anomalous scattering
  - New Monte Carlo tools combining techniques (NMR, scattering.....)

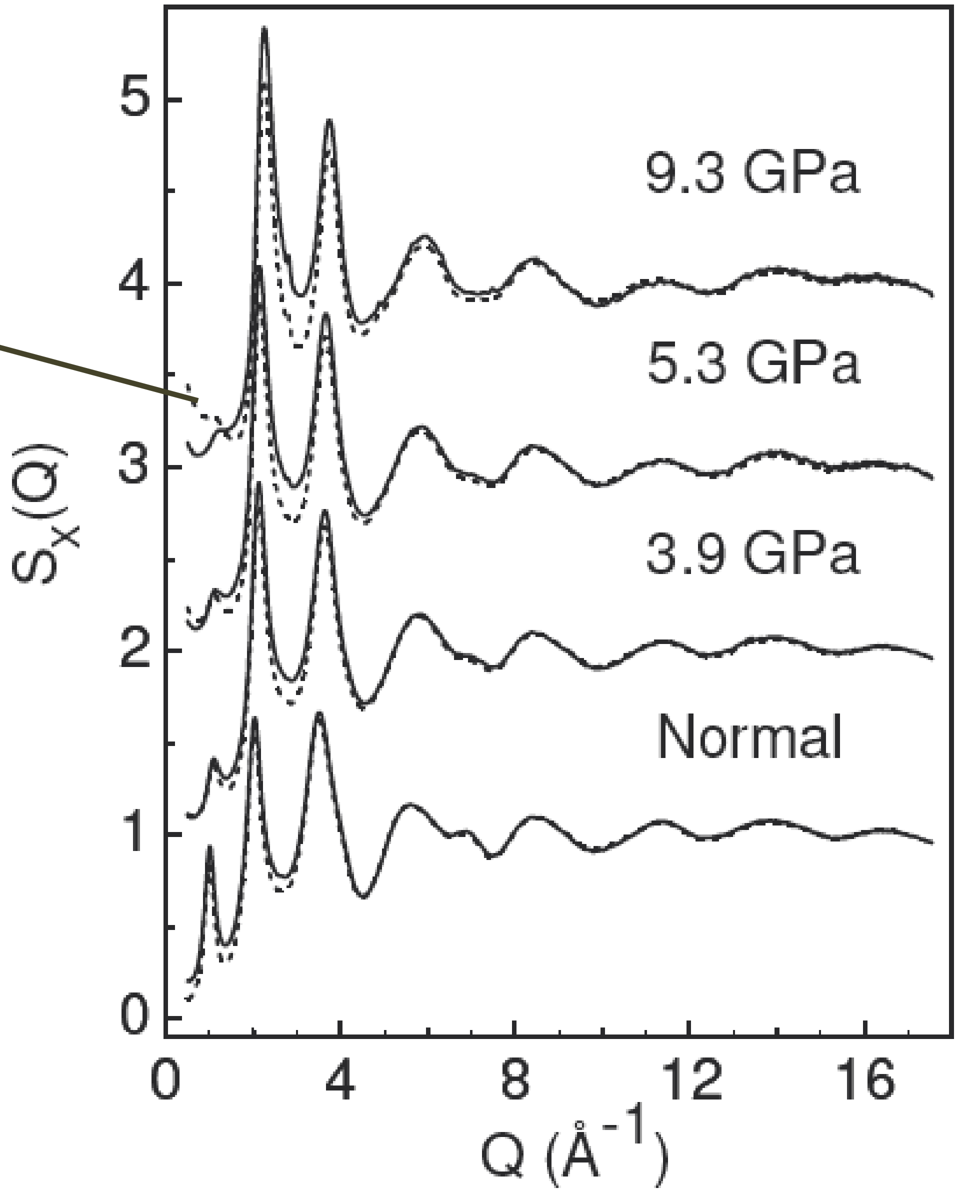
Glasses: HP data from $GeSe_2$ glass in the DAC (5.3 GPa)



Incident x-rays of energy 80.047(3) keV. Bright spots are Bragg peaks from the single crystal diamonds - diffuse rings from $GeSe_2$ glass.

