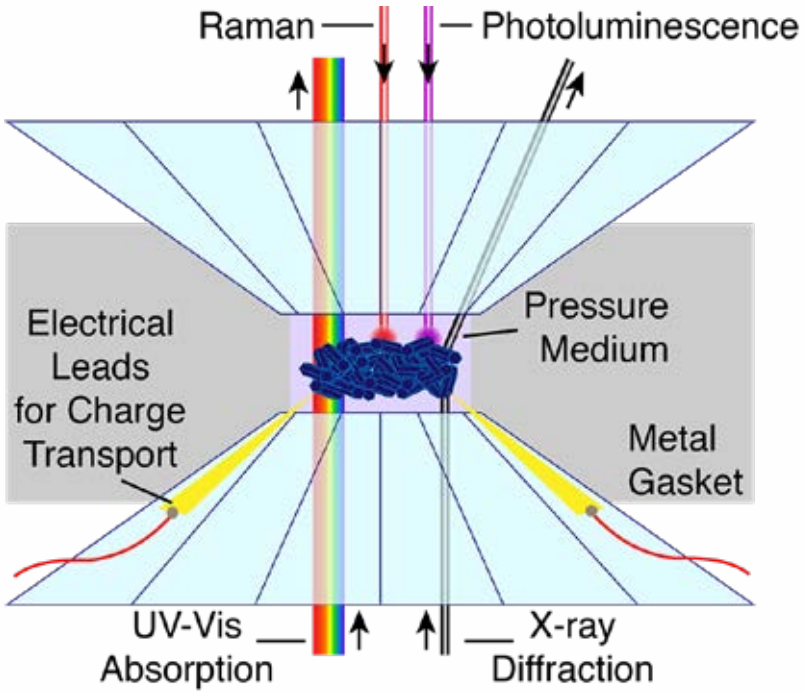
Jaffe Lab

UNIVERSITY OF NOTRE DAME

# A Practical Guide to Working with Diamond-Anvil Cells

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# Acknowledgements


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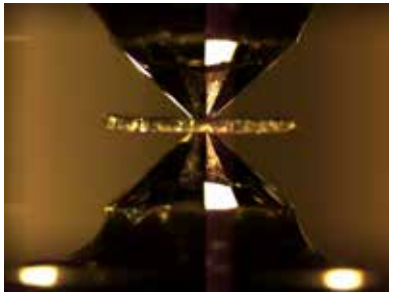
# Pressure

Outer Space

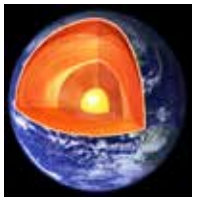
Diamond-Anvil Cell



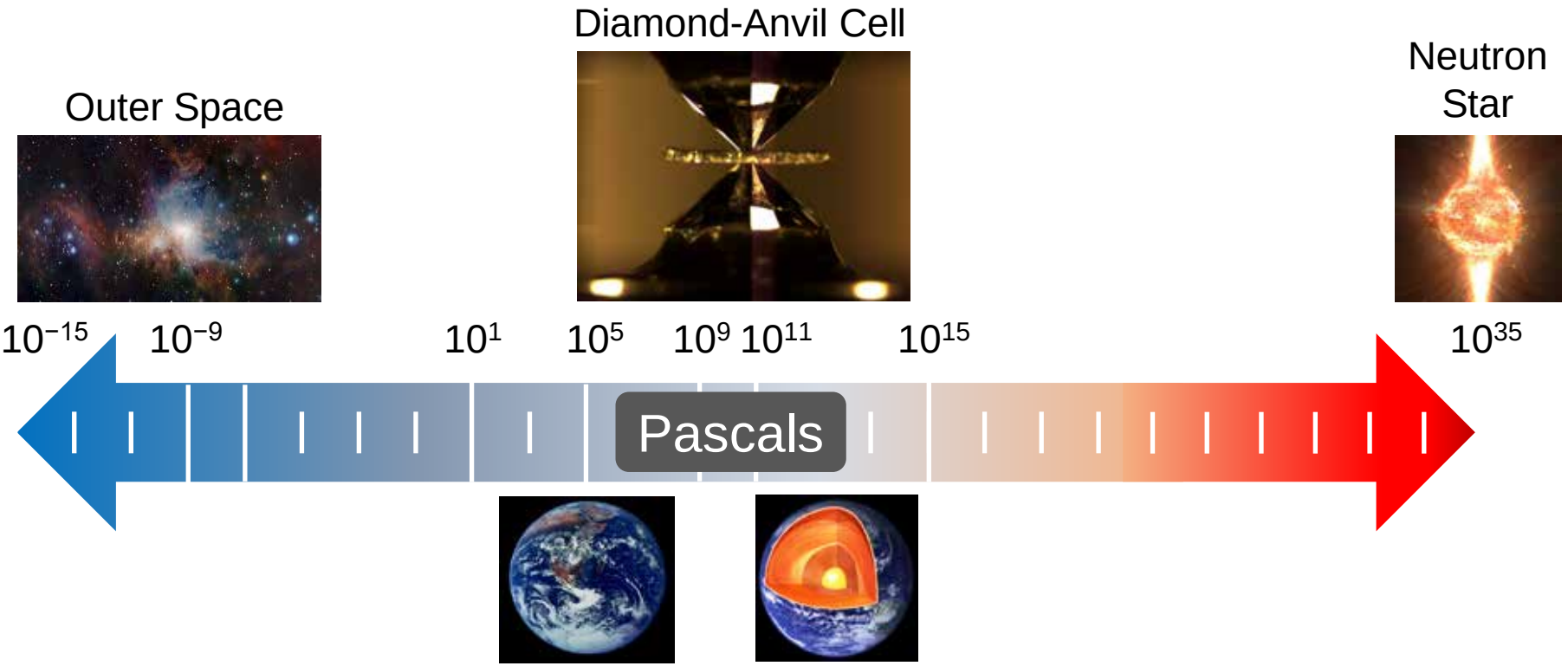
Neutron Star

$10^{-15}$ $10^{-9}$ $10^{1}$ $10^{5}$ $10^{9}$ $10^{11}$ $10^{15}$ $10^{35}$

Pascals

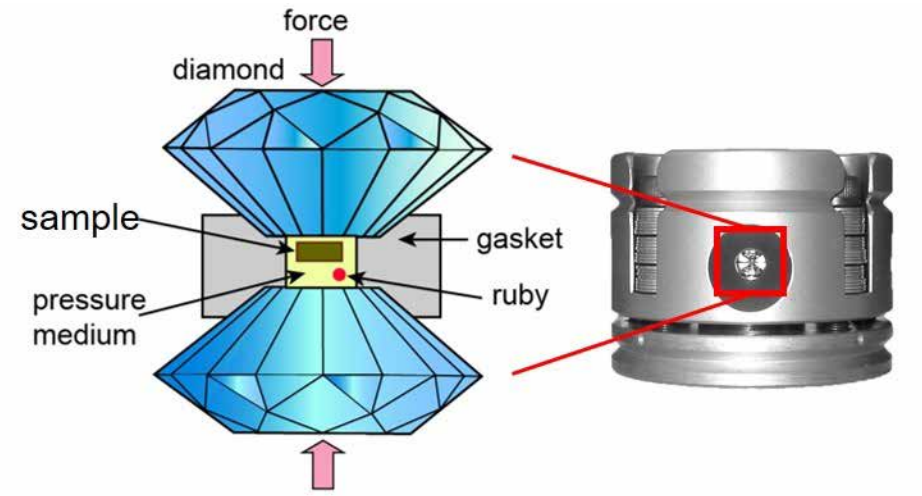


# Pressure

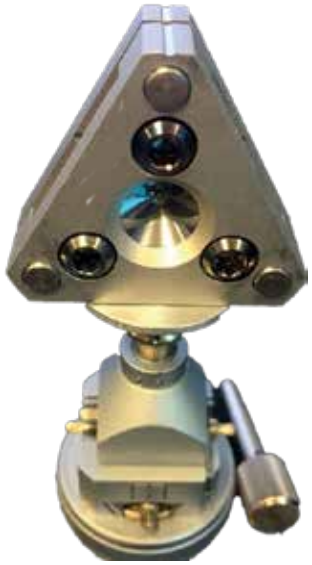


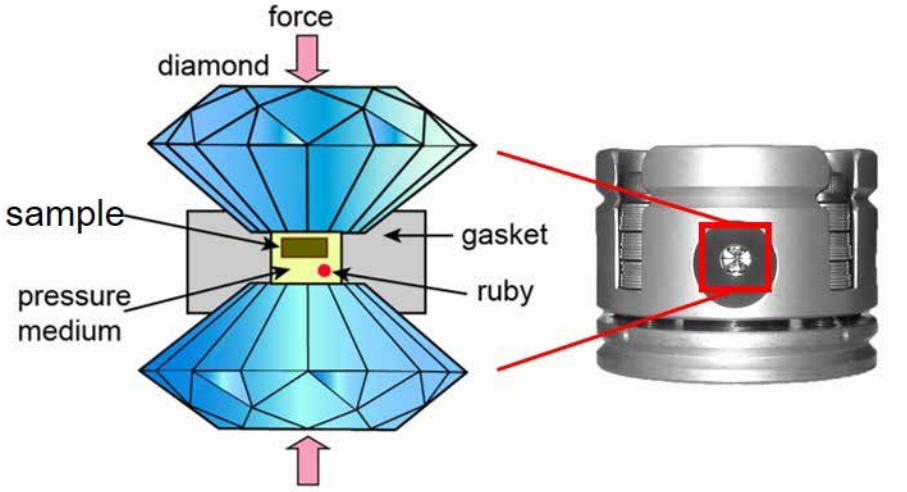

- Compression-induced chemical reactions
- Magnetic and electronic transitions
- Simultaneous modulation of structure and electronic properties
- Perturbation of model systems to gain fundamental understanding

# Diamond-Anvil Cells



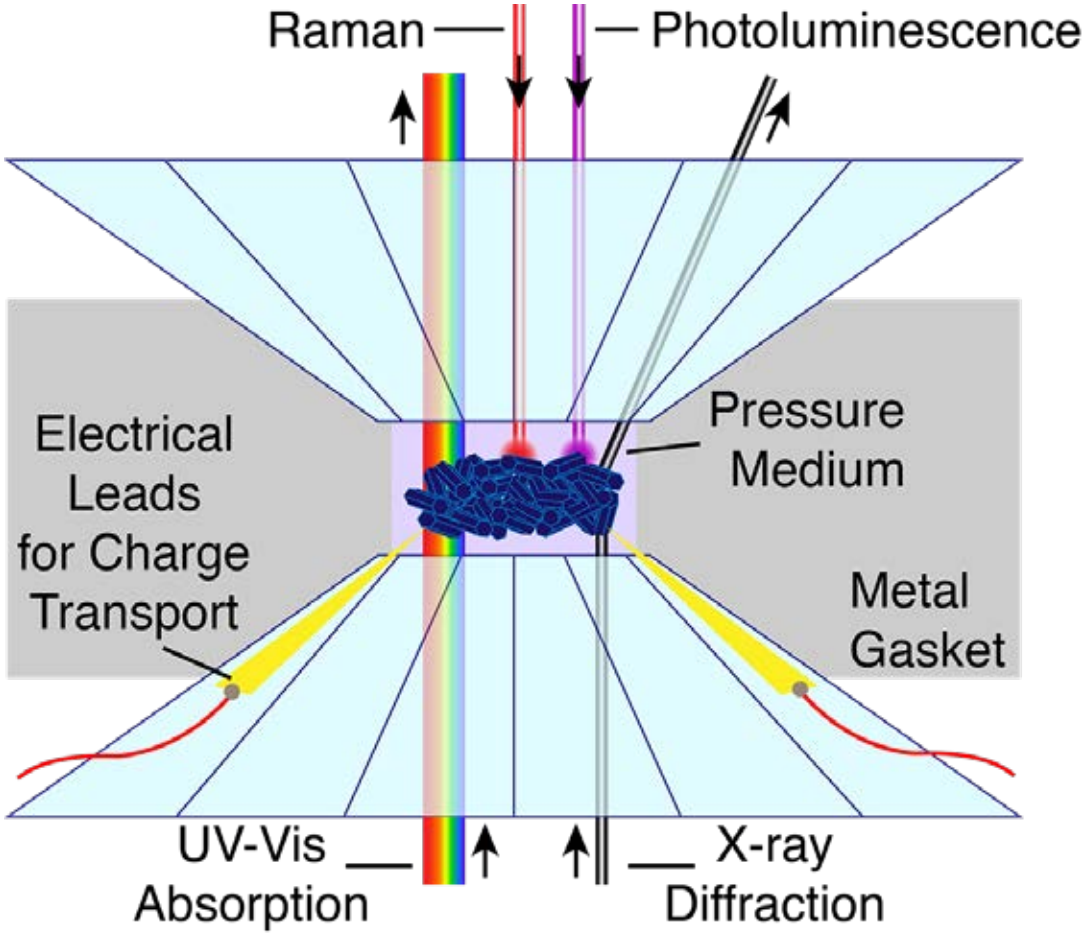
# Diamond-Anvil Cells





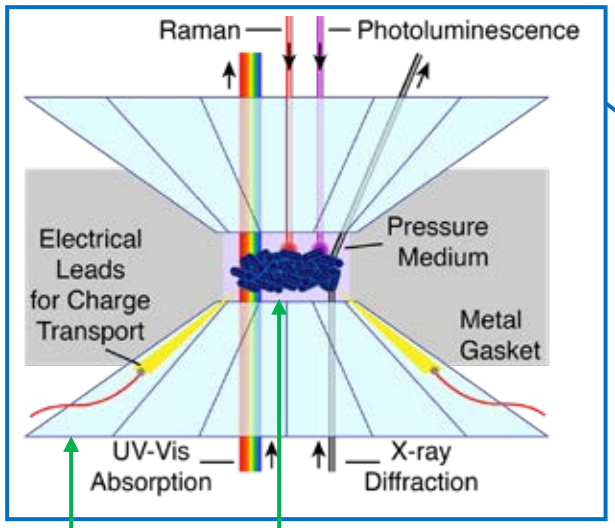



# Diamond-Anvil Cells




- Transparent to large range of radiation
- In situ X-Ray, neutron, optical, electrical, and magnetic probes are possible over large *P*–*T* space

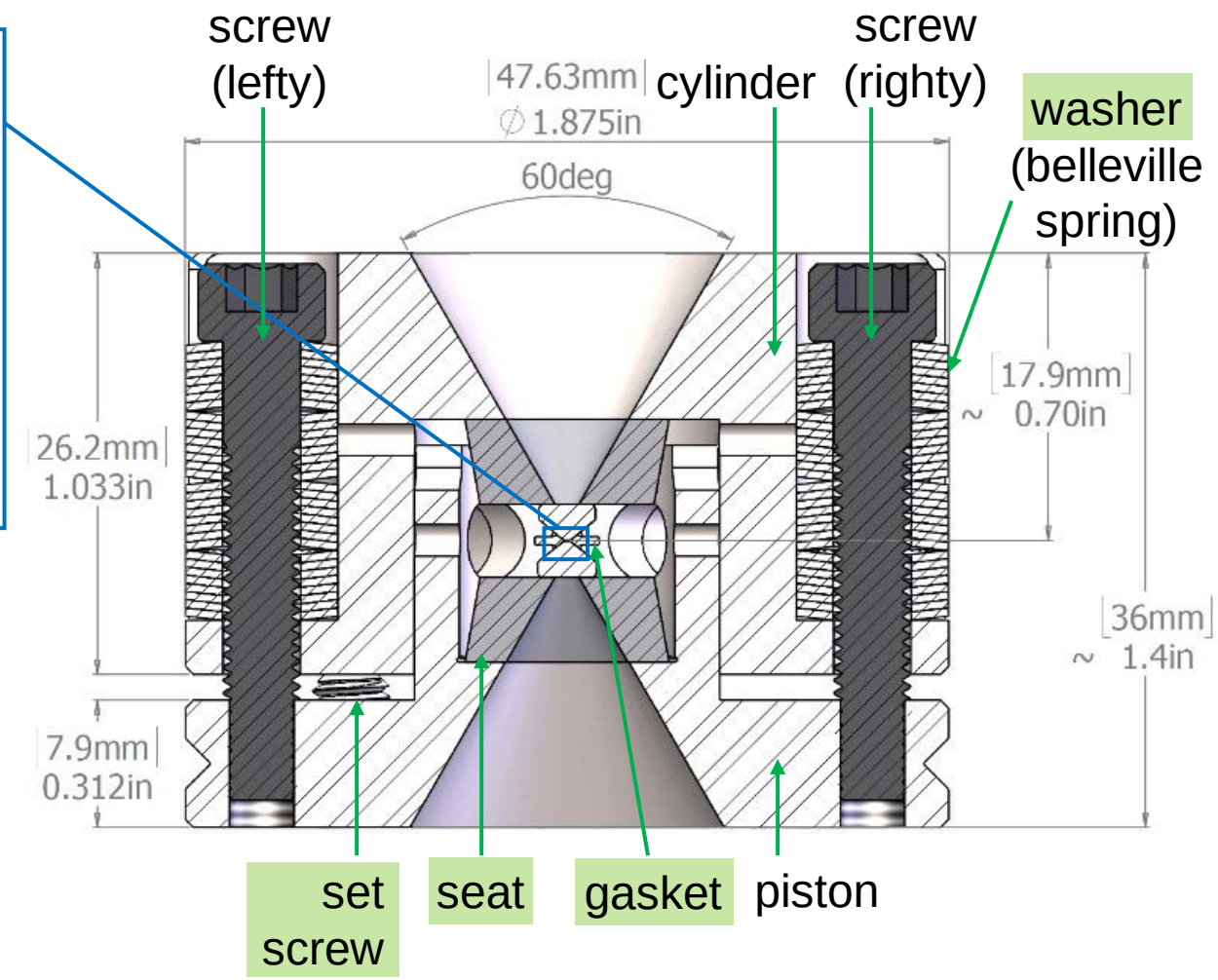
# Components of a DAC




table

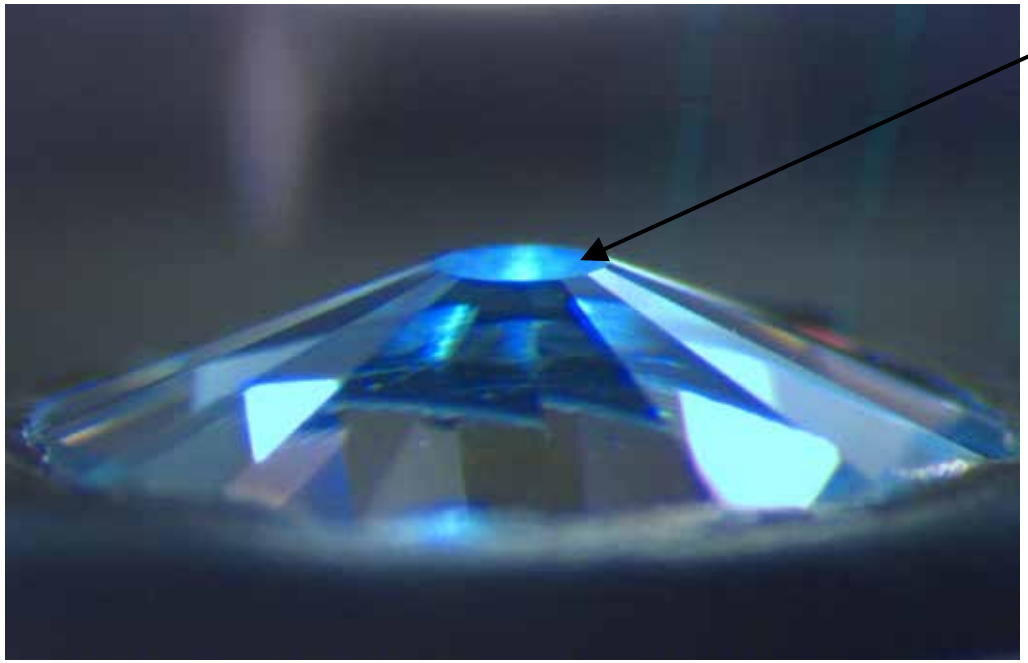
culet

diamond anvil




- Almost every element comes with choice!
- Be creative about picking your components to fit your experiment

