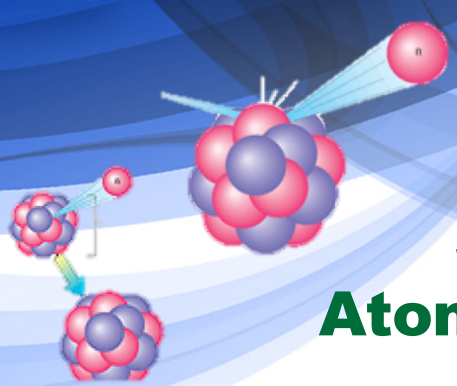


Structure and Dynamics of Metallic Glass – Atomistic insights from scattering experiments

Xun-Li Wang

Department of Physics
City University of Hong Kong

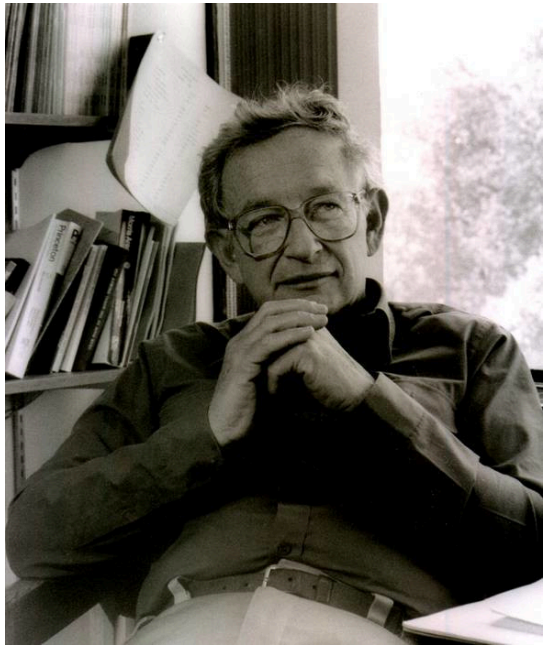
CityU Department of Physics

Top 125 challenges compiled by Science magazine

- What is the universe made of?
- How and where did life on earth arise?
- What is the nature of gravity?
- What is the pairing mechanism behind high-temperature superconductivity?
- What is the structure of water?
- What is the nature of the glassy state?
  - Molecules in a glass are arranged much like those in liquids but are more tightly packed. Where and why does liquid end and glass begin?

The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and glass transition.,.

