Determination of the high-pressure phases (II' and IV') of $CuGeO_3$ using single-crystal techniques

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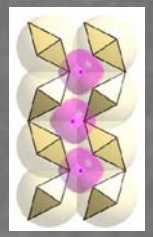
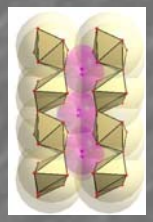
Reasons to Study $CuGeO_3$

- First known inorganic material to exhibit a spin-Peierls transition
- Phase transitions are dependant on the hydrostaticity of the pressure medium
- Majority of previous pressure studies were conducted using Raman spectroscopy and powder x-ray diffraction
  - The structures of the high pressure phases have not been determined

Phase Transitions





~ 7 GPa

Phase II

orthorhombic

~ 14 GPa

Phase II'

monoclinic

~ 22 GPa

Phase VI

tetragonal

hydrostatic

Phase I

monoclinic

quasi-hydrostatic

orthorhombic

~ 7 GPa

Phase III

~ 8 GPa

monoclinic

Phase IV

~ 12 GPa

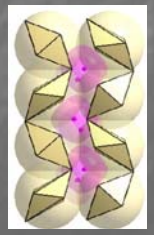
monoclinic

Phase IV'

~ 18 GPa

orthorhombic

Phase V



Experimental Details

- Energy Dispersive X-ray Diffraction
  - Data collected at 16BMB
  - White Beam
  - Single crystal diffraction
    - Ge solid state detector
- Monochromatic X-ray Diffraction
  - Data collected at 13BMD
  - 45 keV beam
  - Single crystal diffraction
    - Image plate detector

Single Crystal Energy Dispersive X-ray Diffraction

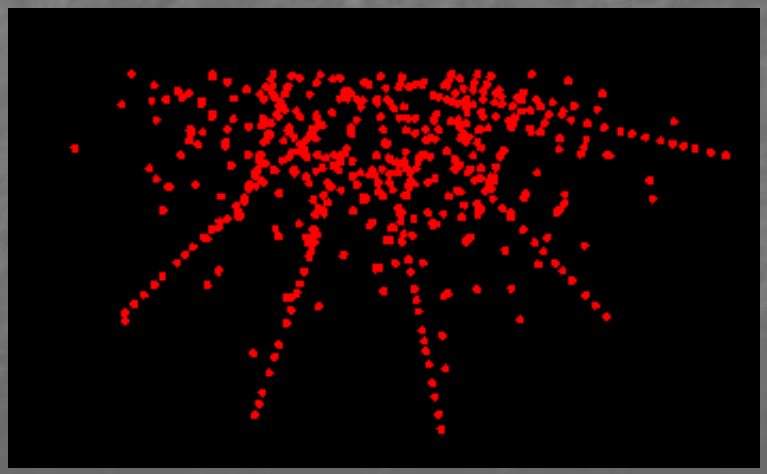
- Determine the d-spacings of the reflections by their energy
- Determine the orientation matrix from the position of the reflections in reciprocal space
- Use of polychromatic beam
  - Allows more reflections to have the Bragg's conditions satisfied in the available geometry than monochromatic radiation
- Use of a Ge solid-state detector as a point detector
  - Better determination of the intensity of the individual reflections than area detectors