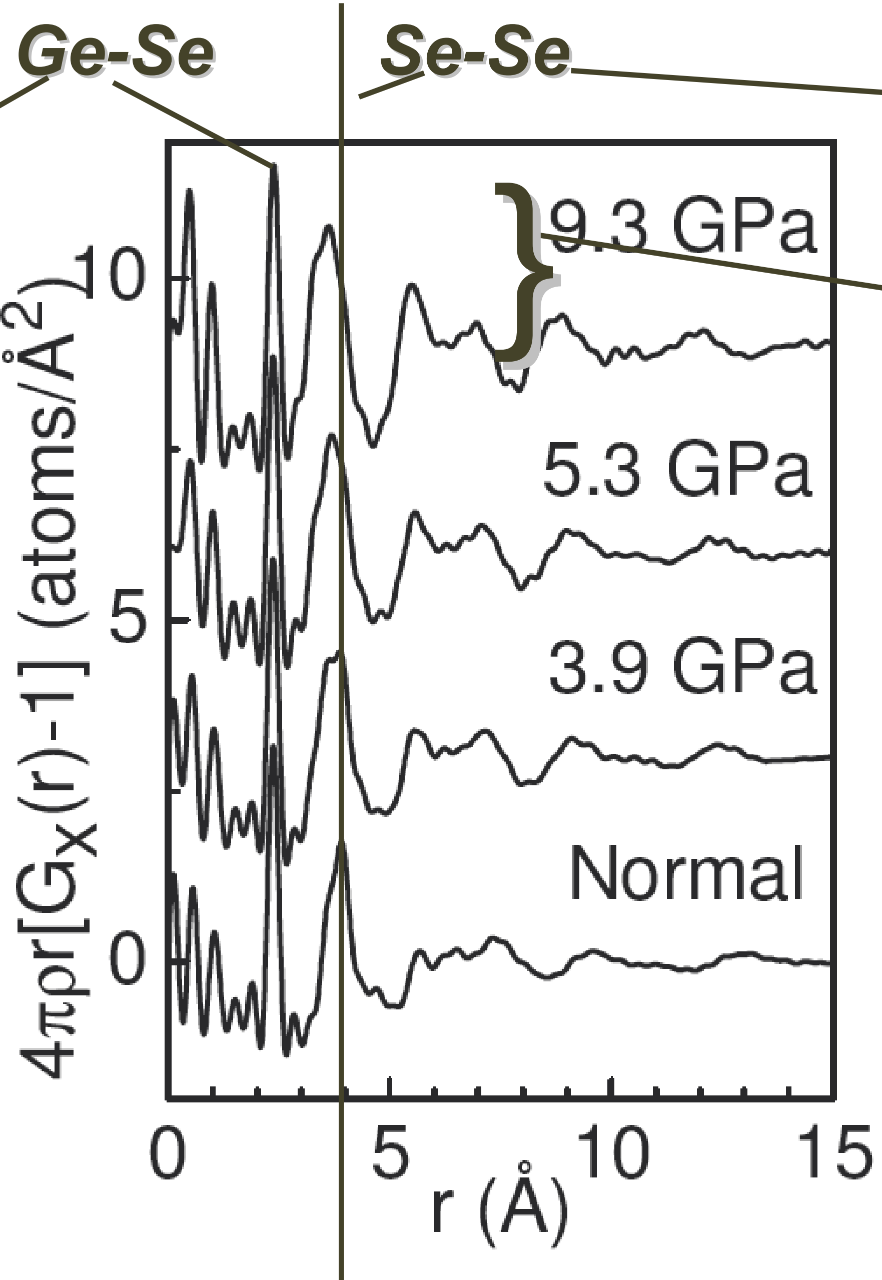
High pressure data from $GeSe_2$ - *Q*- space

Decrease in FSDF indicative of breakdown of intermediate range order



High pressure data from GeSe$_2$ - real space

Ge-Se distance increases slightly: 2.364((5) to 2.376(5)Å; GeSe$_x$ coordination number increases x = 4.0(2) to x= 4.5(2) at 9.3 GPA



results consistent with distortion and breakdown of the tetrahedra during compression.

Peaks shift to low D, increases in intensity with increasing pressure, Consistent with increase in intermediate range order although the FSDP is significantly reduced

Pressure effects on glasses - still an open question

Intermediate range order

- Complicated by overlap of distances
- Need correlations from a number of techniques
- Neutron scattering and isotopic substitution can help
- Anomalous scattering at Ge and Se edges

Phase transitions in glassy materials: a plug for neutrons

X-rays can not do somethings - we need to look at neutrons and Raman as well

Theory

The total structure for neutrons or X-rays is given by:

partial structure factors

$$S_N(Q) = \frac{1}{<b>^2} \sum_{\alpha,\beta} c_\alpha c_\beta b_\alpha b_\beta [S_{\alpha\beta}(Q) - 1]$$

where *c* and *b* are the atomic fraction and coherent neutron scattering length (X-ray form factor). For BOTH X-ray and neutrons, the weighting factor *S(Q) are very similar* Z_{Ge}=32, Z_{Se}=34; b_{Ge}=8.19 fm, b_{Se}=7.97. The pair distribution function is related to the Fourier transform of the total structure factors $S_N(Q)$ and $S_X(Q)$.