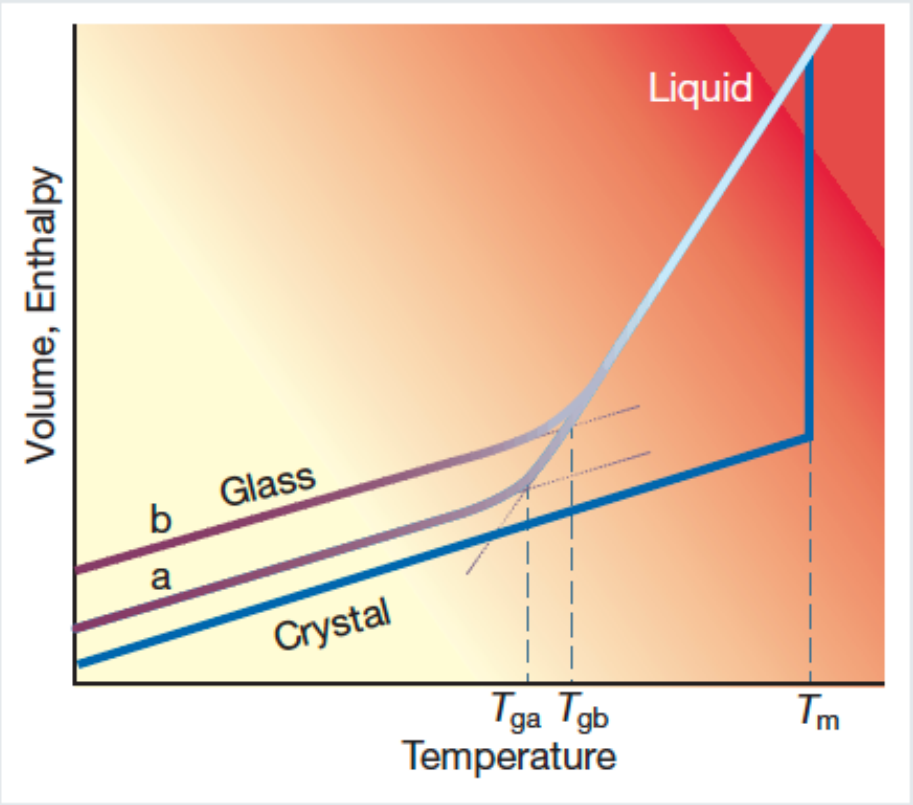
P. W. Anderson, Science, 267 (1995)1615



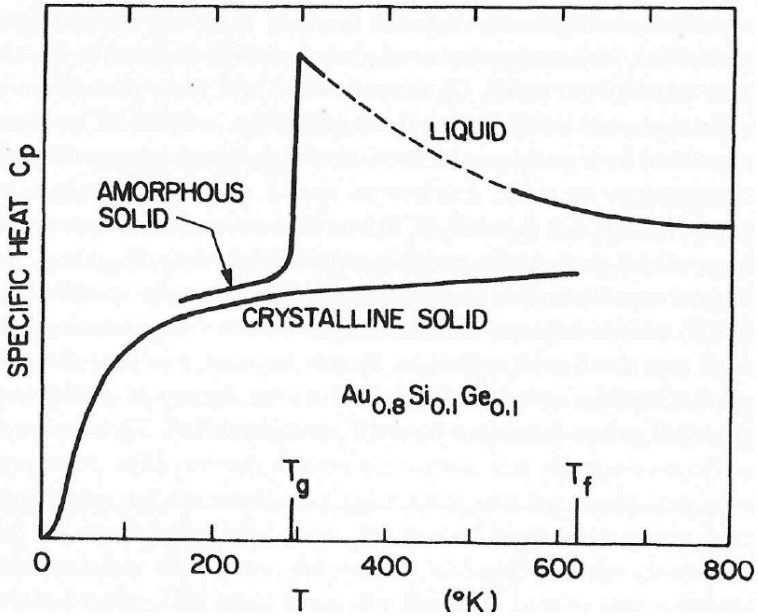
Presentation outline

- Introduction: the fascinating lass problem and metallic glass
- Neutron and synchrotron X-ray scattering techniques
- Short-range order
  - Fundamental building blocks
- Medium-range order
  - Connectivity of the building blocks
- Dynamic properties
  - The correlation between the structure & dynamics
- China Spallation Neutron Source
- Concluding remarks and outlook

What is a glass and the glass transition?



Debenedetti & Stillinger, Nature, 2001



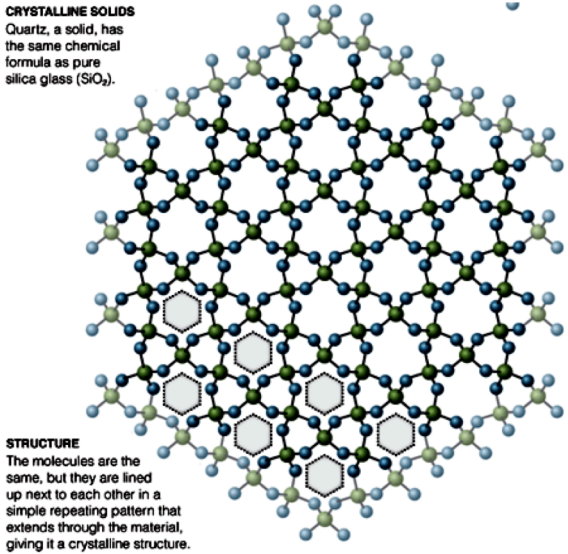
- Is it a thermodynamic transition?
- Is it just a slow down in kinetics?