EDX4DAC

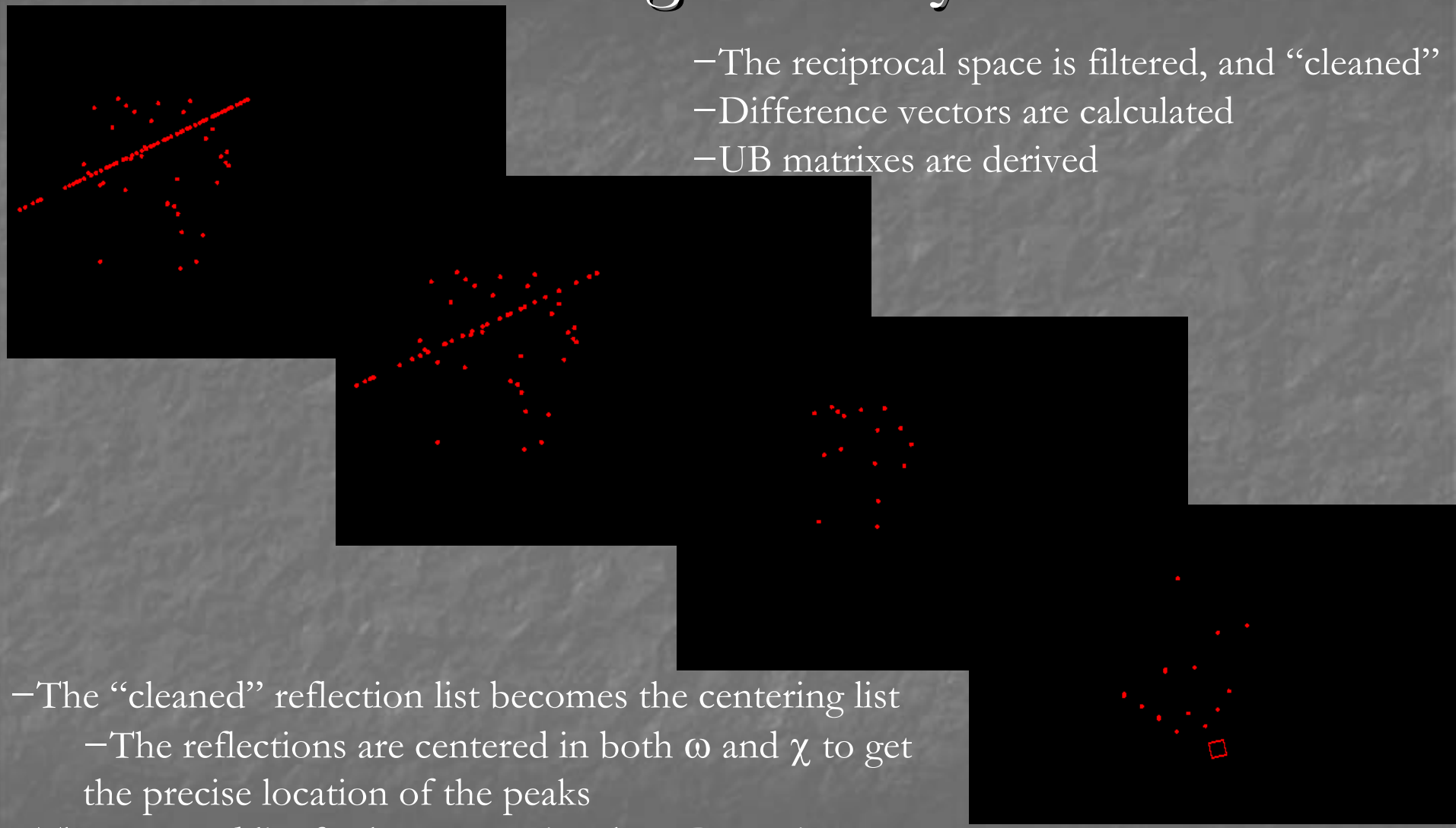
- Typical experiment
  - Center the sample in the chi circle
    - Manually offline then determine how the sample moves during a full 360° χ rotation
  - Peak search
  - Determine orientation matrix
  - Center peaks that constrain the orientation matrix
    - Centered in relationship the ω and χ angles
    - Typically 20 – 30 peaks
  - Calculate a data collection list usually at one energy
  - Collect intensity data

Peak Search

- The sample is scanned for reflections
  - At each 1° χ step the sample rotates through the ω range in 1° steps as well
  - To get a good sampling of the reciprocal lattice the peak search should be allowed to reach at least χ = 90°