# Diamond anvils



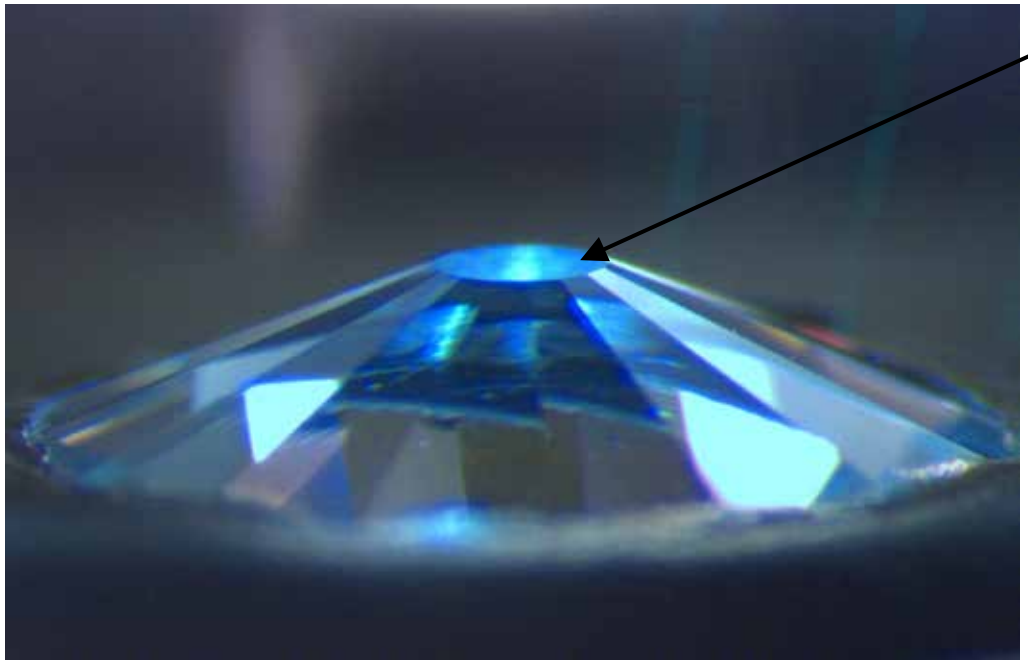
**Culet**

- Ultimately determines achievable pressure

$$P = \frac{F}{A}$$

  - 600 µm culet working pressure ~15 GPa
  - 300 µm culet ~55 GPa

# Diamond anvils

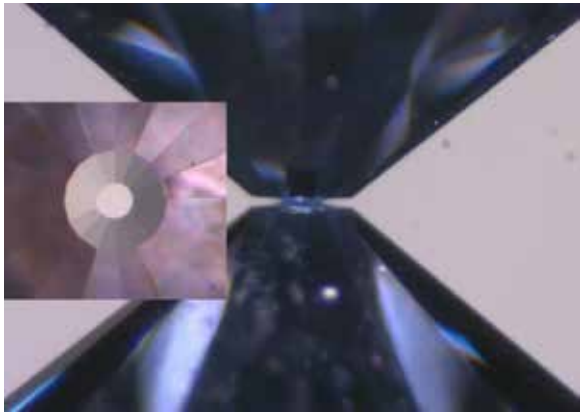


**Culet**

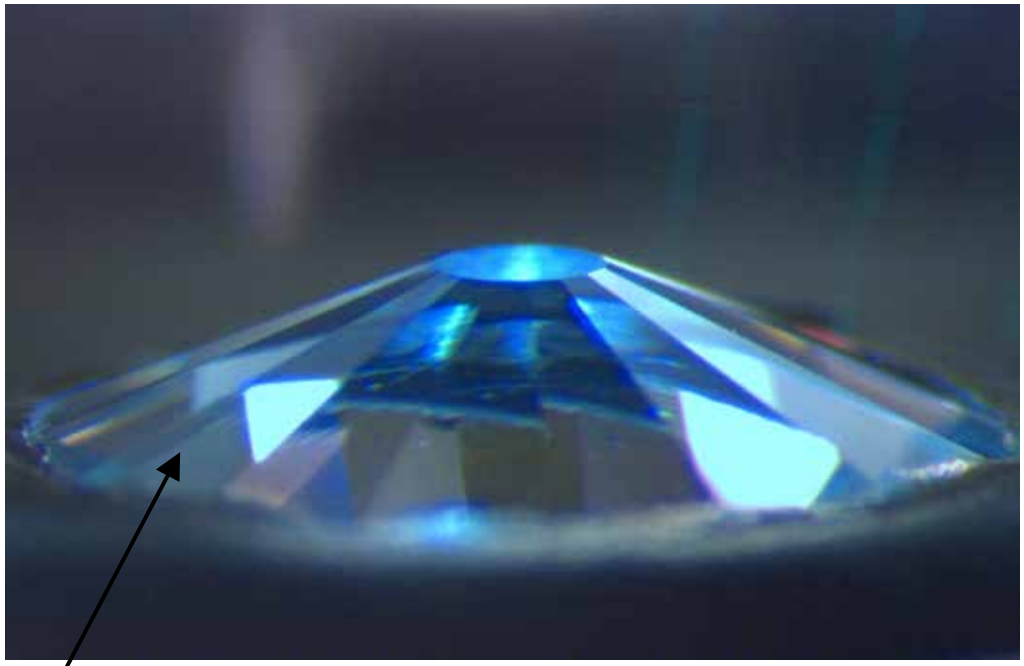
- Ultimately determines achievable pressure

$$P = \frac{F}{A}$$

  - 600 µm culet working pressure ~15 GPa
  - 300 µm culet ~55 GPa
- Beveled anvils can dramatically increase achievable pressure



# Diamond anvils



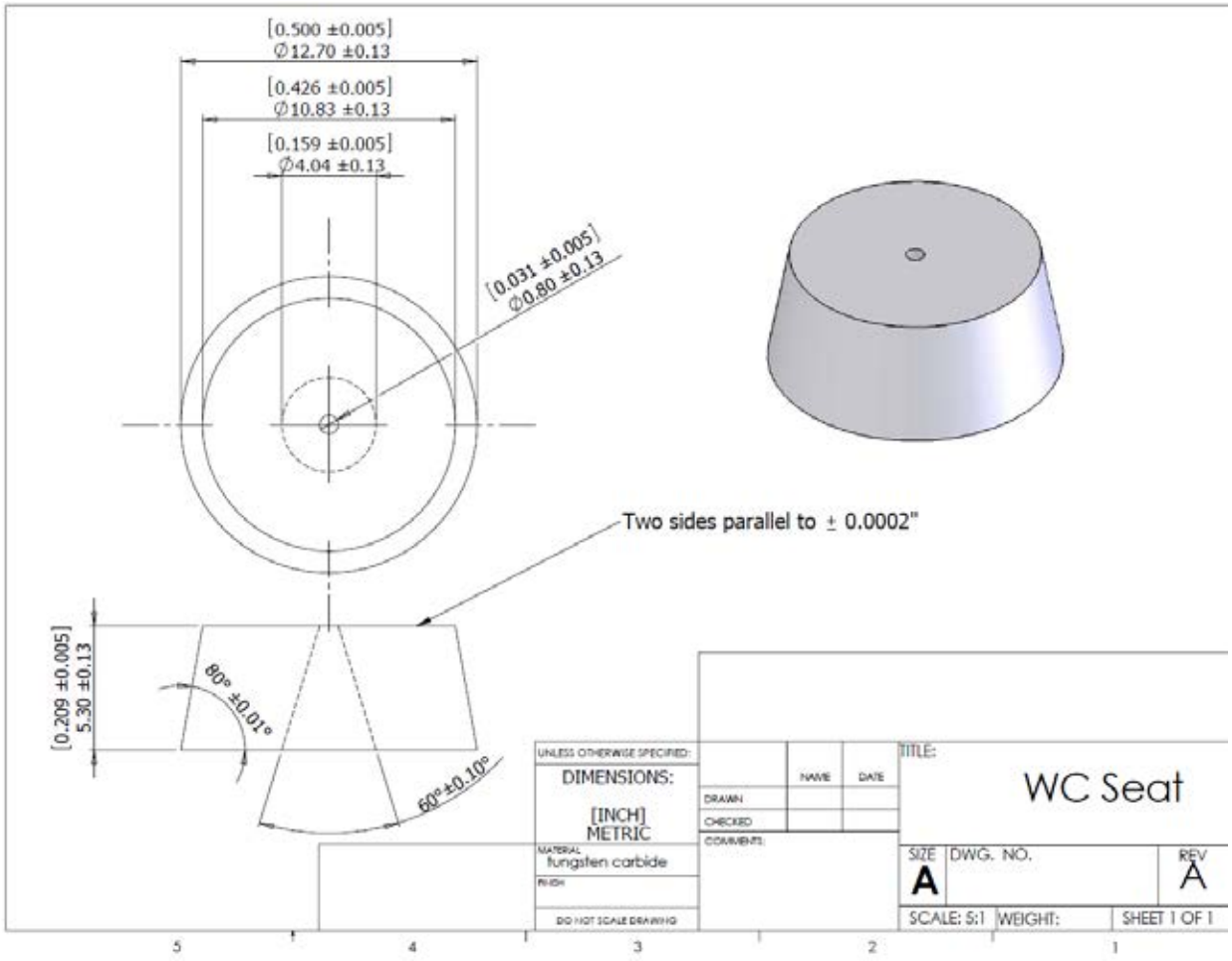
**Diamond type**

- Type I: N impurities → absorb in IR and UV
  - **Ia**: N atoms cluster (IaA and IaB are different clustering motifs)
  - Ib: N atoms are more evenly distributed, tend to be brown or yellow
- Type II: low to near-zero N impurities
  - **IIa**: very low impurities, very low fluorescence, CVD
  - IIb: boron impurities, *p*-type semiconductors

**Importance**

- Want low UV/Visible fluorescence for absorption spectroscopy or photoluminescence measurements
- Want low X-ray fluorescence during diffraction or XAS measurements
- Practical Note: watch out for bluish emitted light during measurements!

# Seats




Practical note:

- WC is better for most optical applications (allowing in more light and from wider angles)
- c-BN is better for X-ray measurements but often has a small (34°) opening angle)

**Choice of seat material**

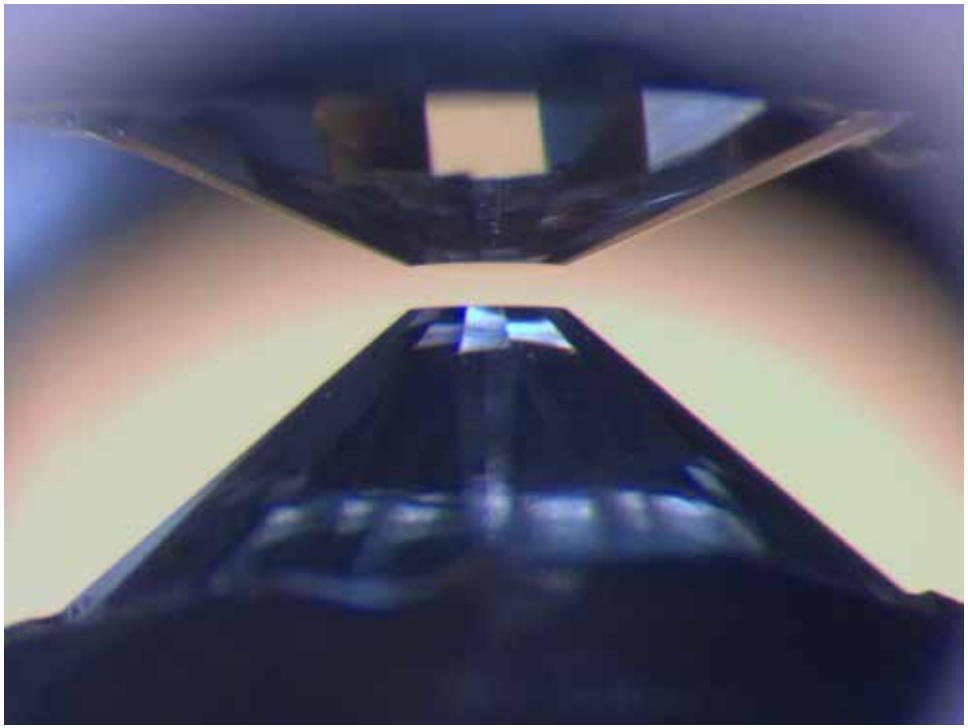
- Tungsten carbide (WC): standard, strong, cheap, large opening angle
- Cubic boron nitride (c-BN): expensive, brittle, but X-ray transparent

# Mounting diamonds

- Two main options:
  - Epoxied to the seat
    - Pros: can easily swap out diamonds, seats, DACs, etc. and the diamond is very accessible (not enclosed)
    - Cons: epoxy can come unstuck or move especially with solvent present or with temperature swings
    - Practical note: a good option is Stycast 2850FT epoxy cured with Catalyst 23LV or 24LV
      - High thermal conductivity, low thermal expansion coefficient, solvent-resistant, electronically insulating
    - Practical note 2: align the diamond to the seat well (many companies sell a “jig” to do so)
  - Force-fitted in a metal ring
    - Pros: stable to temperature and solvent, stays put
    - Cons: not customizable and more difficult to swap/interchange

# Aligning diamonds

- Aligning diamonds within a DAC is incredibly important:
  - Raises the maximum achievable pressure
  - Ensures a lower probability of gasket failure
  - Easier to center sample chamber
  - Less likely to have gasket interference with measurement
  - Less likely to frequently re-glue diamonds

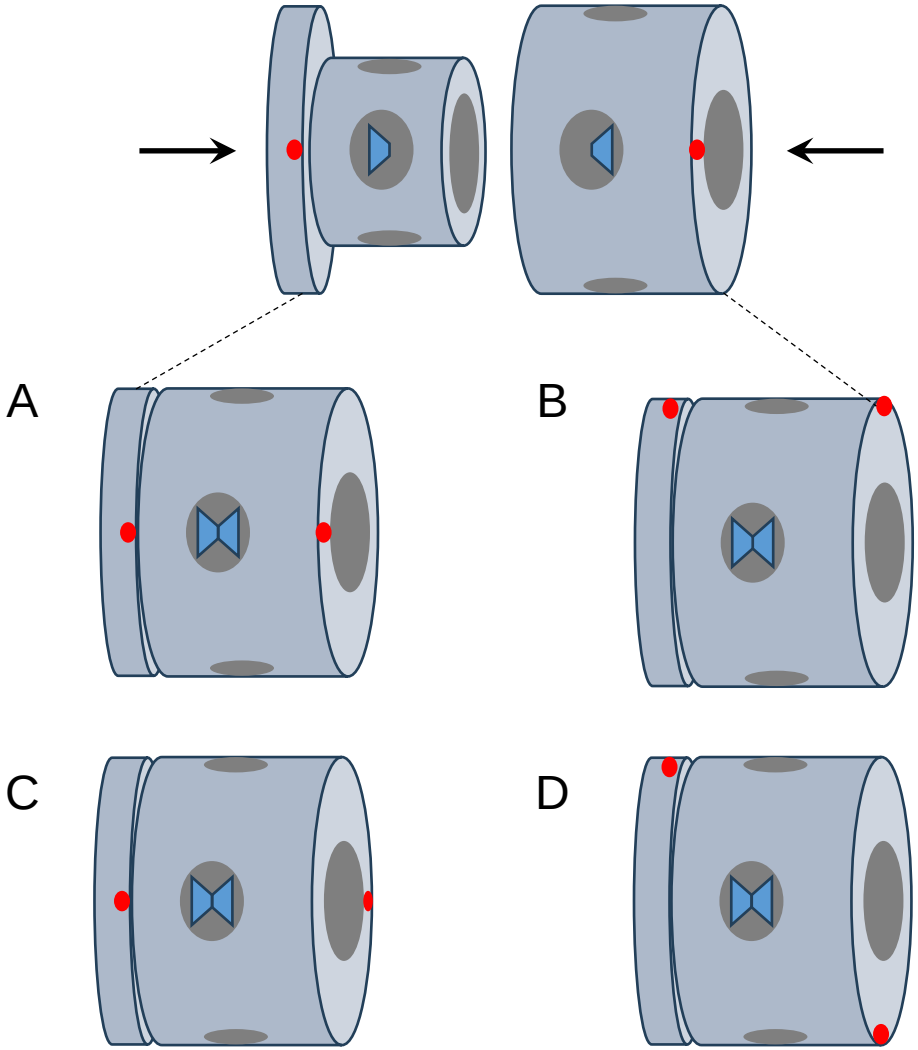


Practical note:

- Spend a lot of time to get this perfect and then you will avoid doing it more in the future!

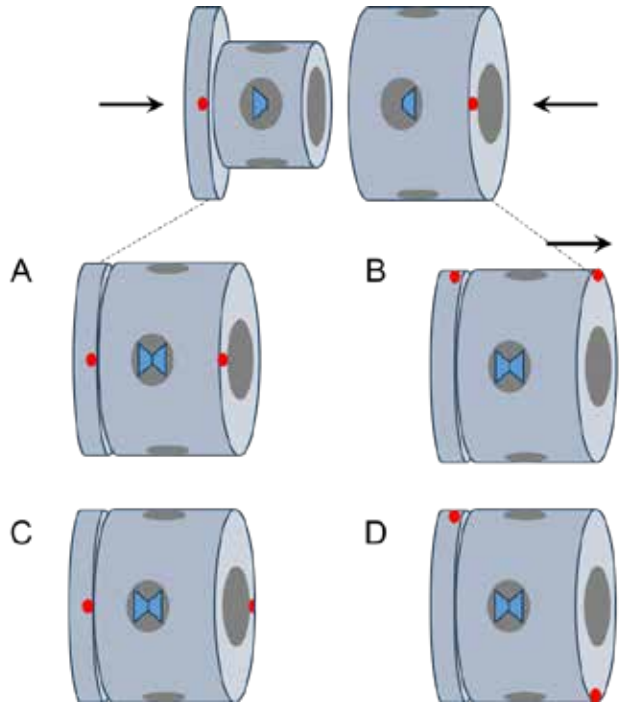
# Aligning diamonds

- With the DAC assembled and the diamonds a few hundred μm apart, align using the following 4 positions



# Aligning diamonds

- **Draw things out!** Imaginary line running down the axis of the diamond from the center of its table to the center of its culet. Represent this with a dash.
- Trying to get that diamond's axis of rotation to be collinear with the DAC's axis of rotation.




- Examples:
  - If you compare positions A and C and you see (– _) and (– ¯), diamond on the right needs to be adjusted to the axis of rotation. From A, you move the diamond on the right up.
  - Then, if B and D look like (¯ –) and (¯ –), you the diamond on the left in B needs to move down a bit
  - If A and C look like (_ _) and (_ –) you know when back in orientation A that both diamonds should move up a little bit.
  - And perhaps B and D would look like (¯ ¯) and (¯ –). So both diamonds should be moved down a little bit when in position B.

# Supplies!

- DAC work is all about fine manipulations
- The basics:


High-mag microcope
- Practical note: lots of light!