The New York Times
nytimes.com

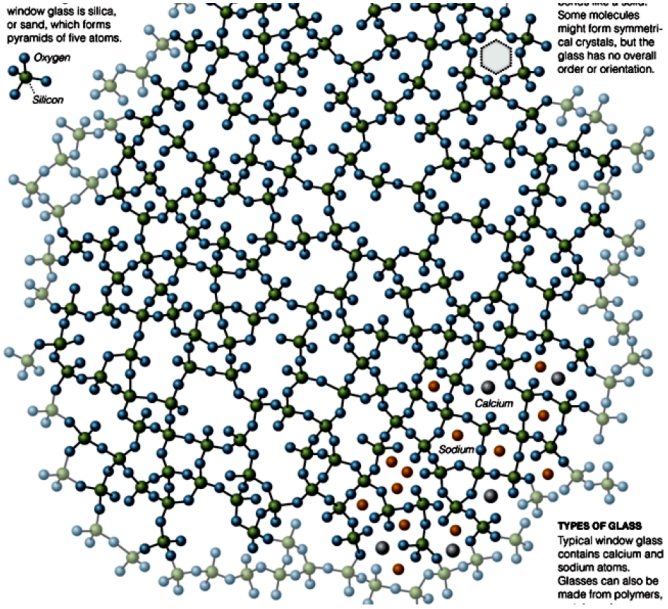
July 29, 2008

The Nature of Glass Remains Anything but Clear

By KENNETH CHANG



Quartz (crystalline SiO_2)



Molten Silica
(amorphous SiO_2)

How to describe

- Structure?
- Dynamics?

Bulk Metallic Glasses Exhibit Unconventional Properties

Excellent mechanical properties

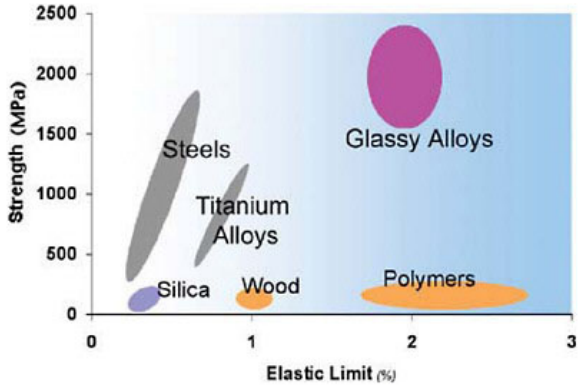
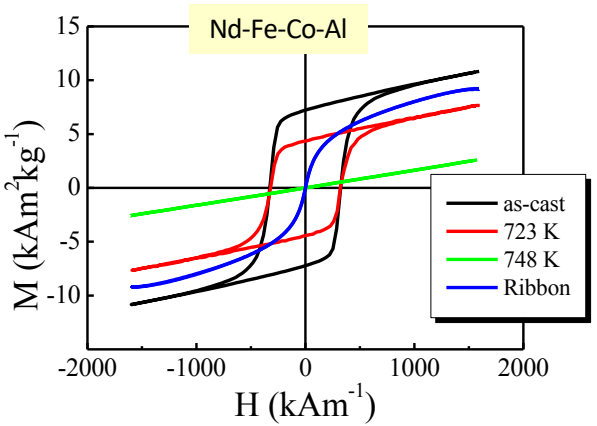


FIGURE 5.5 Far-from-equilibrium processing produces some of the toughest, highest-strength materials (glassy metal alloys). The abscissa corresponds to the yield strain, while the ordinate corresponds to the Young's modulus of the materials identified in the figure. SOURCE: Courtesy of William L. Johnson, California Institute of Technology.

- High strength (> 2000 MPa)
- High elastic strain (> 2%)
- High hardness (600-1500 DPH)

Controllable magnetic properties



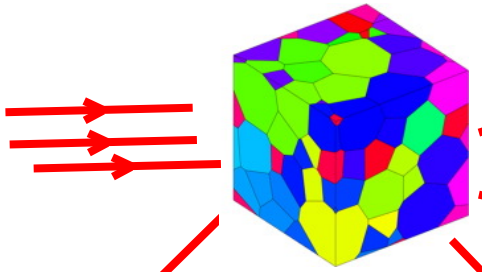
- Magnetic hardness is tunable with annealing
- Application as transformers

W. L. Johnson, Caltech

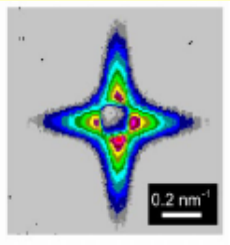
A. Inoue, Tohoku

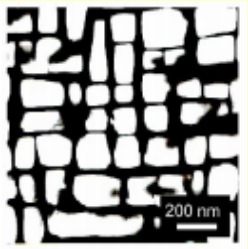
2009 APS James C. McGroddy Prize for New Materials

How are neutrons used to determine the structures?