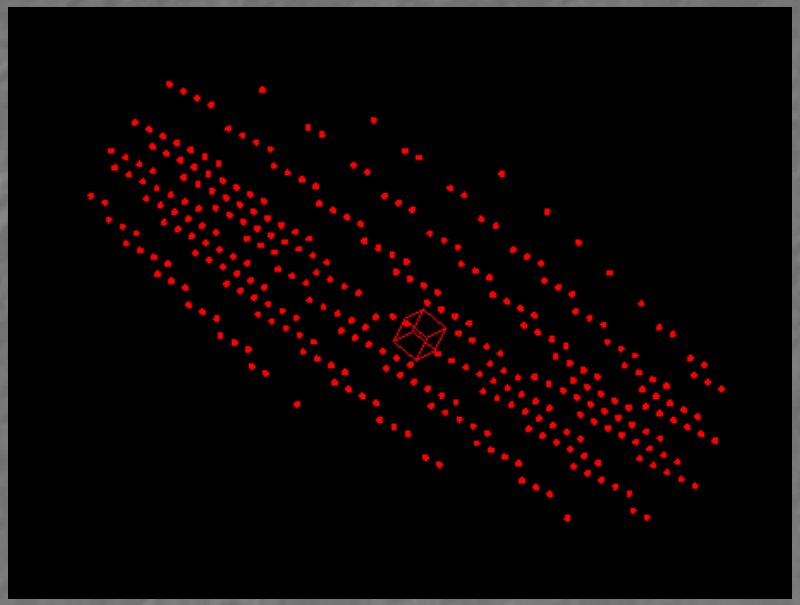
Indexing the Crystal

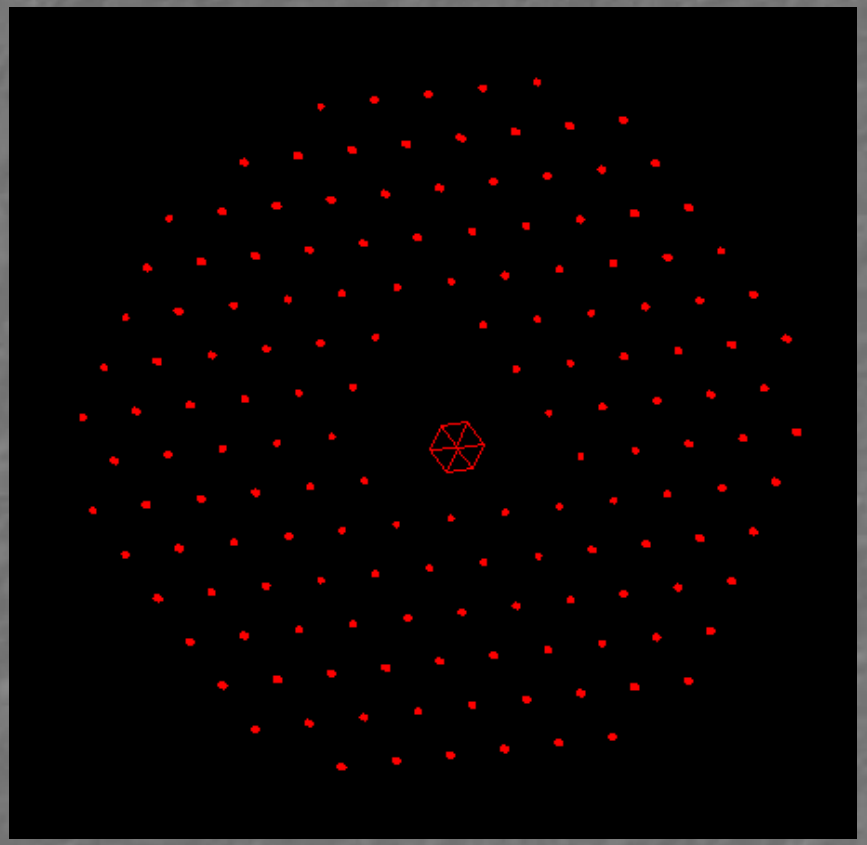


- The reciprocal space is filtered, and "cleaned"
- Difference vectors are calculated
- UB matrixes are derived

- The "cleaned" reflection list becomes the centering list
  - The reflections are centered in both ω and χ to get the precise location of the peaks
- The centered list further constrains the UB matrix