Hex (Allen) key/wrench
- 5/32” (or 4 mm) for main screws
- 3/32” for set screws

Needle for manipulation
- Practical note: tungsten needles are versatile, robust
- Can also use glass capillary

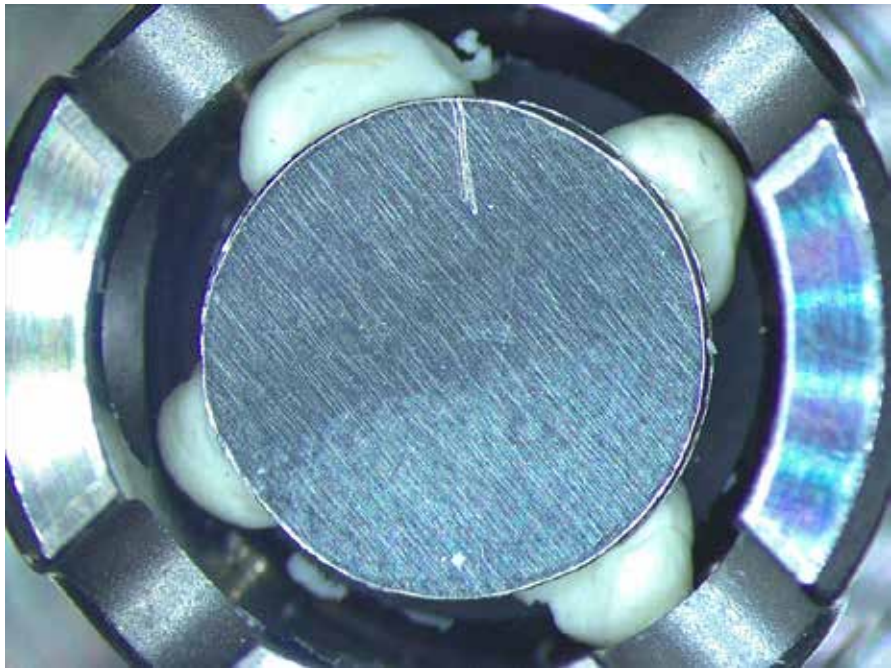
Cotton swabs
- Practical note: type matters! Many leave particles/residue
- Want ones with fine tip

Needle-nose tweezers

<u>Other</u>
- Razor blades
- Toothpicks (metal scratches, these don’t)
- Plastic baggies (so many small parts!)
- Solvents (acetone, isopropanol)
- WD-40 (lubricate piston+cylinder)
- Sand paper (sharpen needle, make piston fit better)

# Gaskets

- Choice of gasket depends on experiment:



**Stainless Steel**

- Versatile, cheap
- Undergoes α-to-ε transition ~13 GPa

**Re/W**

- More robust, less likely to fail
- More expensive

**Be**

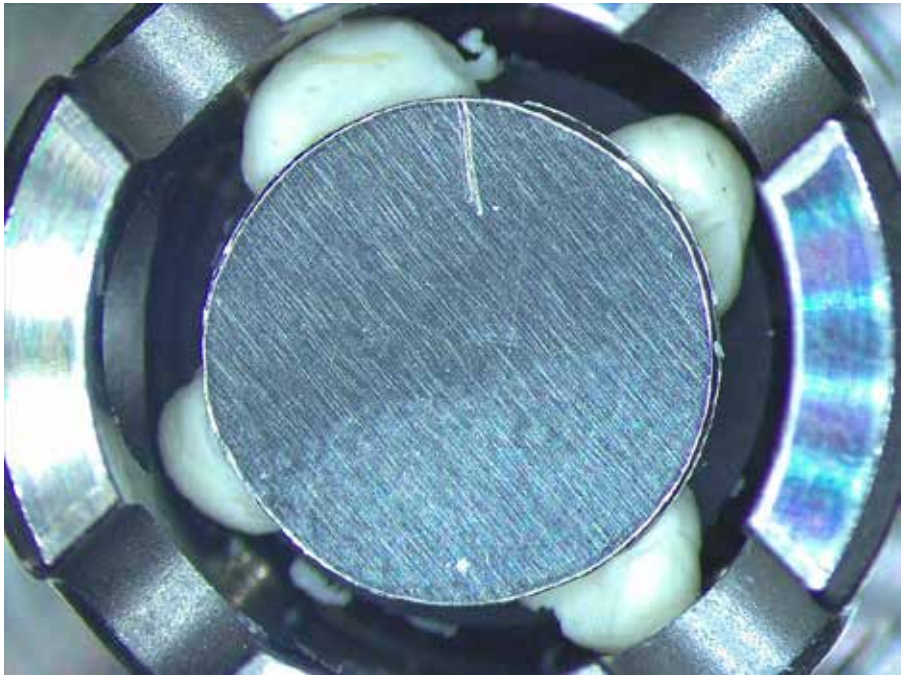
- X-ray transparent (used for XAS measurements)
- Toxic

Practical note:

- Far cheaper to buy sheet of steel (~250 μm typically) and use a hole-punch set to punch out discs

# Gasket supports

- Gasket should be supported (typically on the piston side) to ensure even compression

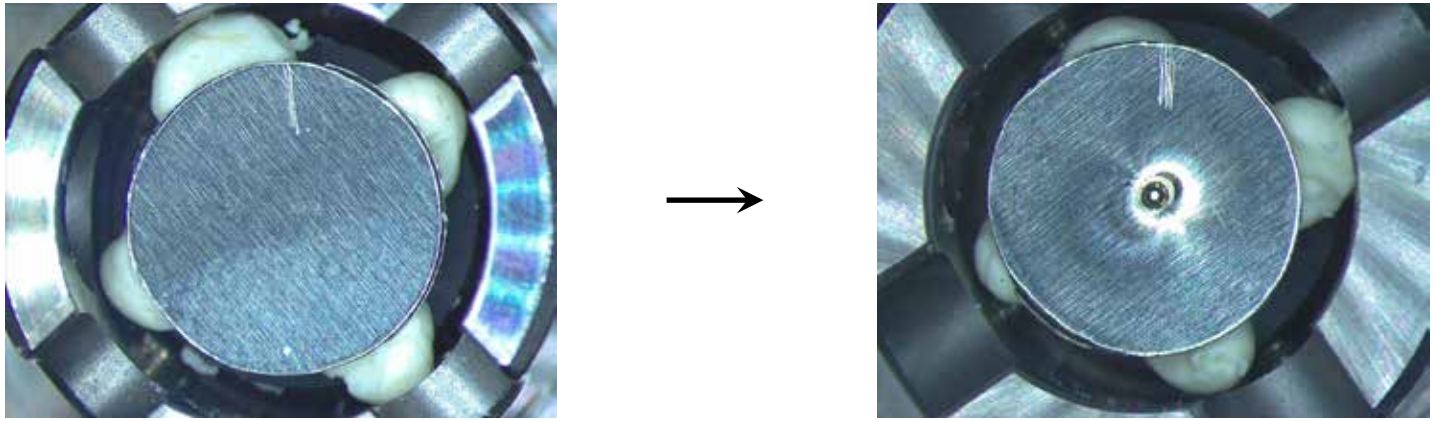


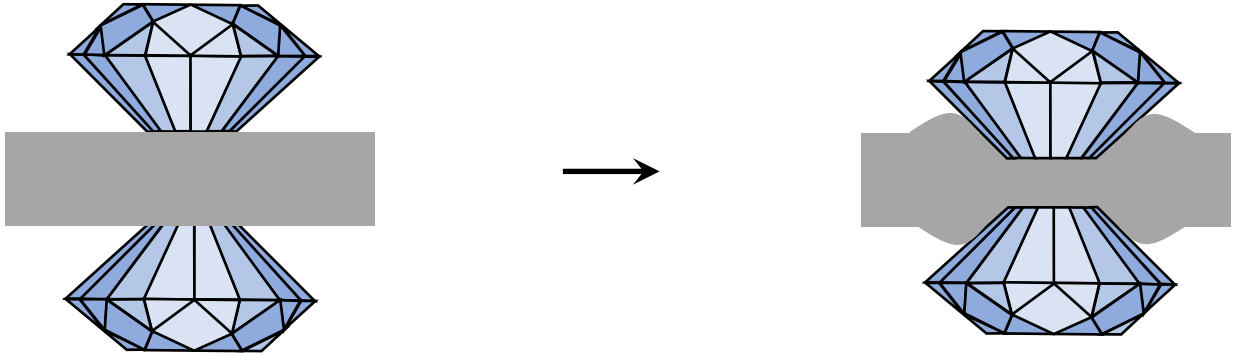
Practical note:

- Modeling clay is inexpensive and get the job done (beware oils from it!)
- Wax also can work but is stiffer and stickier which can frustrate

# Pre-indentation

- It is critical to pre-indent gaskets
  - During compression a lot of material displacement, deformation, and phase transitions occur
  - Pre-indentation helps thin the gasket near the sample to an appropriate thickness, stabilize it (higher max *P*), and guide diamonds back into same spot

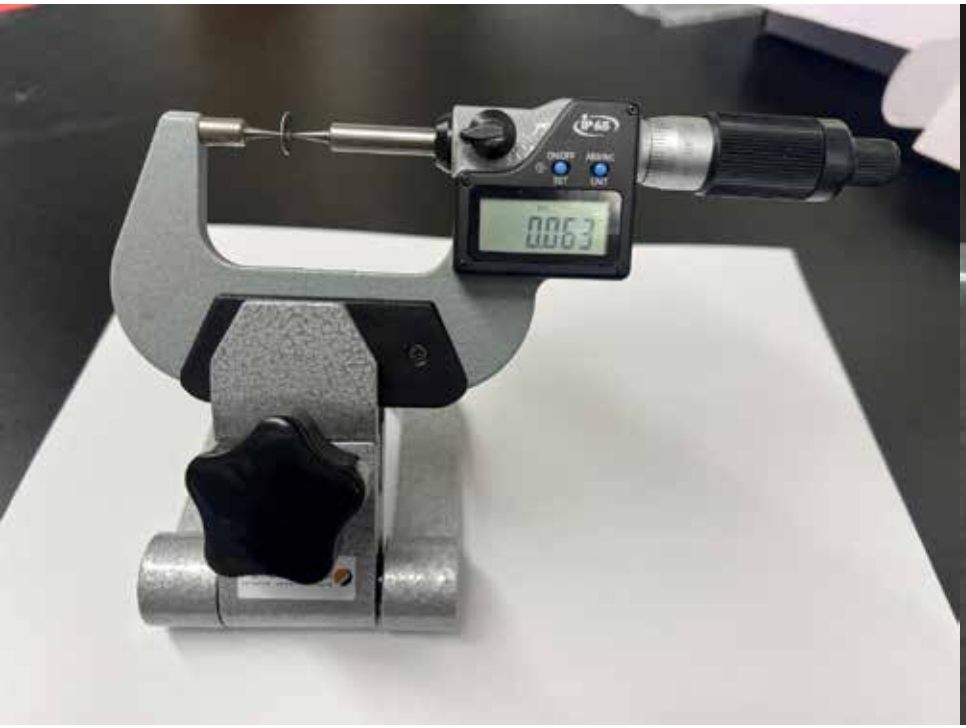


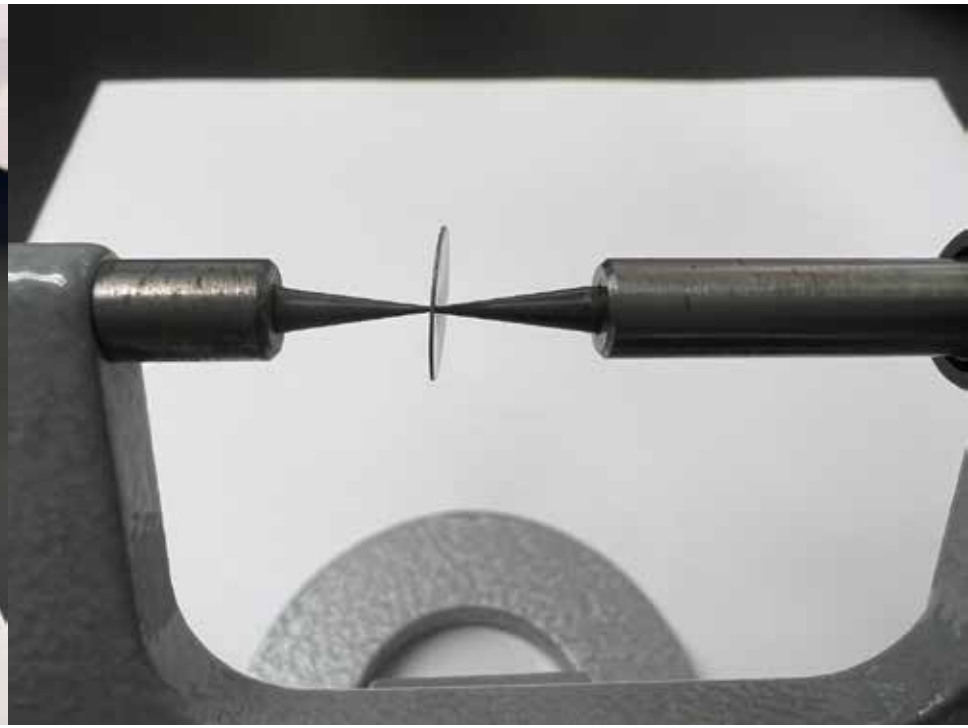


Practical note: for pre-indentation, typically go to at least half of your final target pressure for the experiment

# Pre-indentation

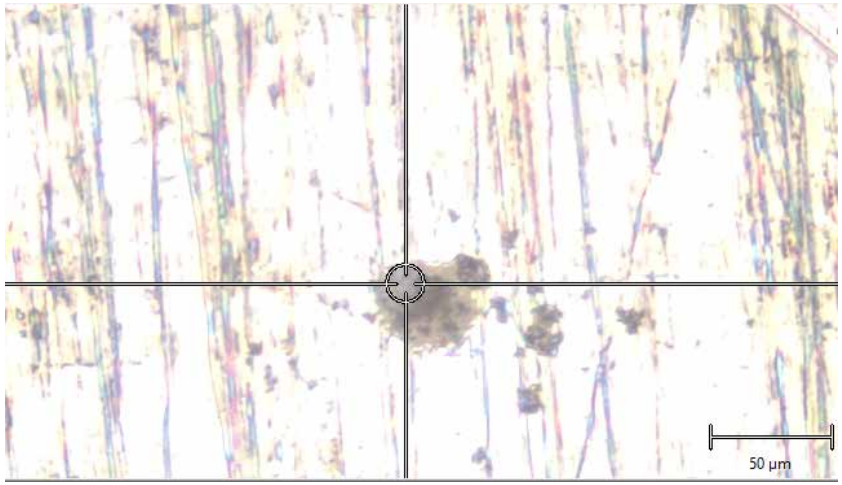
- Target gasket thickness is ~20 to 50 µm
- Measure using micrometer

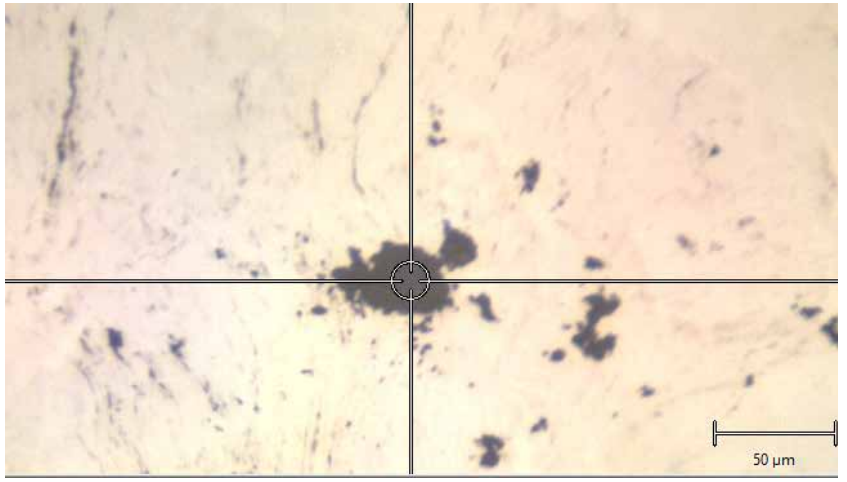


# Pre-indentation

- Phase transition of steel ca. 13 GPa
  - go past this pressure regardless of final target

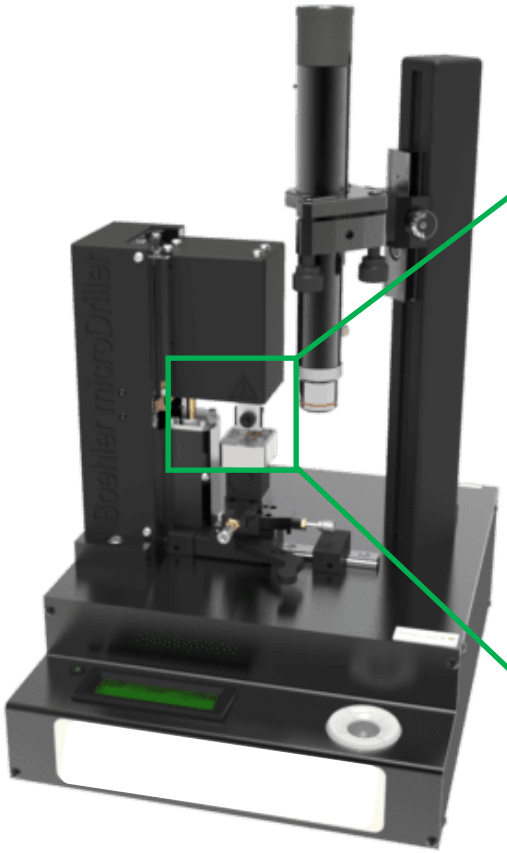


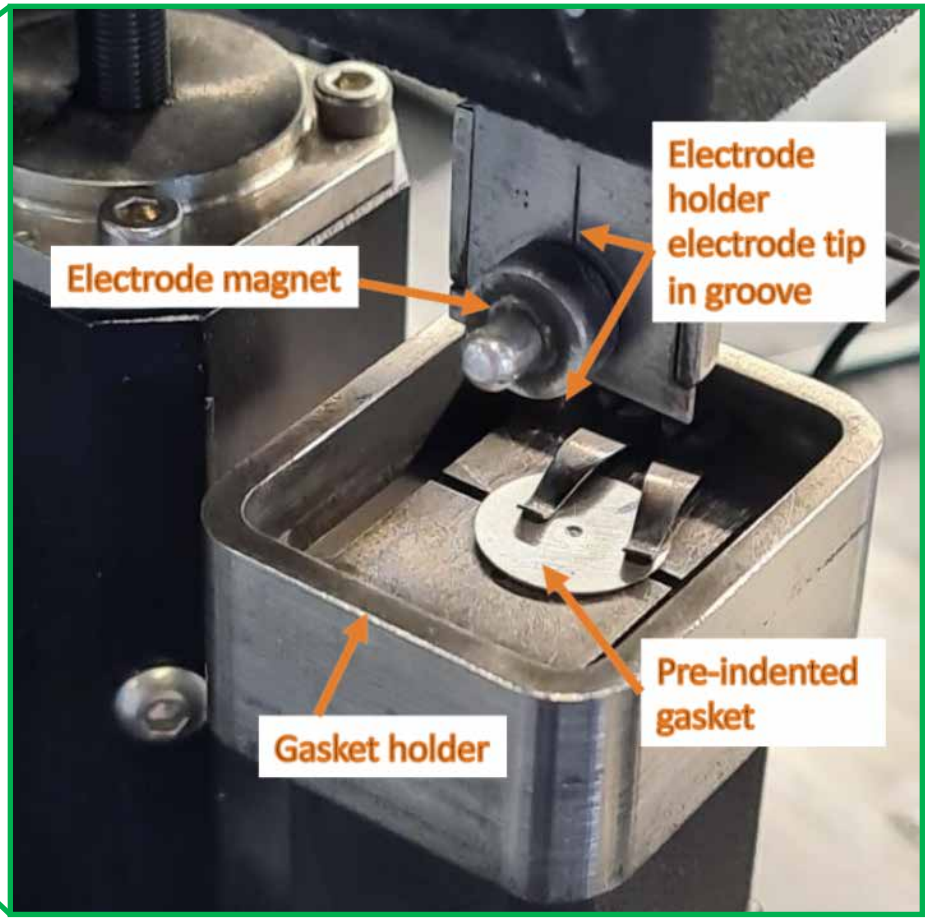

Practical note: you can have a rough sense of pressure by crushing some ruby on the gasket surface (see later)

# Drilling

- Two main options:
  - Laser drilling: precise but few labs have this option
  - Electric discharge machine drilling: finnicky but more readily available



Microdriller from Almax-EasyLab (almax-easylab.com)