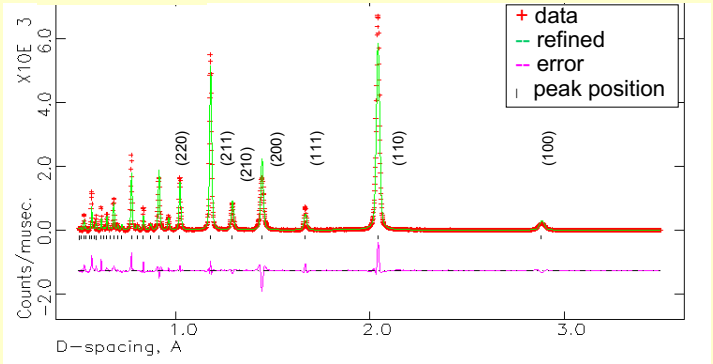
small angle scattering



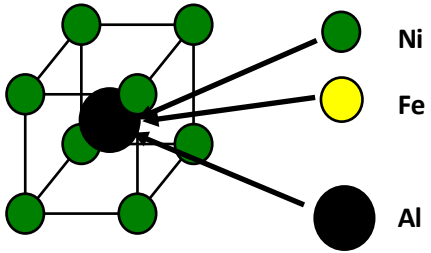


Nanoscale morphology and size distribution

Ni (Al, Fe)



wide angle diffraction



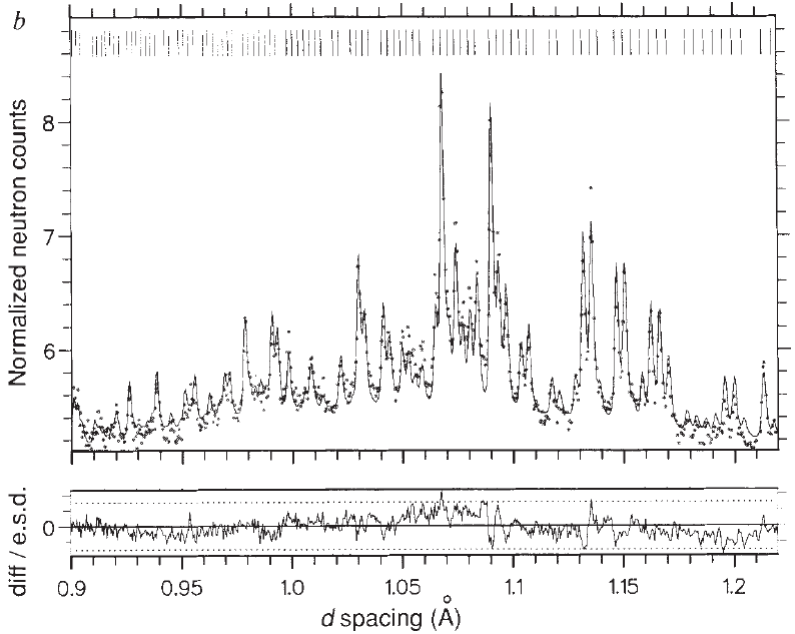
Crystal structure and bonding of ordered C_{60}

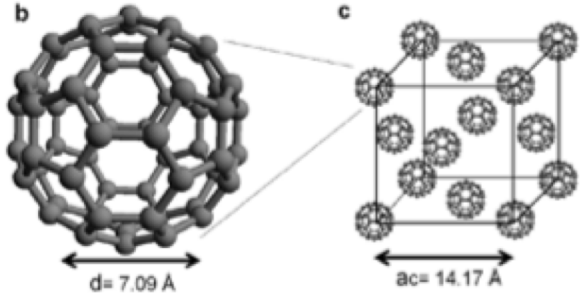
Buckyball

William I. F. David, Richard M. Ibberson, Judy C. Matthewman, Kosmas Prassides*, T. John S. Dennis*, Jonathan P. Hare*, Harold W. Kroto*, Roger Taylor* & David R. M. Walton*