Intensity Data Collection

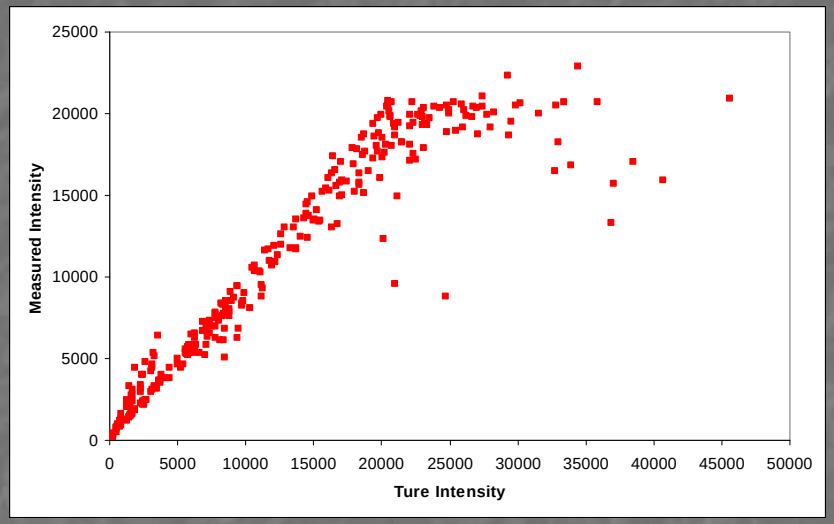




- Can be calculated to produce quasi-monochromatic or constant 2θ data
- Typically contain 300 – 600 peaks

Ge SSD detector

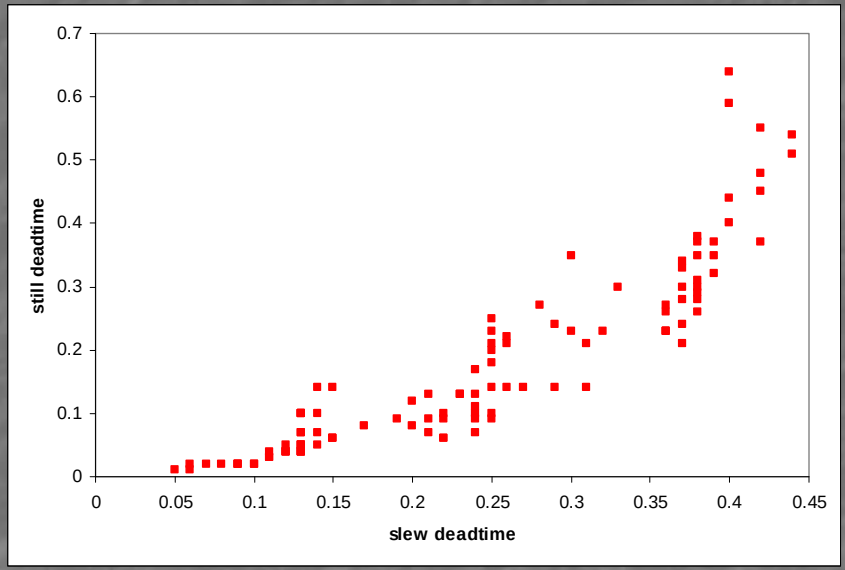
- The dynamic range of the detector
  - As peaks become more intense the detector spends less time measuring the reflection's intensity
- A potential problem for harmonic peaks
  - The detector will spend less time recording the weaker peak's intensity because of the presence of the stronger harmonic