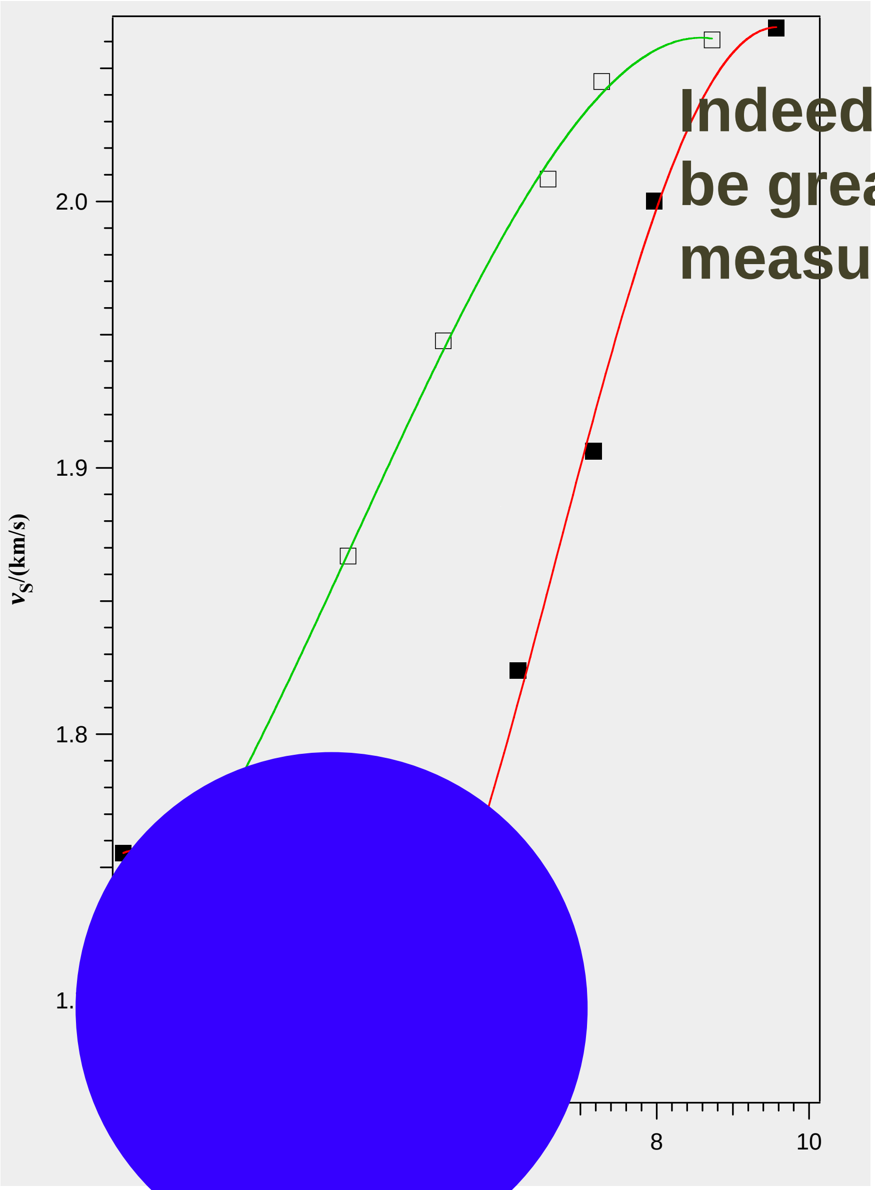
Because Z and b for Ge and Se are so similar the pair correlations

$S_N(Q) \sim S_X(Q) \sim 0.115 S_{GeGe}(Q) + 0.437 S_{SeSe}(Q) + 0.448 S_{GeSe}(Q)$

solutions?: Anomalous X-ray scattering (12 kev); isotopic substitution for neutron *- or choose another glass (perhaps wisest choice!)*

Phase transitions/structure in glassy & liquid materials

nese changes in intermediate range order reflected in property ences?



Indeed they are - and suggests there should be greater integration of property/structural measurements

Shear wave velocity as a function of pressure for $GeSe_2$ glass at RT on compression (red) and decompression (green)

Antao, Li et al (2006)

Conclusions - QHP-PDF

Useful to develop structure models for perturbed structures

Good for debunking models. *A priori studies*?

The nano- and glassy side is still developing

Quantitative

  Properly normalized S(Q) - range of Q >> 15$Å^{-1}$

For moderate pressures (< 10 GPa) WE have found the large volume device (Panoramic/GEM cells, PE cells) give superior data, even with very weak scatterers

The ERL

  See about half of what was discussed in the dynamic group