TABLE 1 Structural parameters from Rietveld analysis of C_{60} at 5 K

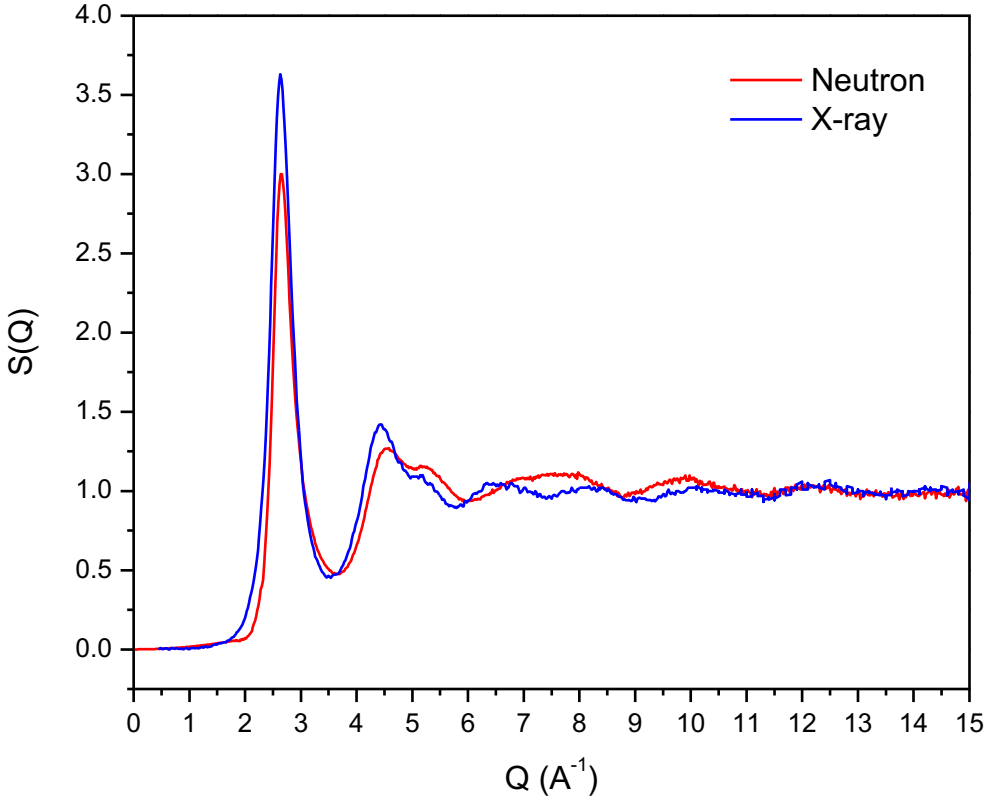
Atom	x	y	z
C11	0.2294 (3)	−0.0325 (2)	0.1010 (3)
C12	0.2467 (3)	−0.0540 (2)	0.0061 (2)
C21	0.2081 (3)	0.0646 (2)	0.1289 (3)
C22	0.2066 (3)	−0.1401 (2)	−0.0360 (2)
C23	0.1710 (2)	−0.0963 (2)	0.1590 (3)
C34	0.2236 (3)	0.1122 (3)	−0.0371 (2)
C24	0.2439 (3)	0.0192 (3)	−0.0636 (2)
C31	0.2053 (3)	0.1349 (3)	0.0616 (2)





What happens when the sample becomes amorphous?

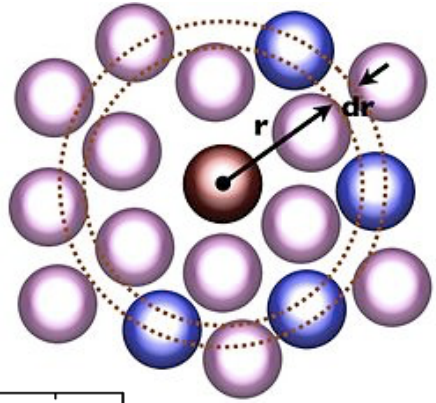
X-ray and neutron diffraction patterns from glass materials have only broad maxima