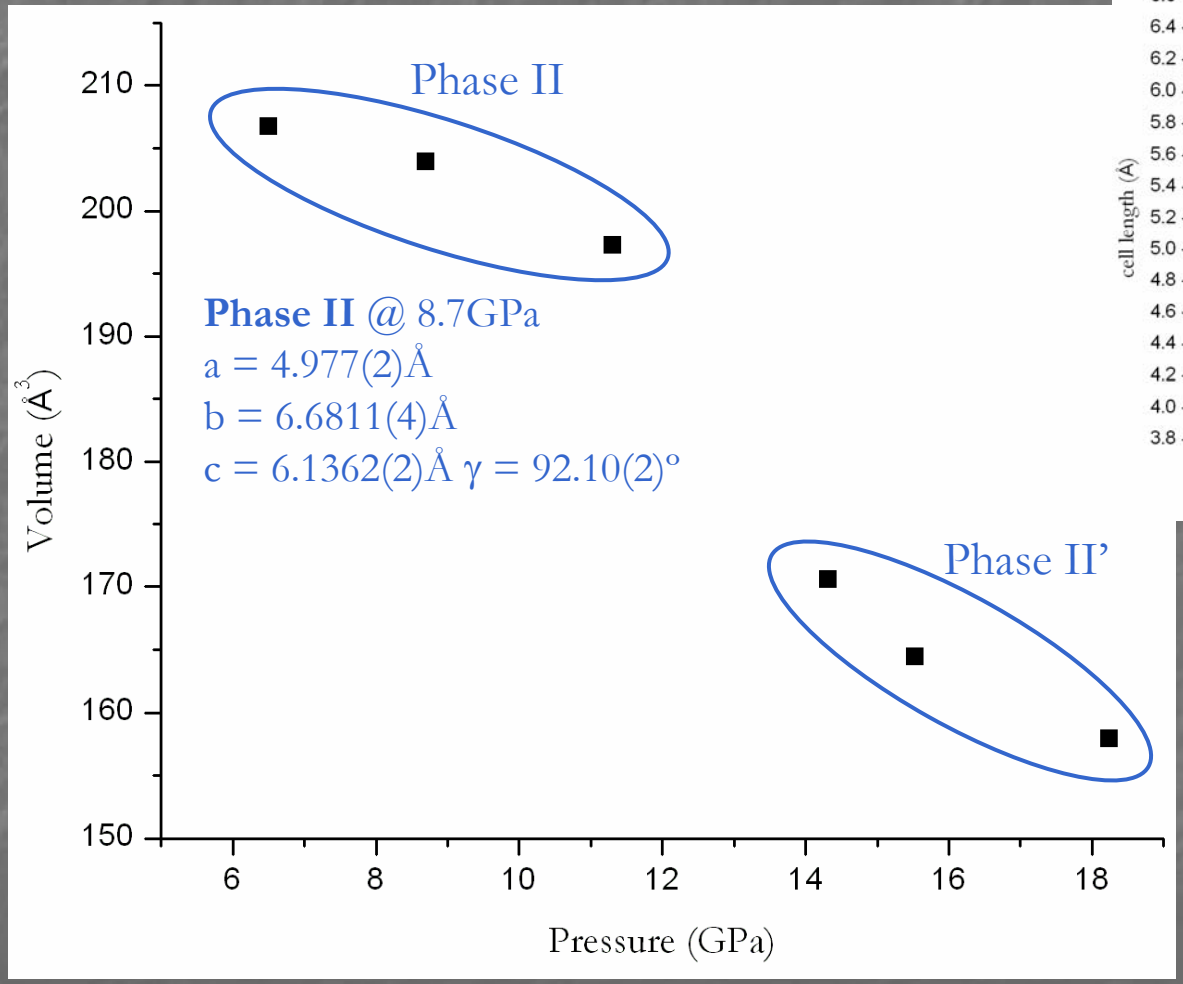
- Adjustment of the measure intensities to the detector's dymanic range
  - Peak centering
    - Automatic adjustment of the silt sizes of the detector
    - One problem is the final intensity can not be scaled back
  - Intensity data collection
    - Slit adjustment is not feasible due to unknown peak widths
    - An absorption foil would be a better solution