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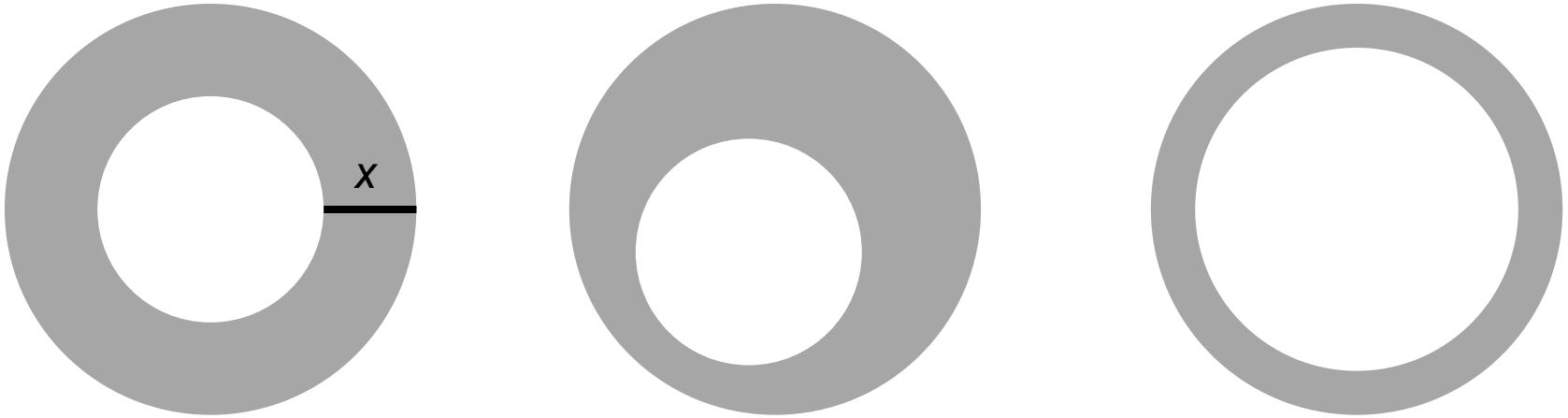



good bad bad

Practical note: ideal *x* value is ~75 to 100 µm (no less than 50 µm when possible)

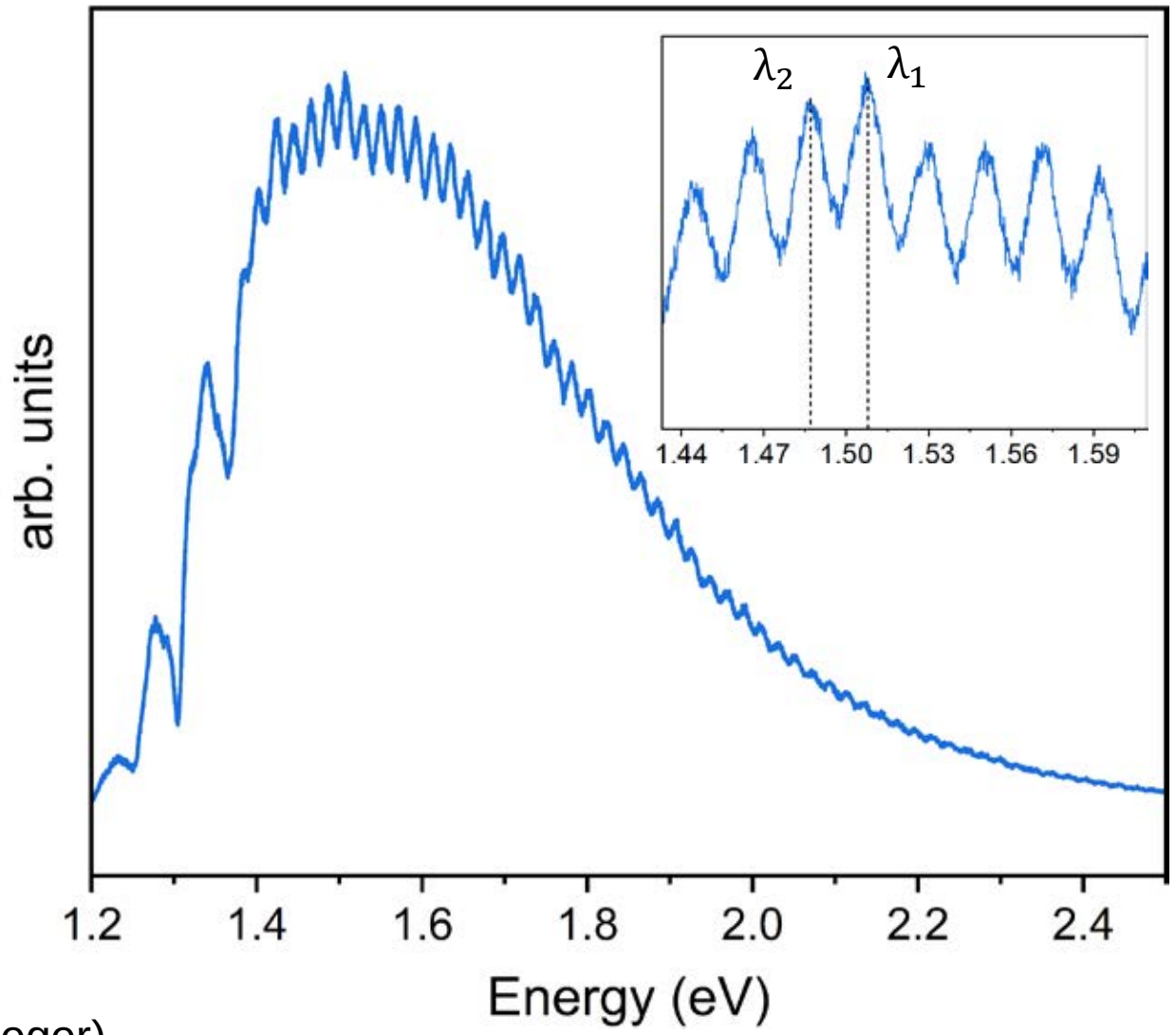
# Another Method to Measure Thickness

- Interference fringes measured using a spectrometer (e.g., on Raman microscope) of transmitted white light give accurate sample chamber height (i.e., gasket thickness)
  - Can measure empty sample chamber or if sample/medium is transparent

$$\boldsymbol{2nd = k\lambda_1}$$

and

$$\boldsymbol{2nd = (k-1)\lambda_2}$$

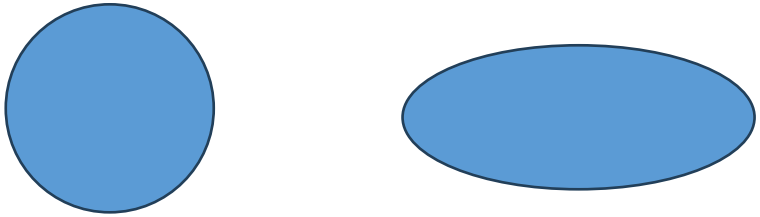



where: $n$ = refractive index
$d$ = thickness
$k$ = order number (integer)
$\lambda_i$ = wavelength at peak $i$

# Even Force

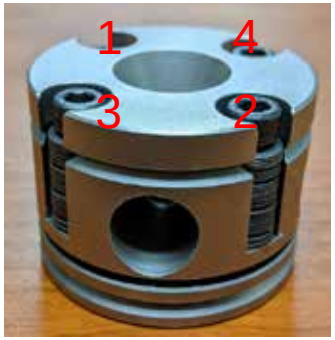
- Make sure you are applying even force to the diamonds, otherwise gasket rupture is likely

**Gasket Hole**



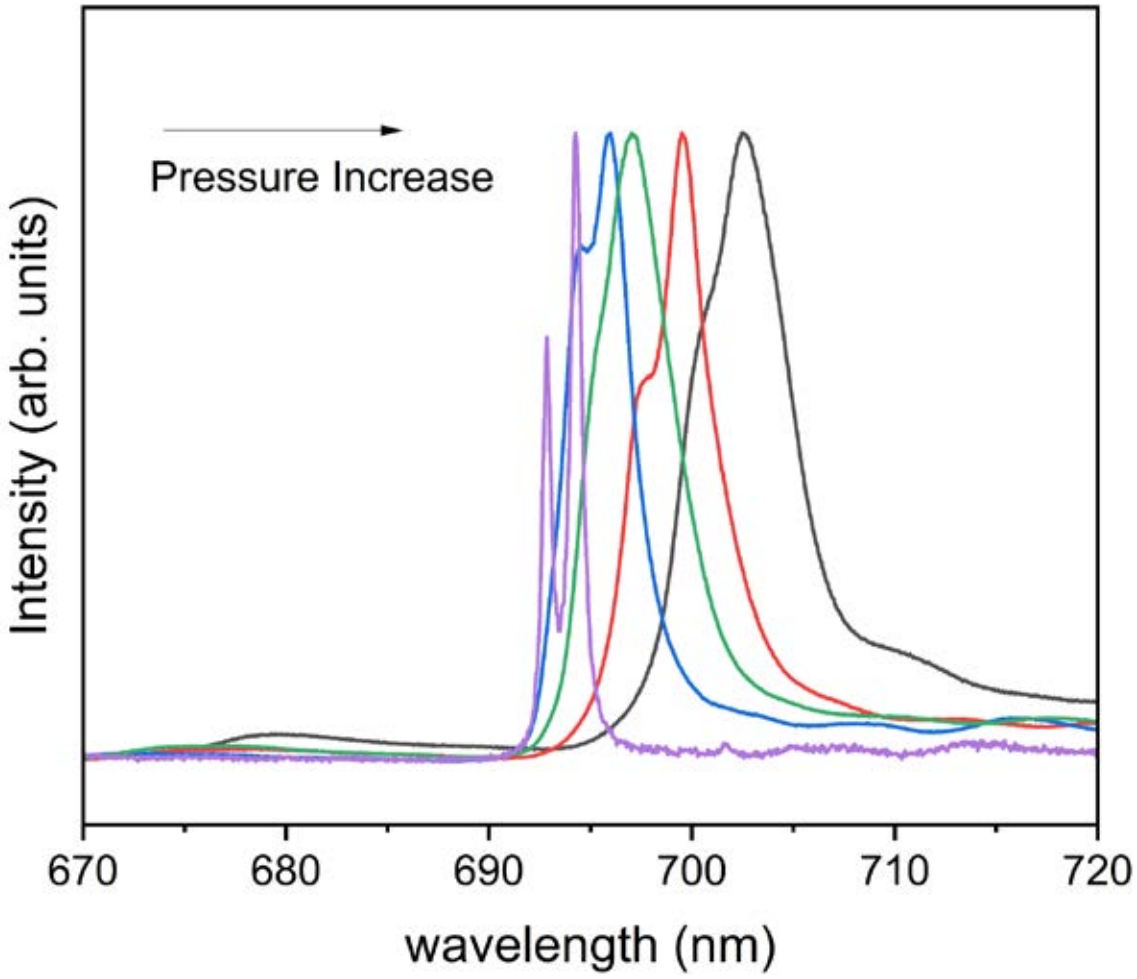
good bad

Practical note: alternate which screws you tighten and keep track of how much you turn each time



# Measuring Pressure

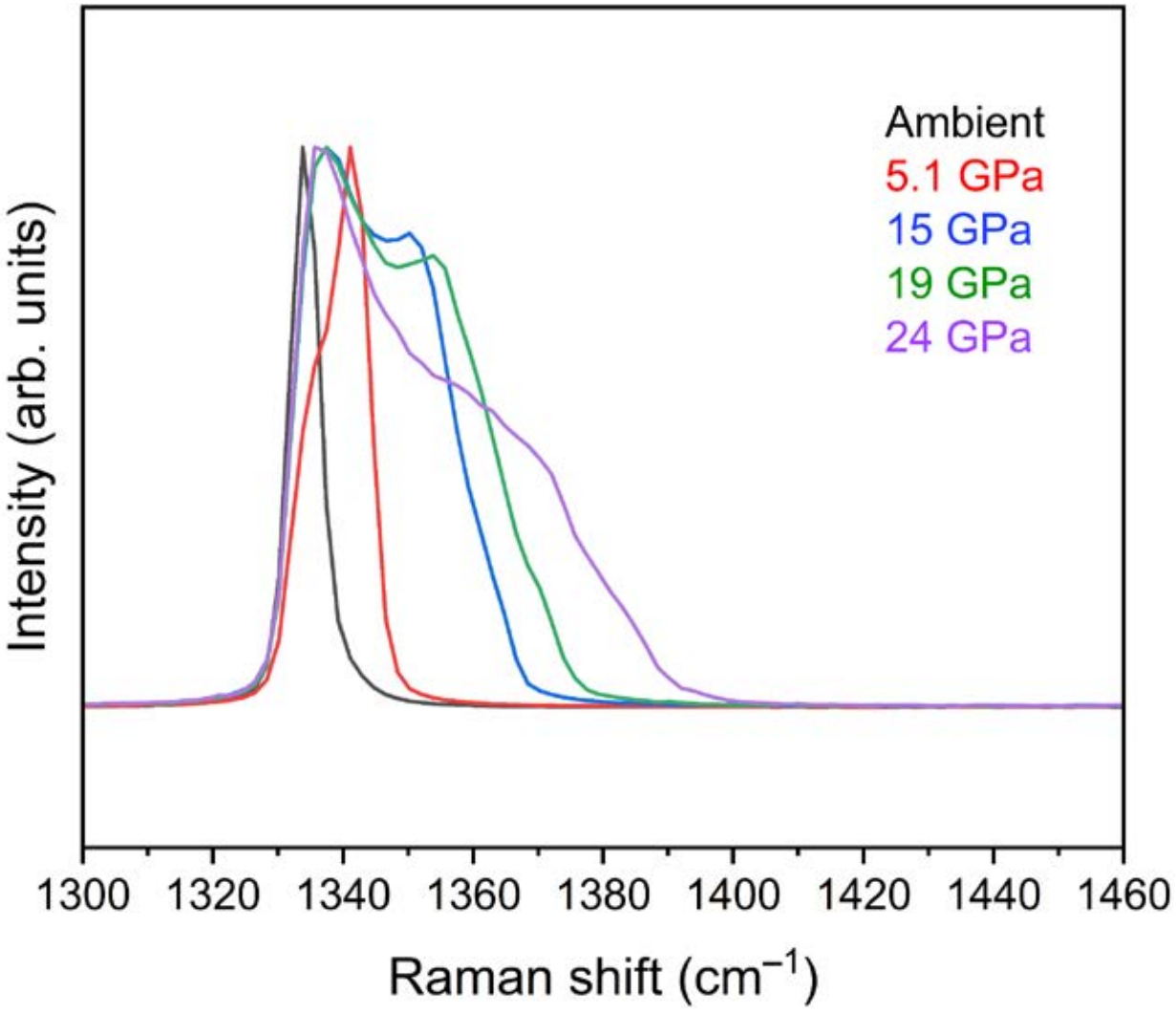
- Ruby fluorescence shifts predictably as a function of pressure!




Practical note 1: can excite using typical Raman laser wavelengths (532, 633 nm)
Practical note 2: isolated ruby spheres fluoresce brightly and can then be avoided for spectroscopy/diffraction measurement (unlike powder)
Practical note 3: on a given pressure value is ca. 5%
Practical note 4: measure pressure before and after experiment to see if it has changed

Mao, Xu, Bell. *J. Geophys. Res.* **1986**, *91*, 4673.
Dewaele, Torrent, Loubeyre, Mezouar. *Phys. Rev. B* **2008**, *78*, 104102

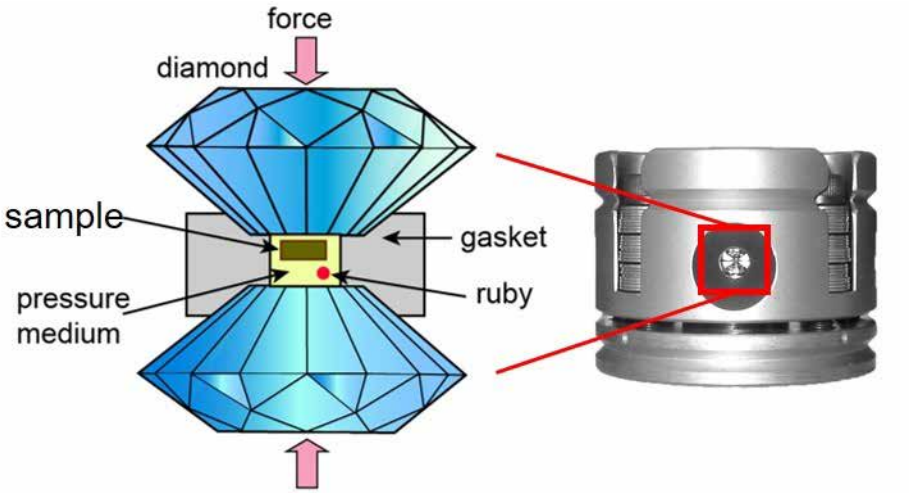
# Measuring Pressure: Other Options




- Diffraction standard (inert, strongly diffracting)
  - Alkali halides; Metals such as Au, Pt, Cu
  - Fit diffraction pattern and extract lattice parameter(s); match to known compression behavior
  - Downside: now you have more peaks in your pattern…
- Raman peak of diamond
  - Only a rough guide

# Pressure Media

- One of the most important aspects of any DAC experiment is the pressure medium!



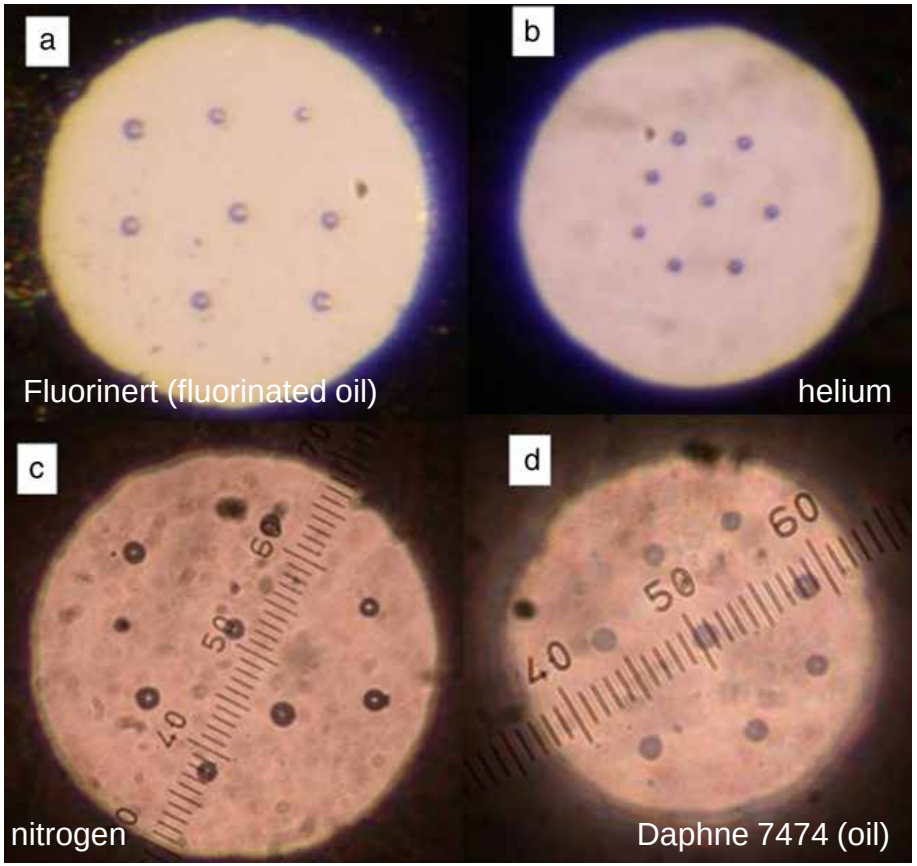

- You apply uniaxial force, but this is simply to reduce the sample chamber volume and compress the medium
- Medium imparts force on sample

- **All media will become solid at some pressure** and will therefore not uniformly compress the sample
- Choice of medium is based on: reactivity with sample, ease of loading, hydrostatic limit, and numerous other factors

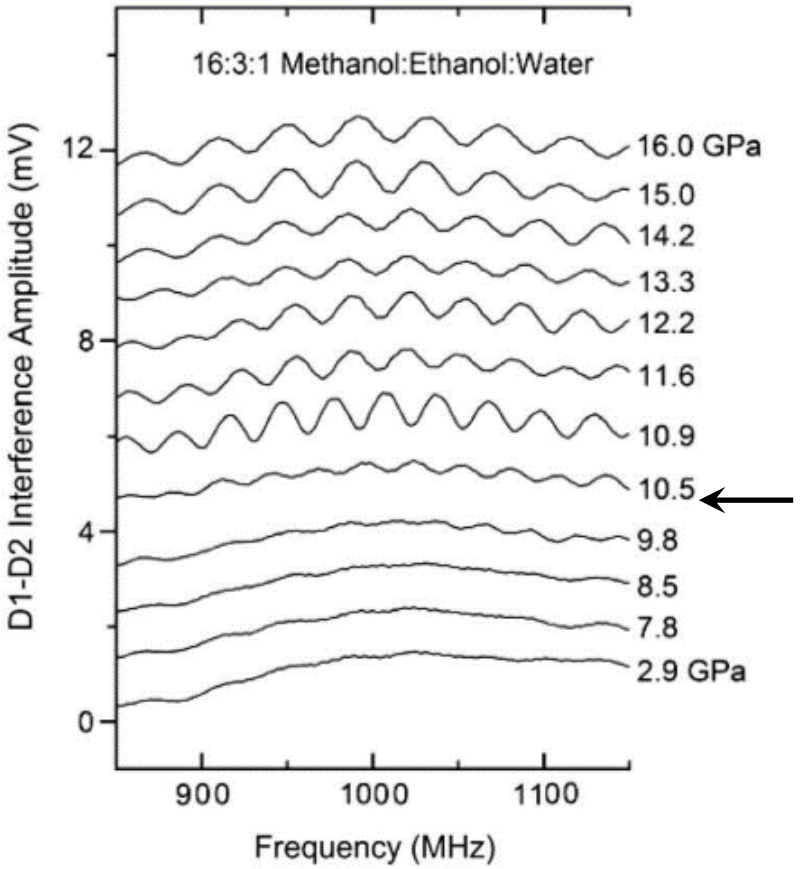
Angel, Bujak, Zhao, Gatta, Jacobsen *J. Appl. Crystallogr.* ***2007****, 40*, 26.
Klotz, Chervin, Munsch, Marchand *J. Phys. D: Appl. Phys.* ***2009,*** *42*, 075413.