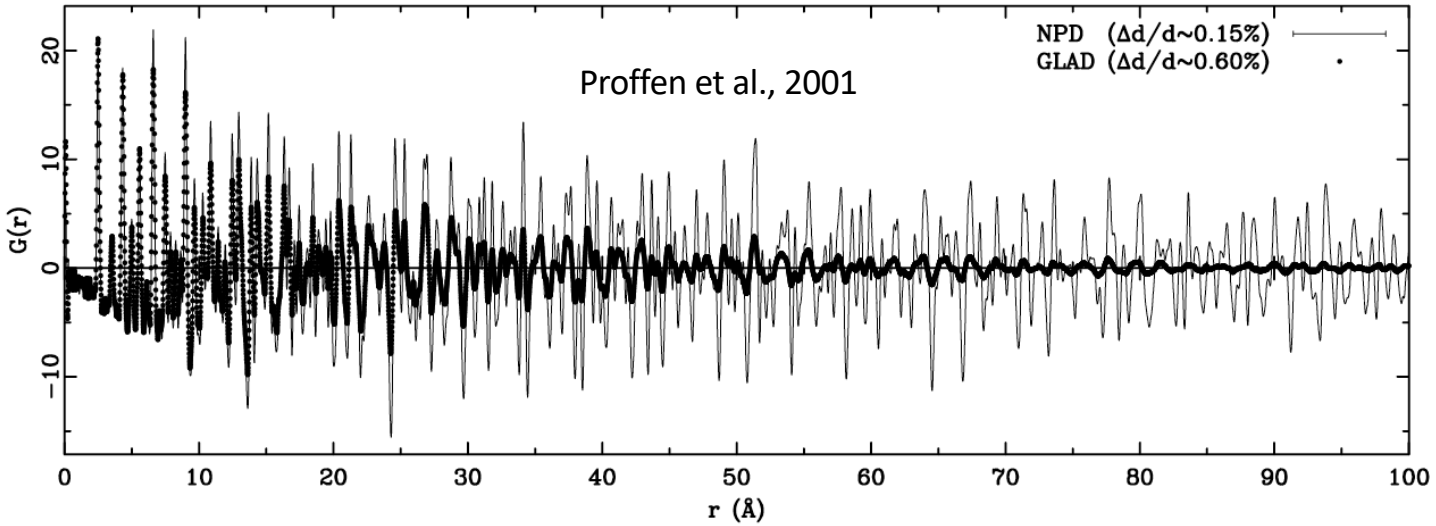


Real space data analysis – the Pair Distribution Function approach

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

$$= \frac{2}{\pi}\int_0^\infty Q[S(Q) - 1]\sin(Qr)\,\mathrm{d}Q,$$





VOLUME 91, NUMBER 26 PHYSICAL REVIEW LETTERS week ending 31 DECEMBER 2003

In situ Synchrotron Study of Phase Transformation Behaviors in Bulk Metallic Glass by Simultaneous Diffraction and Small Angle Scattering

X.-L. Wang,[1,2] J. Almer,[3] C. T. Liu,[2] Y. D. Wang,[1] J. K. Zhao,[1] A. D. Stoica,[1] D. R. Haeffner,[3] and W. H. Wang[4]

Partially crystallized bulk metallic gass contains high-density nanometer sized crystallites

- **e.g., upon isothermal annealing**
- **Density 10^{23}-10^{24} m^{-3}**
- **Crystallite size ~10 nm**
- **How do they form?**
  - **Crystalline order (~ Å)**
  - **Chemical order (~nm)**

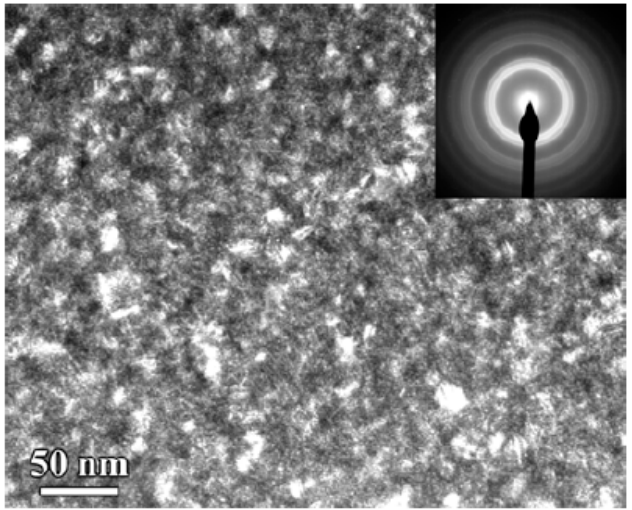


Figure 4
Dark-field transmission electron microscopy image with diffraction pattern (inset) of Vit105, annealed for 15 h at 673 K (Pekarskaya *et al.* 2003).