Still versus slew

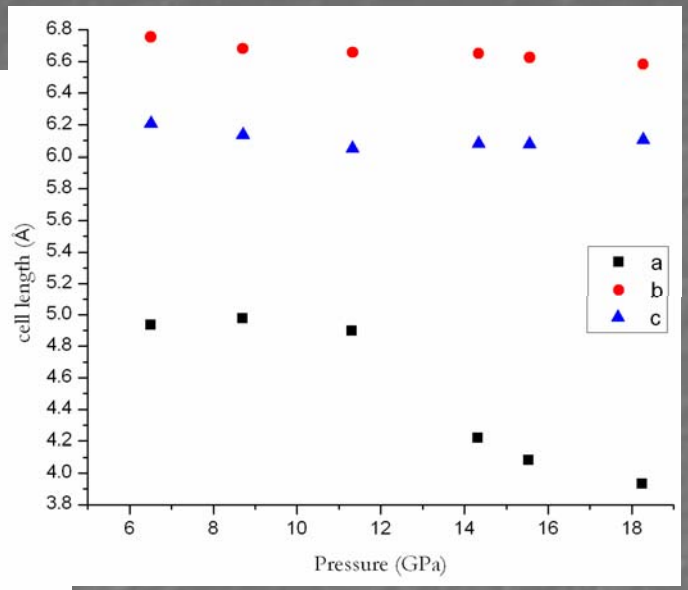
- With strong peaks the dead time of the detector reaches the real time
  - The dead time is the difference between the defined exposure time and true exposure time
  - Can cause intense peaks to appear to have little or no intensity
- Two ways to combat this effect
  - A material that will absorb some of the incoming beam thus lowering its intensity
  - Slew exposures instead of still exposures
    - "smears out" the intensity of the peak over an angular range