# Pressure Media

- How were limits determined?




ruby fluorecence

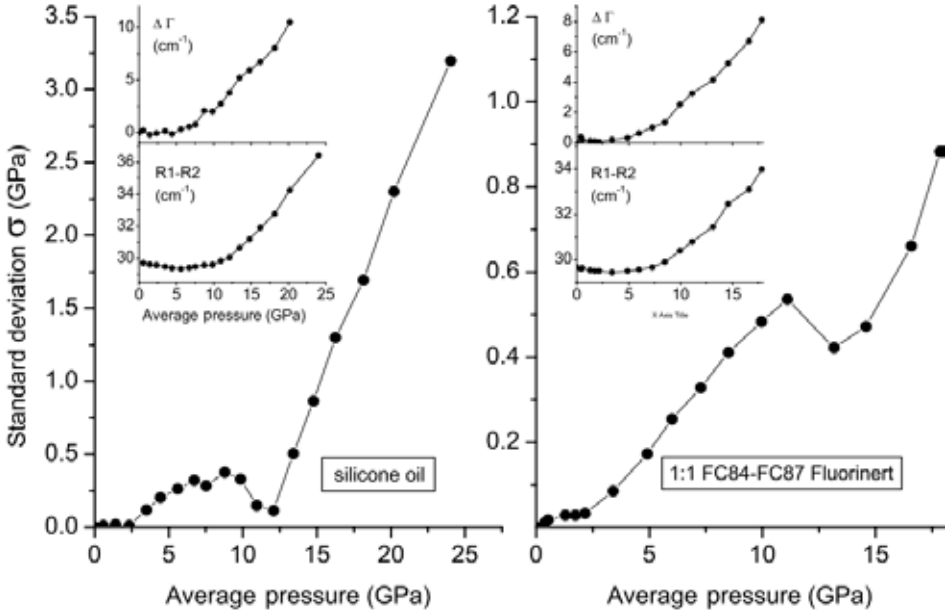



interferometry

Klotz, Chervin, Munsch, Marchand *J. Phys. D: Appl. Phys.* ***2009,*** *42*, 075413.

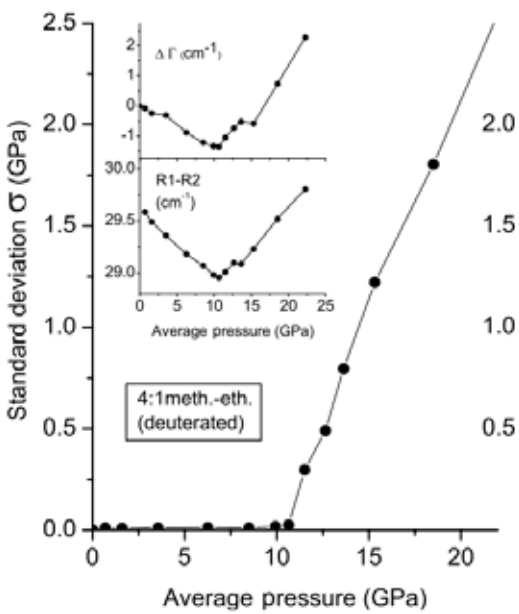
Angel, Bujak, Zhao, Gatta, Jacobsen *J. Appl. Crystallogr.* ***2007****, 40*, 26.

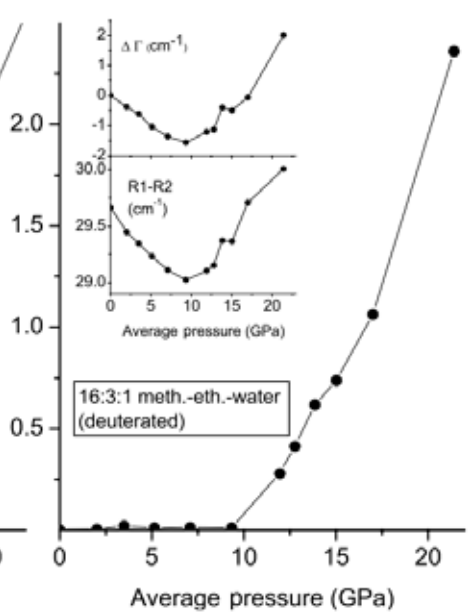
# Pressure Media

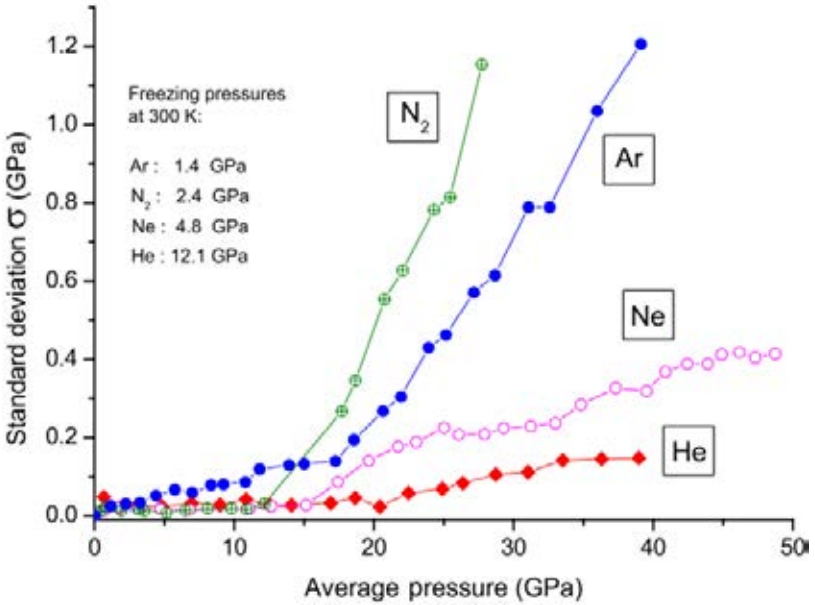








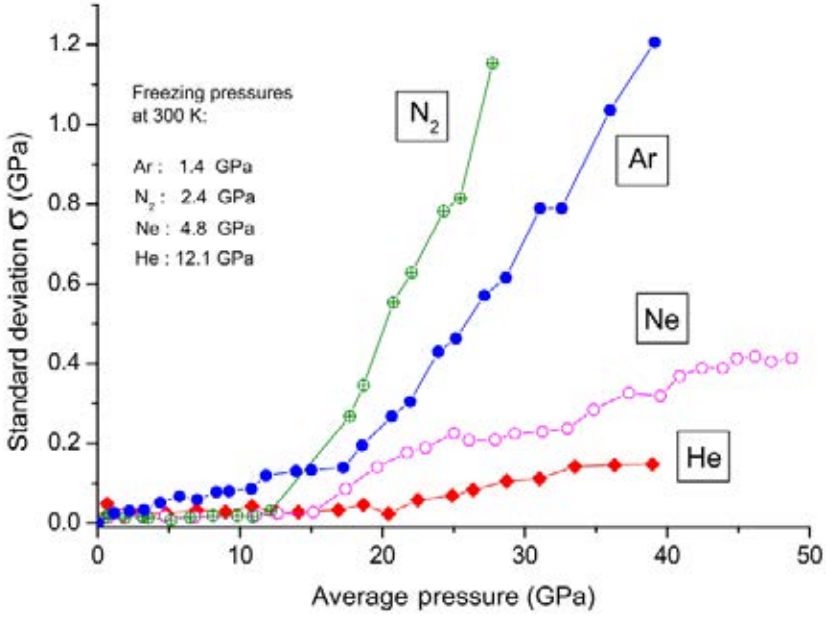




Klotz, Chervin, Munsch, Marchand *J. Phys. D: Appl. Phys.* ***2009,*** *42*, 075413.

# Pressure Media

- Summary
  - Helium is the best but cumbersome to load (fun fact, it embrittles diamonds over time by intercalating!)
  - Oils are easy to load but not very hydrostatic
  - MeOH:EtOH:$H_2O$ is okay but somewhat volatile and can cause solids already in sample chamber to move

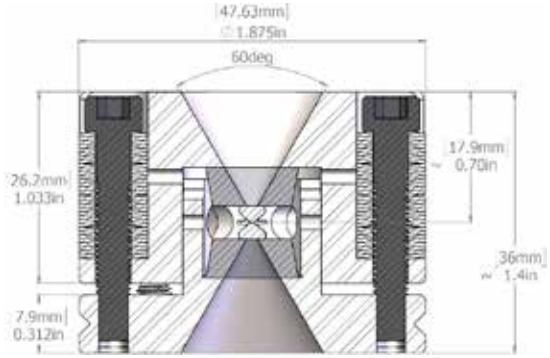



Practical note 1: can use the sample itself to be its own medium (works well if sample is soft)
Practical note 2: alkali halides are pretty soft, transparent, and can act as diffraction standard. 3-in-1!

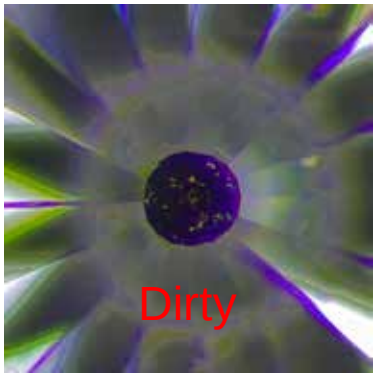

Angel, Bujak, Zhao, Gatta, Jacobsen *J. Appl. Crystallogr.* ***2007****, 40*, 26.
Klotz, Chervin, Munsch, Marchand *J. Phys. D: Appl. Phys.* ***2009,*** *42*, 075413.

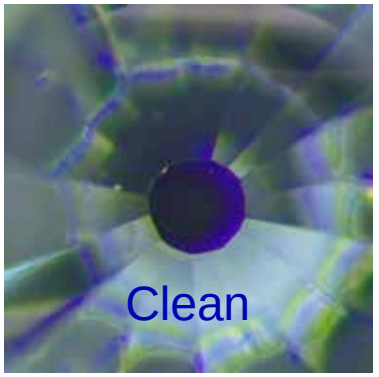
# Sample Loading

1. Ensure same number and configuration of washers on each screw



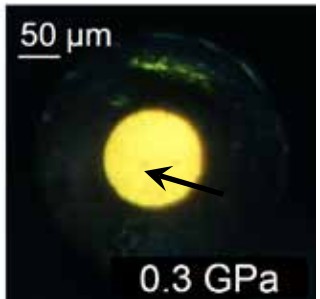

2. Clean diamonds well!! (not so easy)




3. Add sample bit by bit using tip of tungsten needle
   - Periodically compact sample with top diamond to fill chamber completely (but avoid applying pressure)
   - Clean top diamond regularly (avoids sticking)

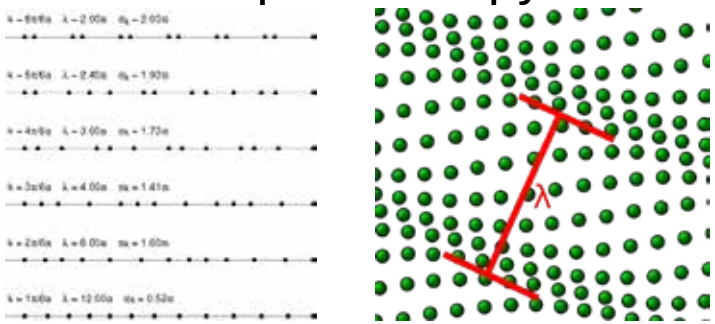
4. Place ruby sphere on top diamond and bring cell together
   - Choose spot carefully (off-center to avoid interference, avoid edge)
   - Keep track of ruby as you close and take a photo!



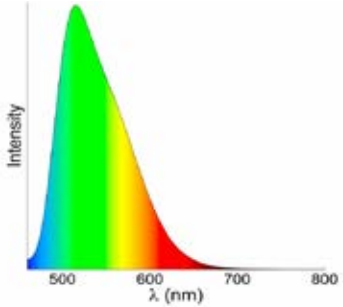
# “Normal” vs. “Difficult” Measurements

## “Normal”

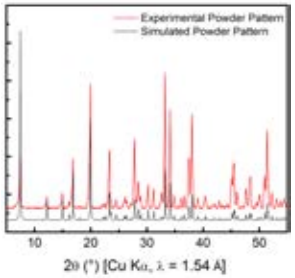
- Raman spectroscopy




- Photoluminescence

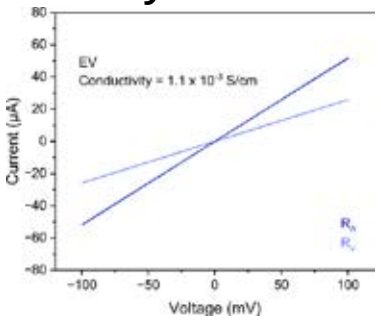



- Powder X-ray diffraction

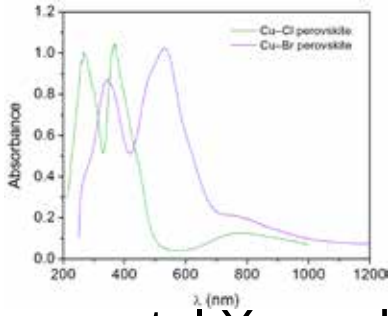



## “Difficult”

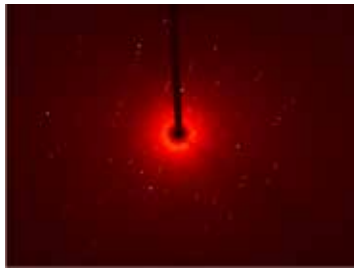
- Conductivity



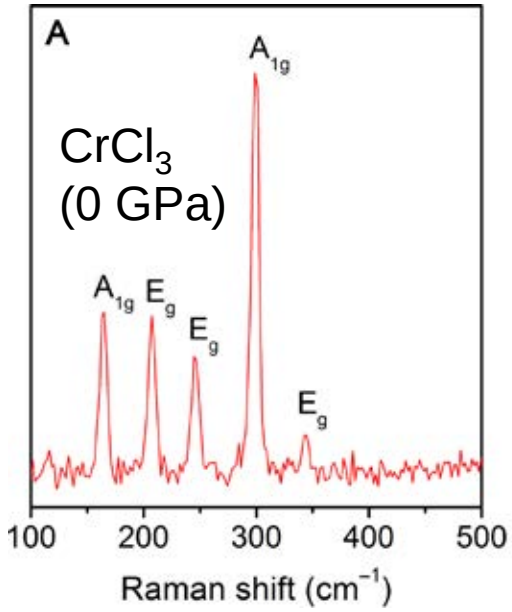

- Absorption spectroscopy

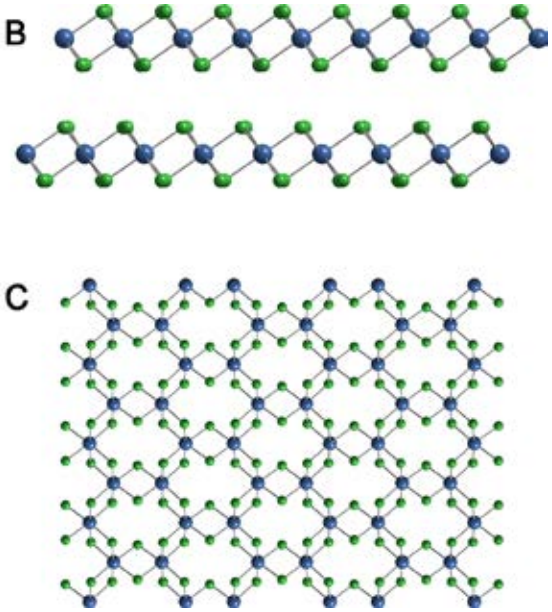


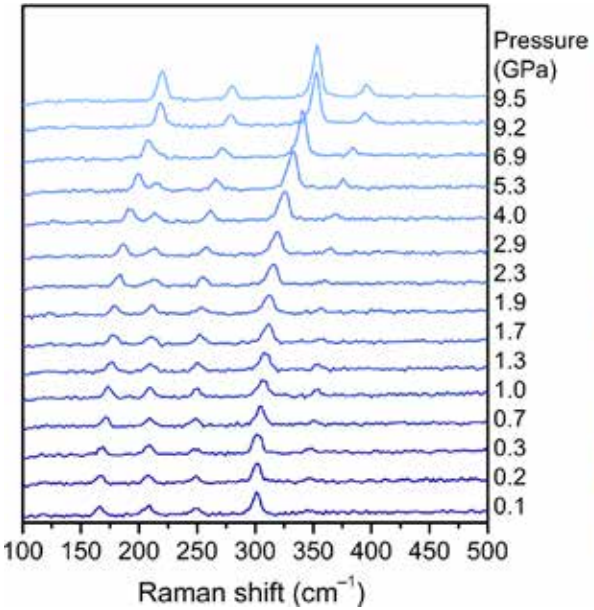

- Single-crystal X-ray diffraction

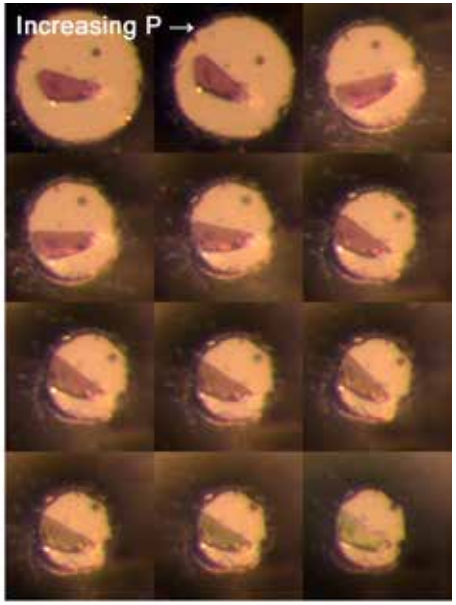


# Raman Spectroscopy



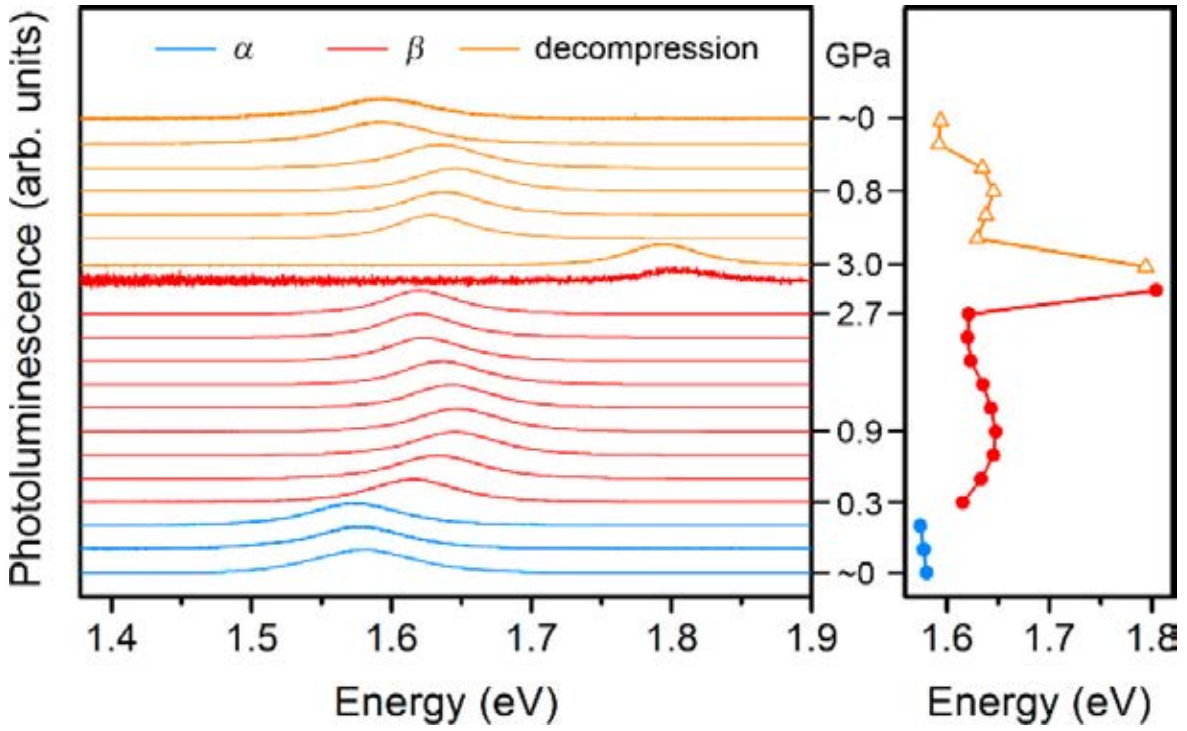




Practical notes:

- Measure using Raman microscope (available in many individual or user labs)
- Typical Raman laser wavelengths (532, 633 nm) so ensure your sample is compatible
  - Ideally does not absorb and is stable to laser light
- Start low power and ramp up to avoid laser damage (look at sample often!)
- Measure different spots
- Generally, peaks should move to higher Raman shift at higher pressure (lattice stiffening)
- Measure over a wide range
- Beware cosmic rays (very sharp)
- Wait for sample to equilibrate pressure*

*applies to virtually all high-pressure experiments

# Photoluminescence Spectroscopy




$(CH_3NH3)PbI_3$

Practical notes:

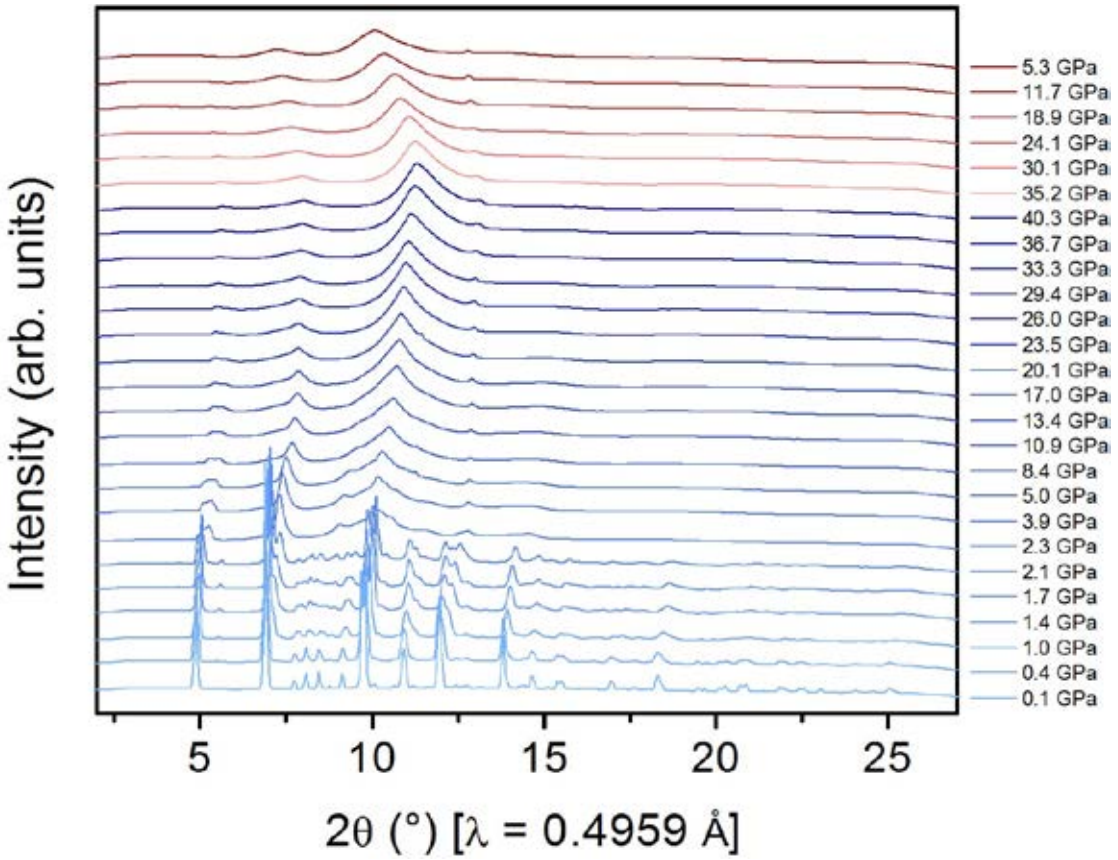
- Also measure using Raman microscope (if laser is of sufficient energy to excite sample)
  - Can also use custom setup, but that gets tricky
- Sample must photoluminesce
- Similar concerns as with Raman experiment w.r.t. laser stability
- Watch out for photo-induced reactivity
- Measure different spots
- Know your radiative mechanism in order to be able to comment on its evolution



Jaffe, Lin, Beavers, Voss, Mao, Karunadasa *ACS Cent. Sci.* ***2016,*** *2*, 201.

# Powder X-ray Diffraction

- Typically requires synchrotron, though some lab sources can work (Ag anode and long collection times)
- Most common method to more directly probe structural evolution

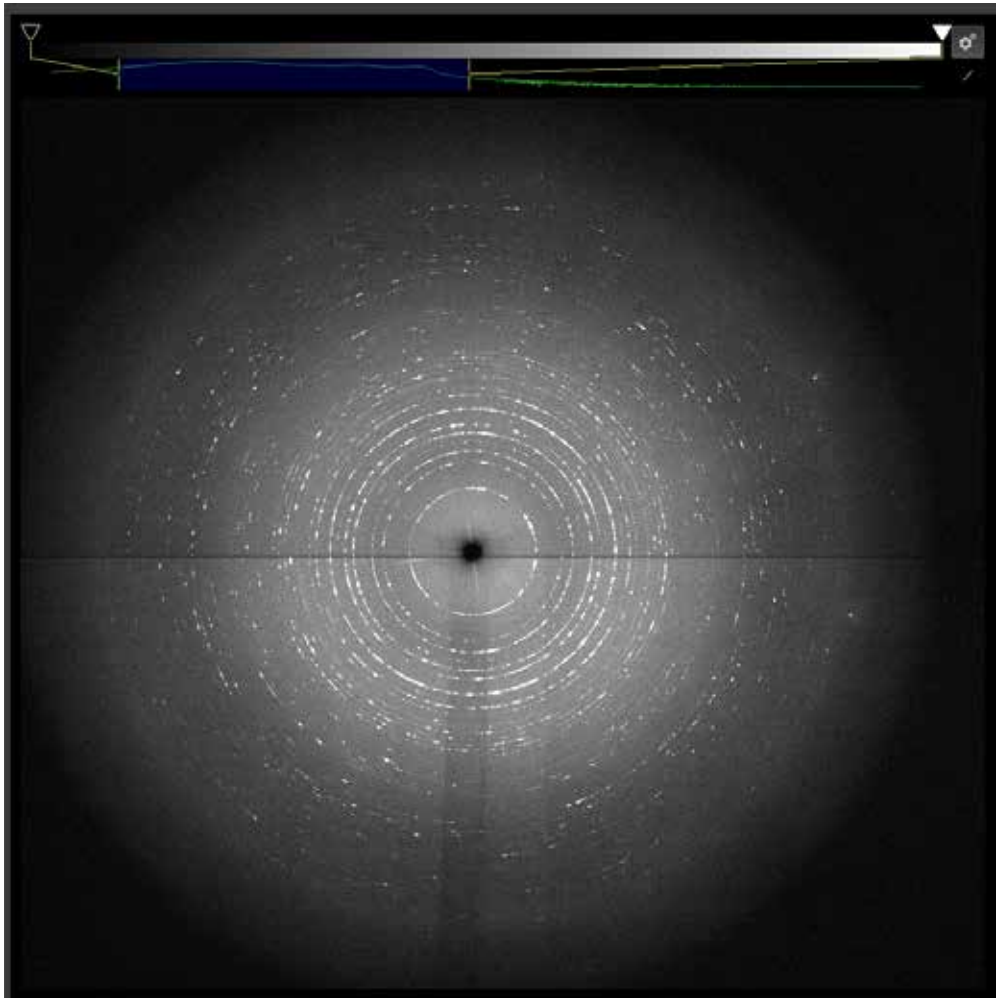



Practical notes:

- Choose X-ray wavelength based on absorption edges, X-ray damage, beam intensity, etc.
- If your crystallites are too large, you will get “spotty” Debye-Scherrer rings
  - Solution: grind sample (but this can induce strain/defects) or…wobble (rock back and forth on motorized stage)!

# Powder X-ray Diffraction

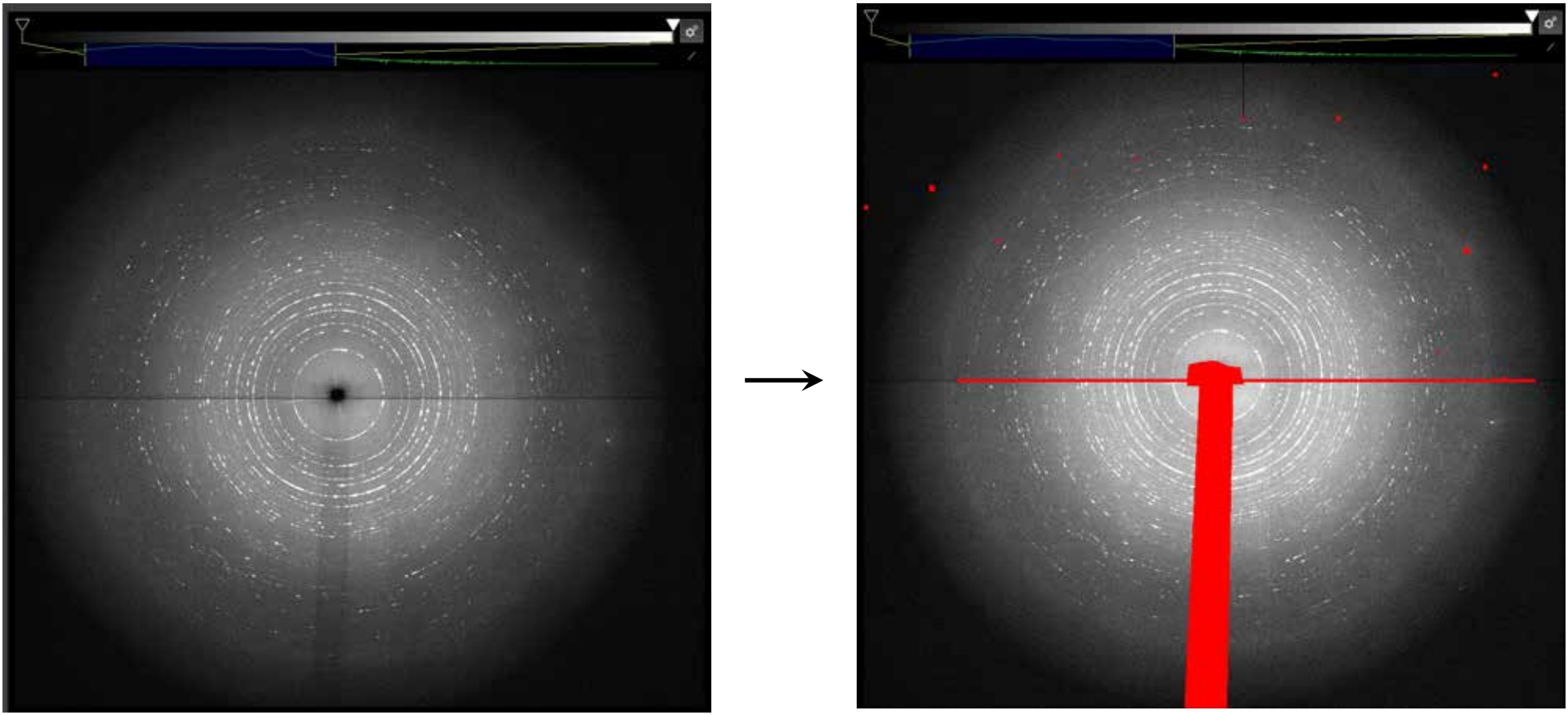
- Typically requires synchrotron, though some lab sources can work (Ag anode and long collection times)
- Most common method to more directly probe structural evolution



Practical notes:

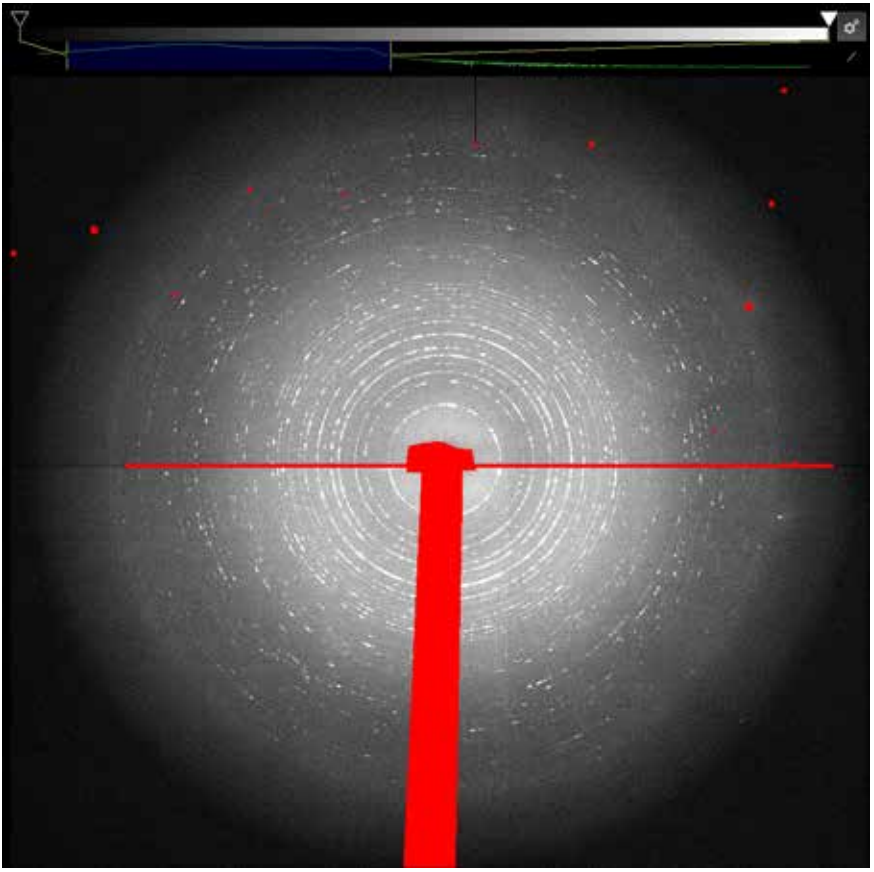
- Choose X-ray wavelength based on absorption edges, X-ray damage, beam intensity, etc.
- If your crystallites are too large, you will get “spotty” Debye-Scherrer rings
- Process data carefully
  - First calibrate detector, distance to sample, wavelength, etc. using a standard (e.g., $LaB_6$ or $CeO_2$)
- Dioptas is a very helpful free processing program for these data

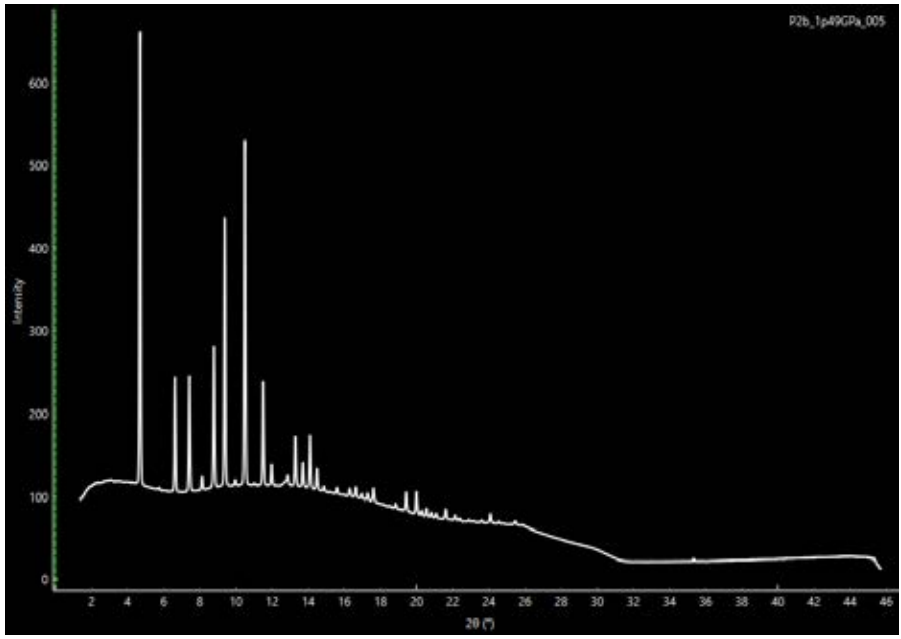
# PXRD Data Processing



- Mask out center of beam and beamstop as well as cosmic rays, diamond reflections, gasket peaks, dead pixels, etc.