Phase II – Phase II' Transition

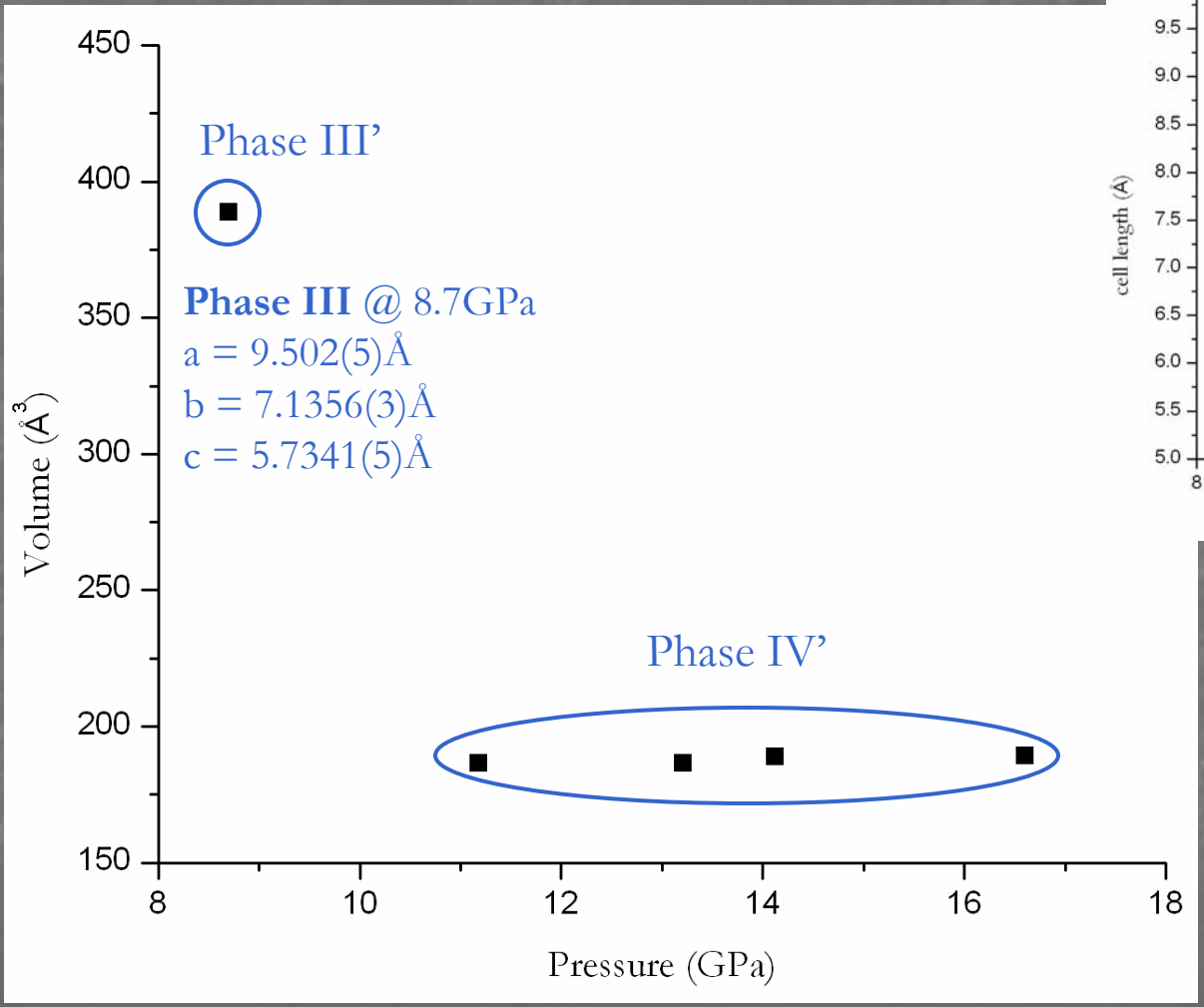


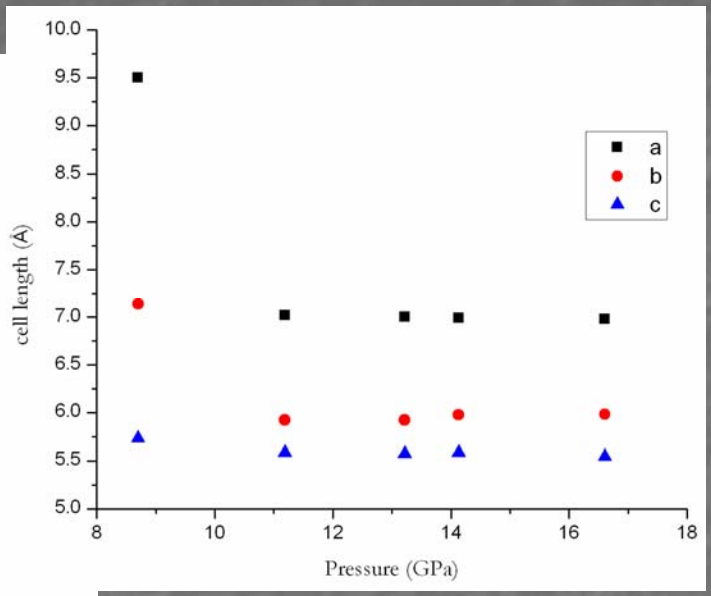
Phase II @ 8.7GPa
a = 4.977(2)Å
b = 6.6811(4)Å
c = 6.1362(2)Å γ = 92.10(2)°



Phase II' @ 19.9GPa
a = 3.952(3)Å
b = 6.596(2)Å
c = 6.064(2)Å
V_0 = 297(30)Å^3
K_0= 15(3)GPa
K' = 2.78(5)

Phase III – Phase IV' Transition





Phase IV' @ 14.13GPa
a = 6.9855(4)Å
b = 5.975(5)Å
c = 5.5809(3)Å γ = 125.82(7)°
V_0 = 547(11)Å^3
K_0= 23(8)GPa
K' = 2.800(4)

Conclusions

- By loading crystals of phases I and III allowed the investigation of both phase transition pathways under identical conditions
- A combination of monochromatic and energy dispersive single crystal diffraction was employed to determine the lattice parameters of phases II' and IV'.
  - The lattice parameters of phase II' previously reported by Ming, et. al. (1999), determined by powder x-ray diffraction, do not agree with our determination of the lattice parameters. We attribute this discrepancy to the higher quality of single crystal data with respect to powder data.
- From the experiments we have been able to determine preliminary values of V0, K0 and K' for both phases II' and IV'.
- In the coming future we should be able to increase the quality of our data to the point at which we will be able to complete structure refinements of both high pressure phases.

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