# PXRD Data Processing





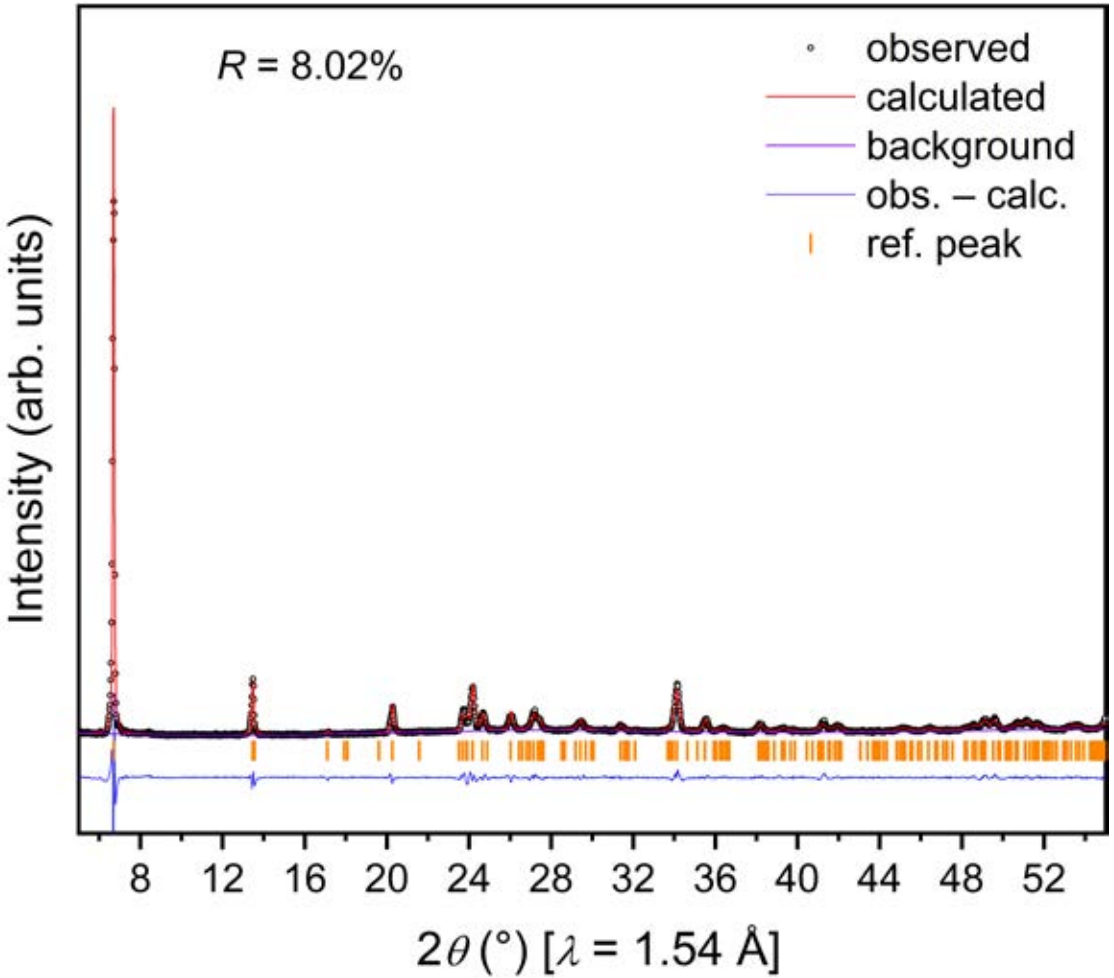

- Integrate Debye-Scherrer rings

Practical note:

- Always check your pattern against your expected pattern, as well as against gasket (e.g., bcc-Fe) and perhaps pressure medium

# PXRD Data Analysis: *Attempt* Rietveld

- Do your best to extract lattice parameters (Le Bail/Pawley) for use in equation of state fitting
- ***If*** no phase transitions have occurred, attempt Rietveld refinement, but strain, deviatoric stress, masking, small sample volume, etc. all affect intensities




Practical notes:

- Programs for determining unknown symmetry: Jade (best, but expensive), DICVOL, McMaille, TREOR (these latter 3 are often implemented in GSAS, Fullprof, etc.)
- Symmetry is often lowered by a high-pressure phase transition

# *Practical* Equations of State

1. Plot *P* vs. *V* (incorporate errors!)  *program: EoSFit (free!)
2. Fit points to 2nd order BM EOS first
3. Try 3rd order and see if the error values on $K_0$, $V_0$, and $K'$ look ridiculous

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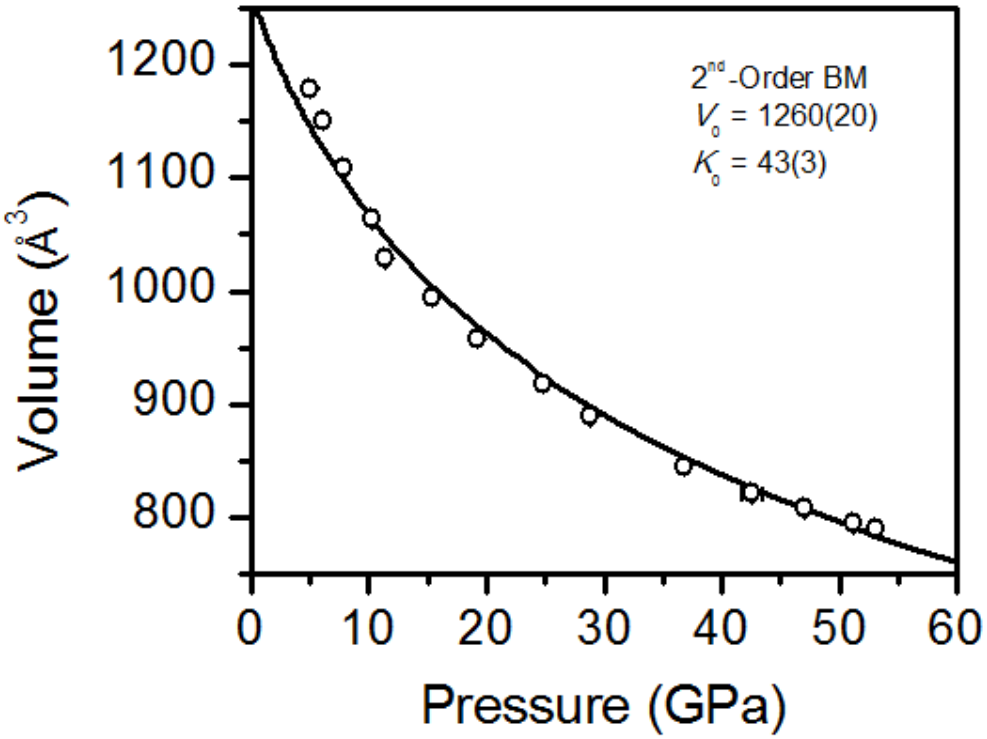

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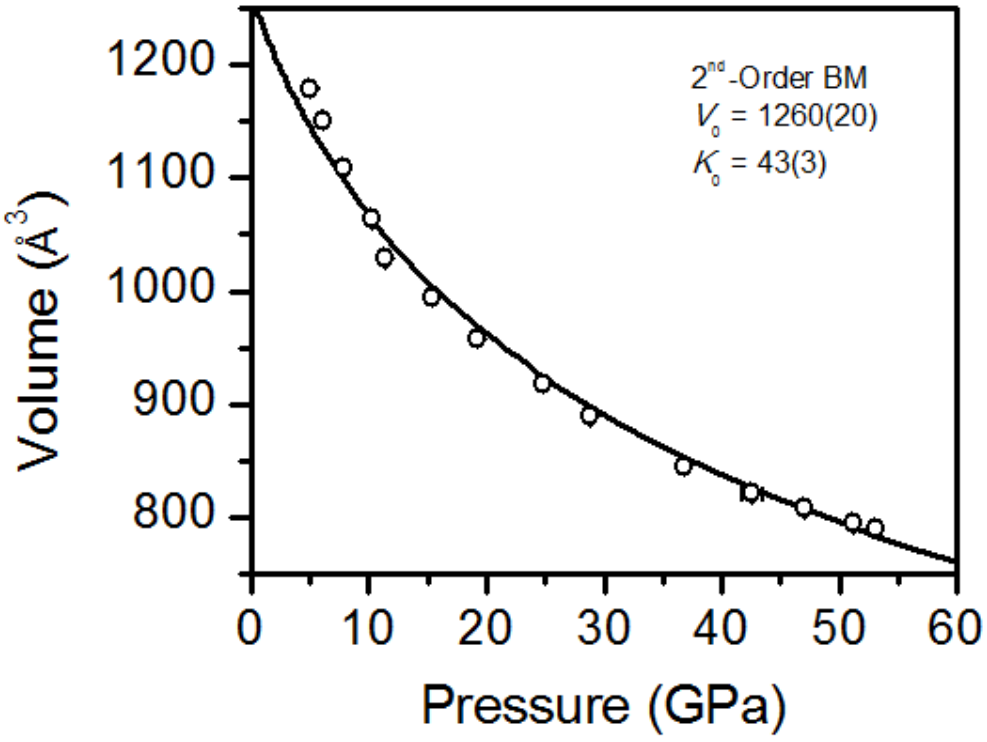
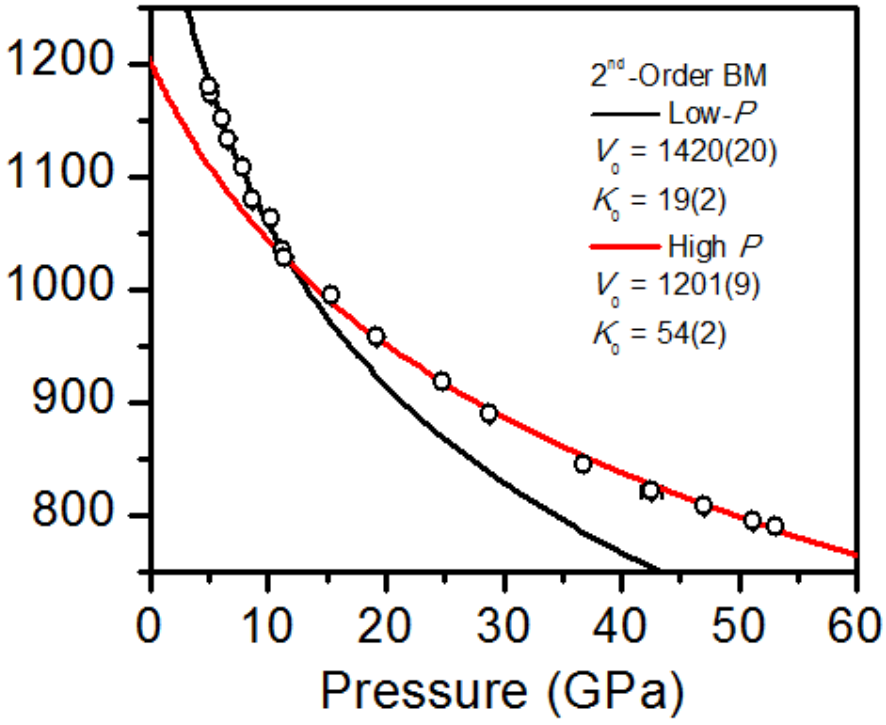
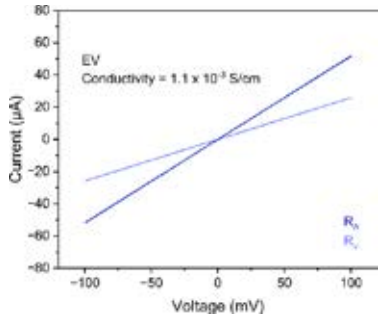



Practical note: it is possible for second-order phase transitions to occur, where symmetry/structure of material stays the same but bulk modulus has a sharp change

# “Difficult” Measurements

- Conductivity

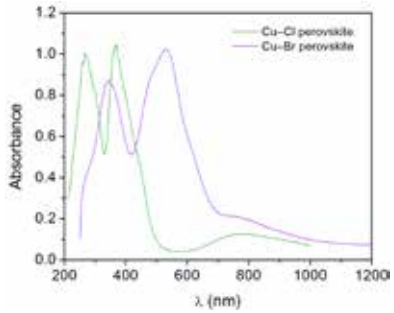



**Why?**

→

- Metal gasket is conductive!
- Leads are delicate

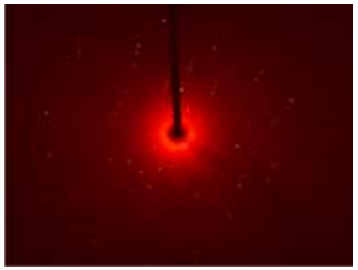
- Absorption spectroscopy




→

- Sample is very small (instrumentation limitation)
- Need proper background
- Sample is often *too* absorbing

- Single-crystal X-ray diffraction



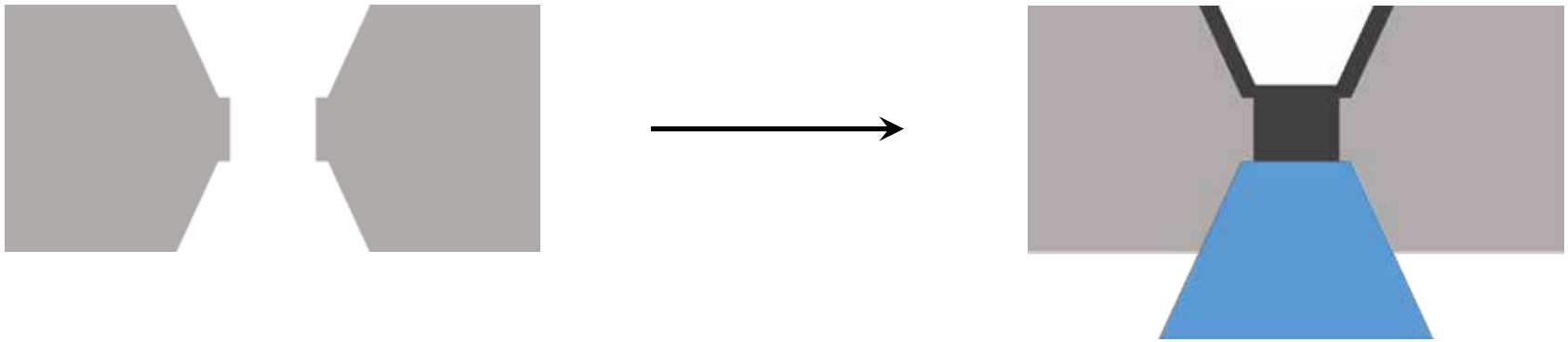
→

- Absorption correction and masking is incredibly challenging
- Intensity of beam is an issue
- Need to access wide angle-range

# Conductivity

1. Pre-indent as normal but drill out almost all of the culet-facing gasket (e.g., if culet is 300 μm, drill out 290 μm)

# Conductivity



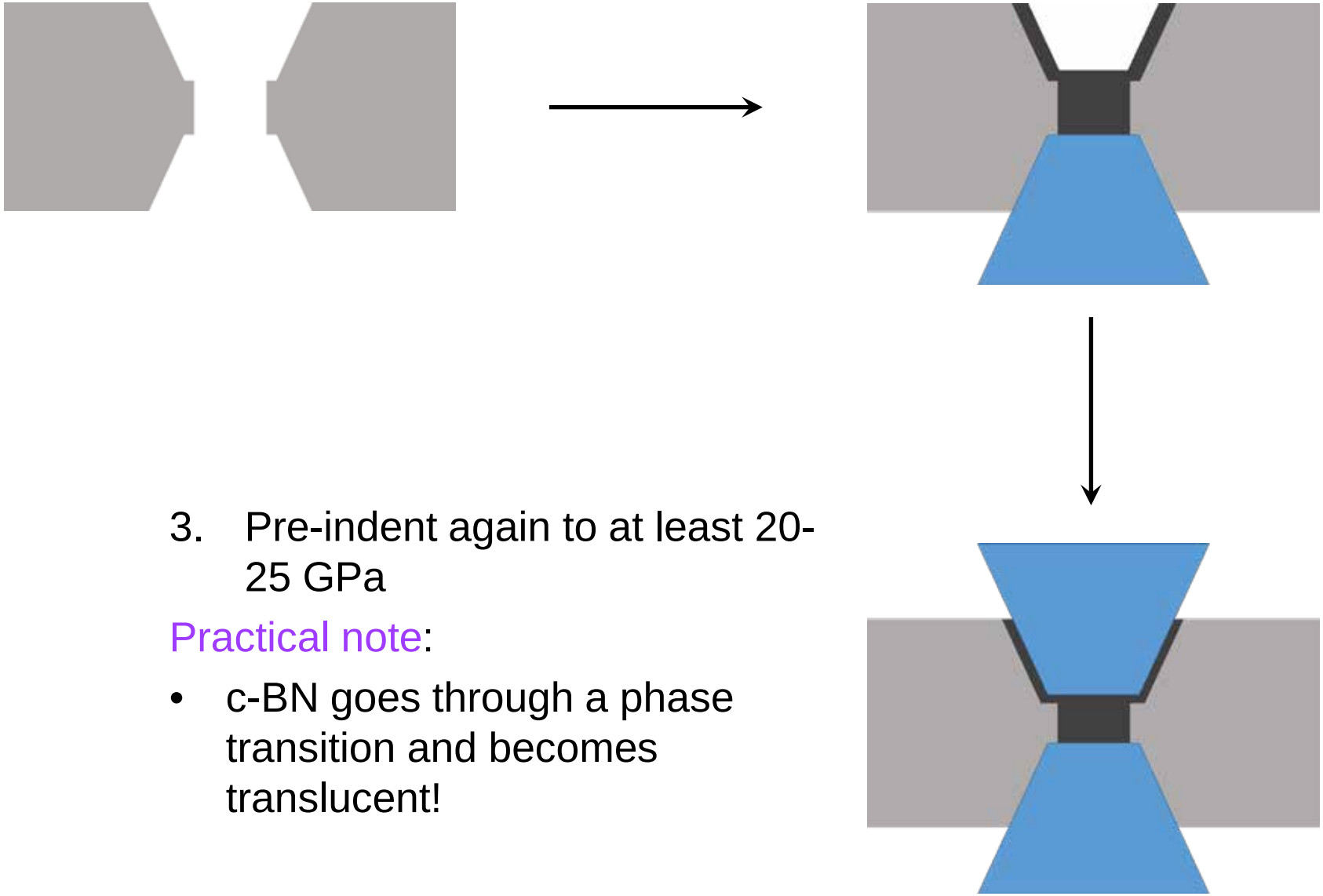
2. Coat indentation and fill sample chamber with cubic-BN powder in epoxy matrix

Practical note:

- Purchase c-BN powder from an abrasives company!
- Epoxy: EPO-TEK 353ND works well
- Takes some playing around to get consistency of matrix right—want max c-BN without it being crumbly
- This part is *hard*. One piece at a time and press down with diamond, try not to have it come apart when you raise the top diamond

Wang, Yang, Xiao, Liu, Chow, Shen, Mao, Mao *Rev. Sci. Instrum.* ***2011****, 82.*

# Conductivity

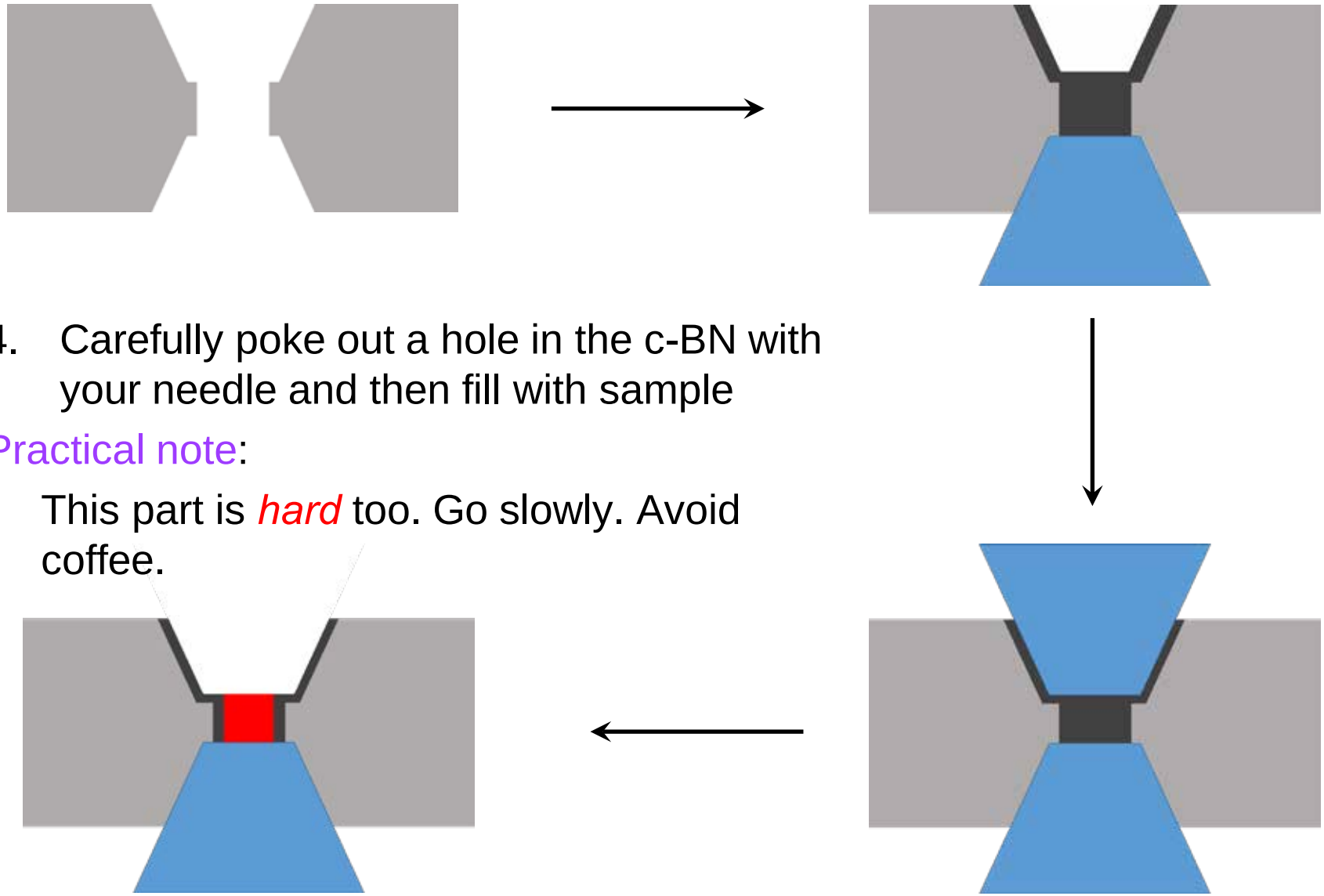


3. Pre-indent again to at least 20-25 GPa

Practical note:

- c-BN goes through a phase transition and becomes translucent!

# Conductivity

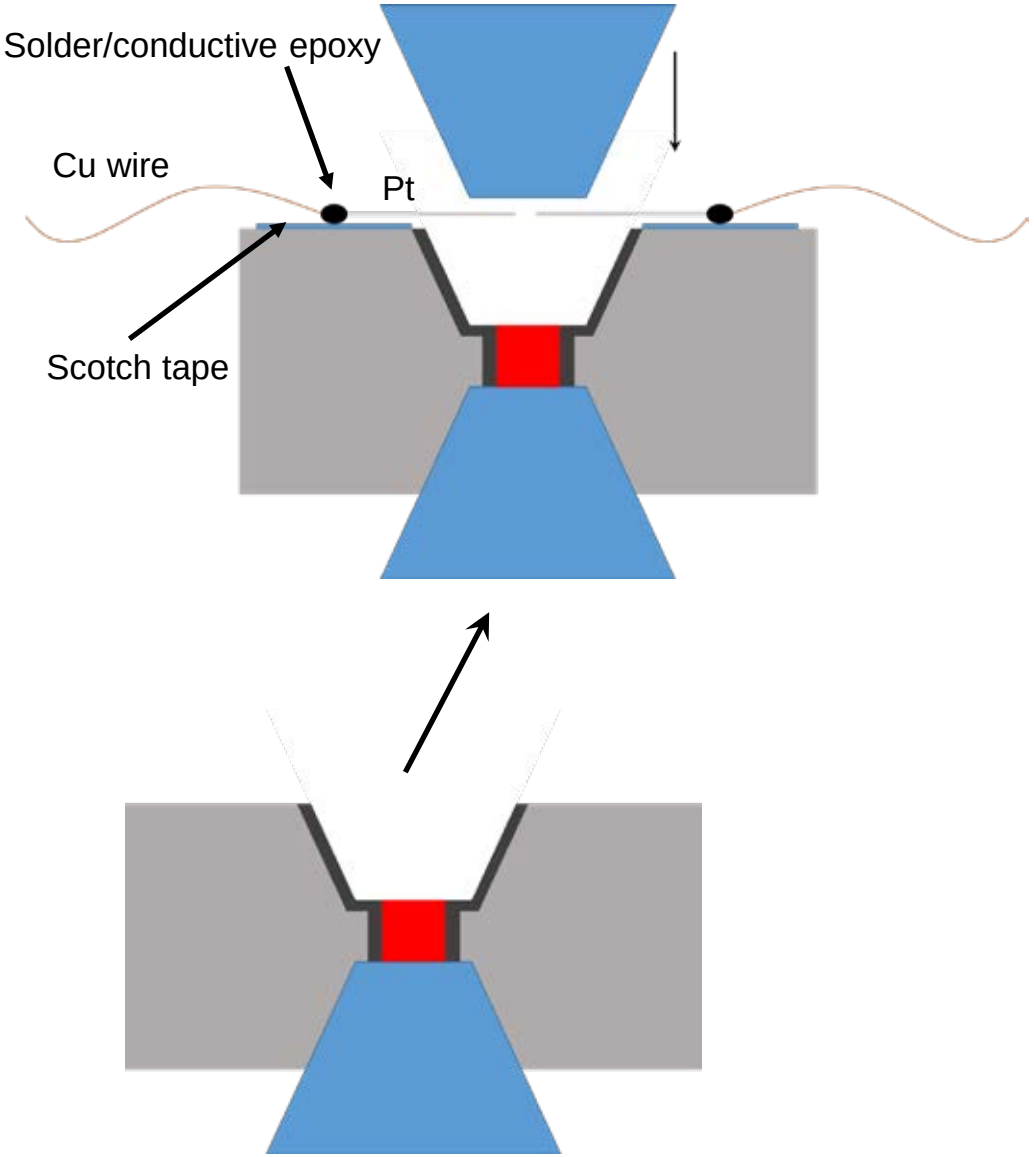


4. Carefully poke out a hole in the c-BN with your needle and then fill with sample

Practical note:

- This part is *hard* too. Go slowly. Avoid coffee.

# Conductivity

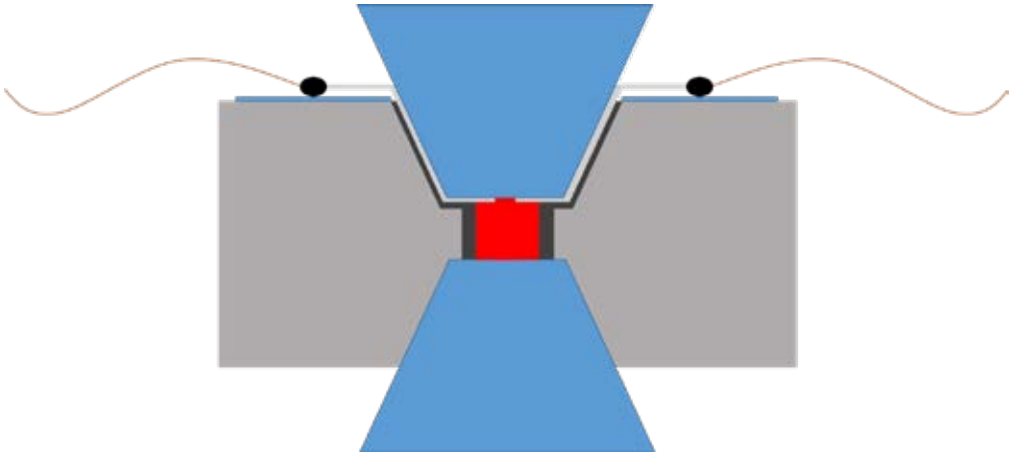



5. Affix Pt “slivers” such that they extend long enough and will contact the sample

Practical note:

- Cut little “pizza wedges” with a razor blade
- ~4-5 micron thick foil is good
- Coil the exterior ends of the Cu wire so that you have extra length to play with when unraveled but so that they fit inside of the DAC)

# Conductivity

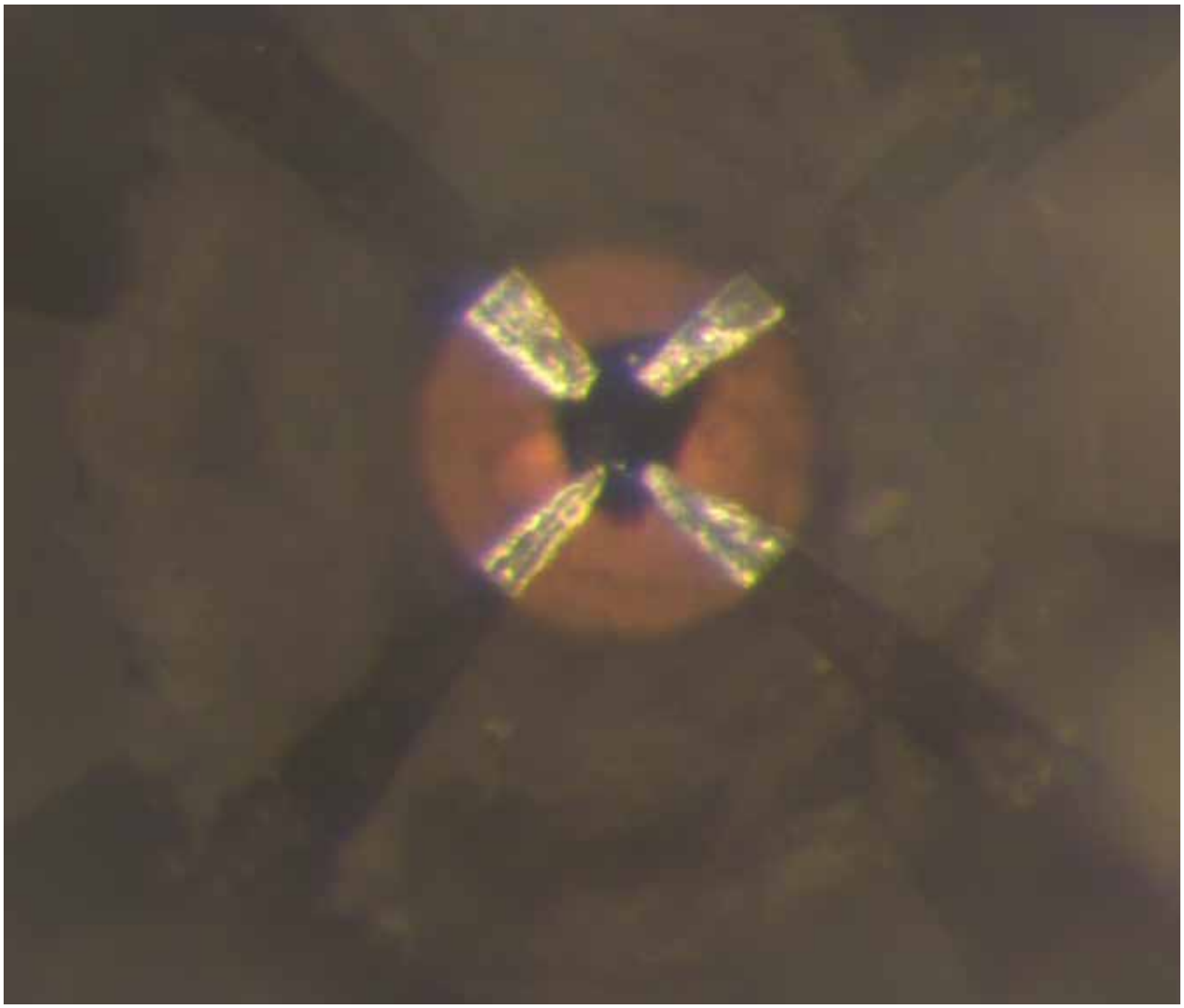


6. Nudge and bend Pt leads until you see that they will contact the sample properly when the top diamond is down, add ruby, seal

Practical note:

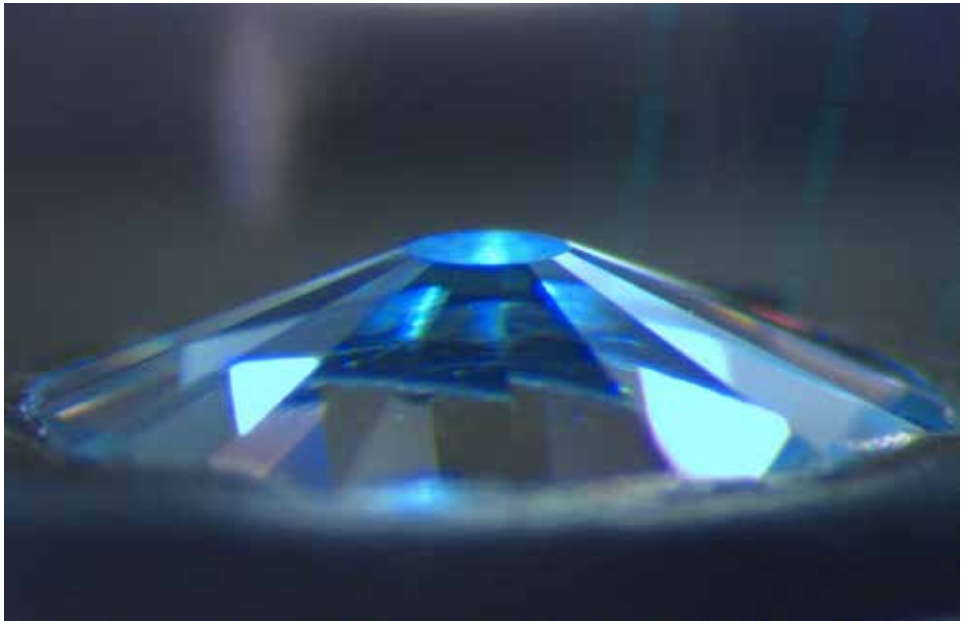
- This task is very repetitive and requires patience
- You will then need to connect the fine Cu wires to more robust external leads. Uncoil the Cu wires, carefully epoxy external leads to exterior of cell. Connect external leads to Cu wires with silver paint.

# Celebrate! And hope…



# Conclusion

- High-pressure experiments are *finnicky*!
- Don’t overanalyze your data:
  - Is a data signal from the gasket, medium, cosmic ray, interference fringe, or ruby?
  - Is a result because of lack of equilibration, a temperature change, X-ray/laser damage, or pressure medium?
  - Rietveld should not be trusted unless conditions are right
  - Space group search algorithms are “dumb” are will come up with weird options. Use your knowledge and don’t trust the computer!



# Conclusion

- High-pressure experiments are *finnicky*!
- Don’t overanalyze your data:
  - Is a data signal from the gasket, medium, cosmic ray, interference fringe, or ruby?
  - Is a result because of lack of equilibration, a temperature change, X-ray/laser damage, or pressure medium?
  - Rietveld should not be trusted unless conditions are right
  - Space group search algorithms are “dumb” are will come up with weird options. Use your knowledge and don’t trust the computer!
- Be creative! A lot of this stuff is cobbled-together “hacks” to make life easier.


https://www.youtube.com/@LabHacks

Jaffe Lab

# Thanks!

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# Equations of State

- Need to describe how volume (e.g., of the unit cell) relates to pressure, i.e., *P*–*V* relationship
  - First order: constant compressibility (think like a spring where $F = kx$)

change in volume (such as different in unit cell volumes)

$$\frac{\Delta V}{V_0} = -\frac{1}{K}\Delta P$$

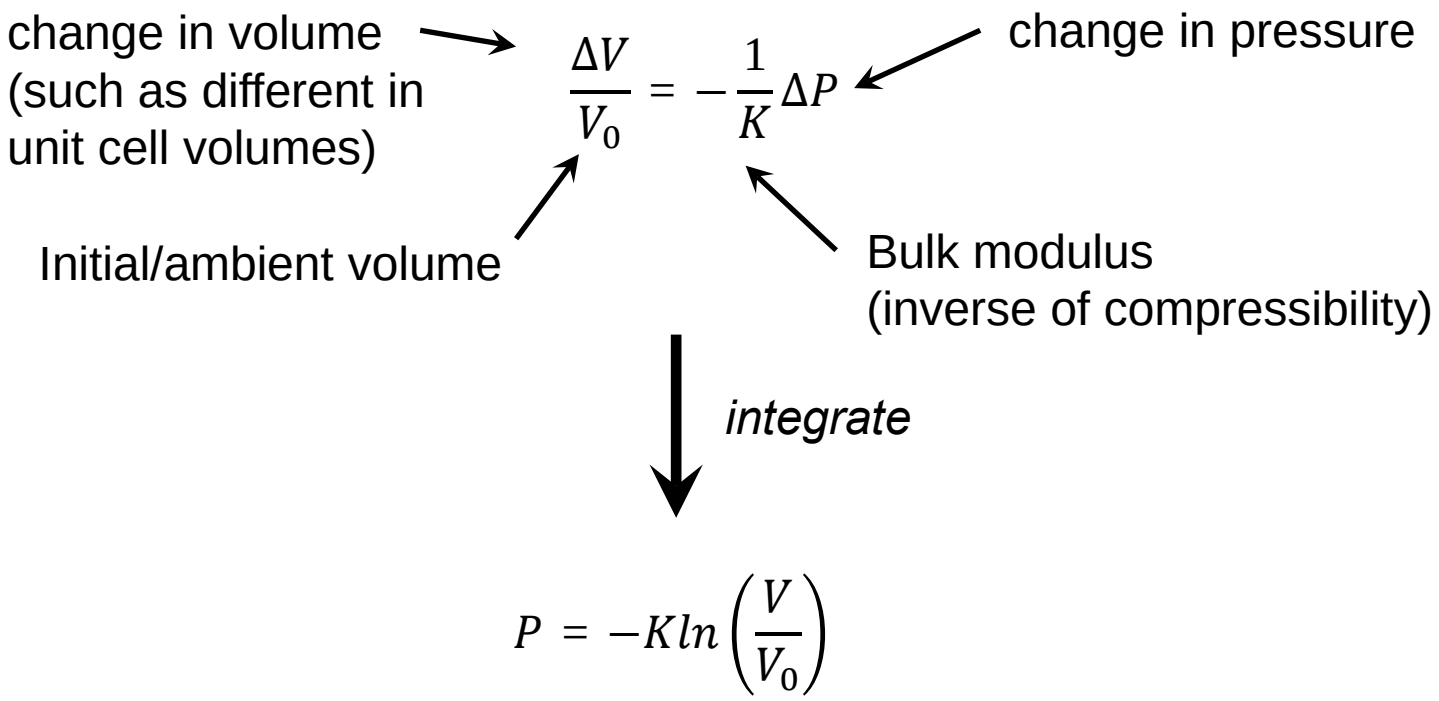
change in pressure

Initial/ambient volume

Bulk modulus (inverse of compressibility)

# Equations of State

- Need to describe how volume (e.g., of the unit cell) relates to pressure, i.e., *P*–*V* relationship
  - First order: constant compressibility (think like a spring where $F = kx$)



# Equations of State

- Higher orders:
  - Second order: linear compressibility (Murnaghan EOS)
  - Third order: non-linear compressibility (Birch-Murnaghan EOS)

Bulk modulus at ambient pressure

Derivative of bulk modulus (fixed at 4 for 2nd order)

$$P = \frac{3K_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left[1 + \frac{3}{4}\left(K_0^{'} - 4\right)\left(\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1\right)\right]$$

2nd order

3rd order

*Required Taylor series expansion to account for non-linearity in Eulerian strain (spatial rather than material dependent reference

# Back-of-the-Envelope Calculations

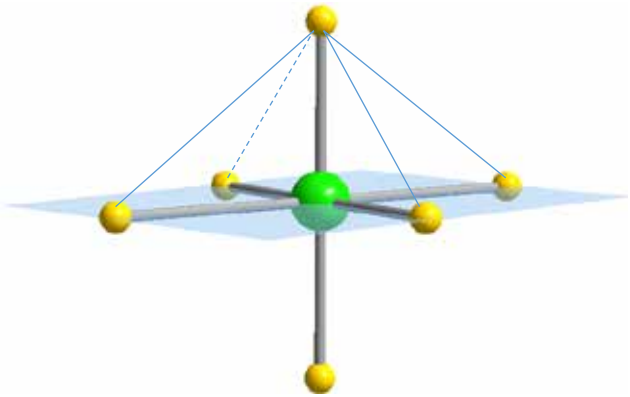
Energy required to compress octahedron

$$E_{JT} = -\int_{V_0}^{V_{crit}} P(V)dV$$

Assumes compressibility doesn't change with pressure (not true, but this will simply underestimate $P_{crit}$)

$$\boxed{E_{JT} = P_{crit}(V_0 - V_{crit})}$$

Assume all energy goes to compressing JT-elongated axis

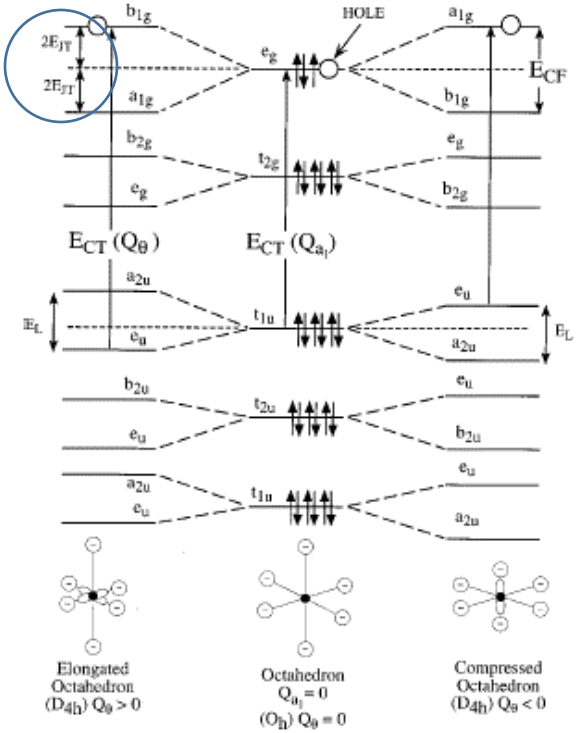


$$V_0 = 2\left(\frac{1}{3}b_{distorted}h\right)$$

$$V_{crit} = 2\left(\frac{1}{3}b_{non-distorted}h\right)$$

$$E_{JT} = \frac{E_{a1g\rightarrow blg}}{4}$$

Comes from perturbative model for piezospectroscopic shifts as a function of electron-phonon coupling

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