Small Angle Scattering and Wide Angle Diffraction Are Complementary

- Small angle scattering is a great tool for study of phase separation (over length scale of nm-μm)

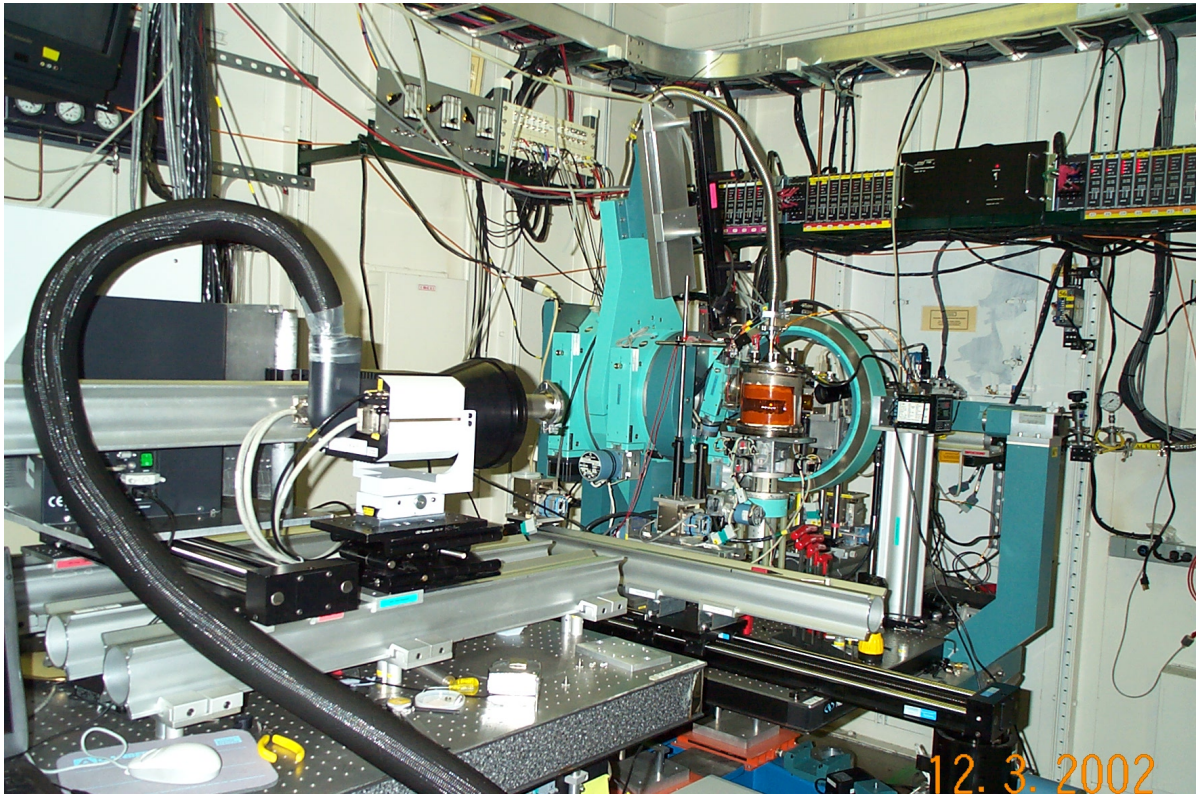
but no phase information is given

- Diffraction is good for probing atomic ordering (over length scale of 1-10 Å)

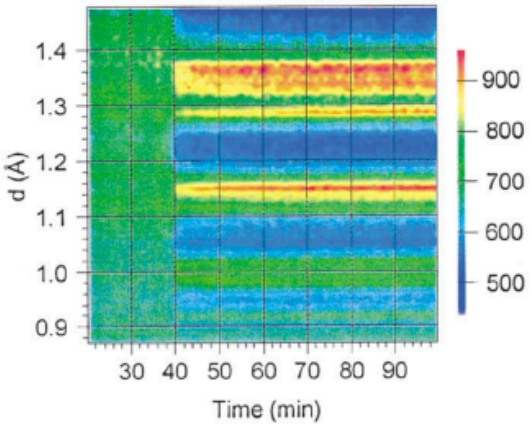
but provides little information unless the local atomic structure changes

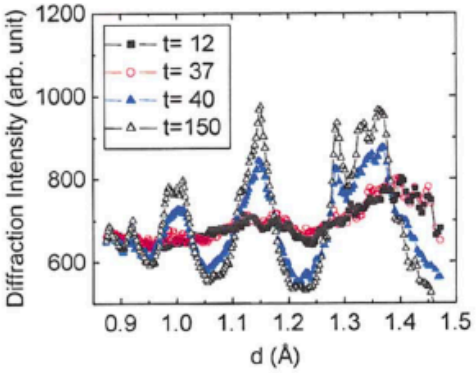
- Simultaneous measurements of both reveal behaviors over multiple length scales

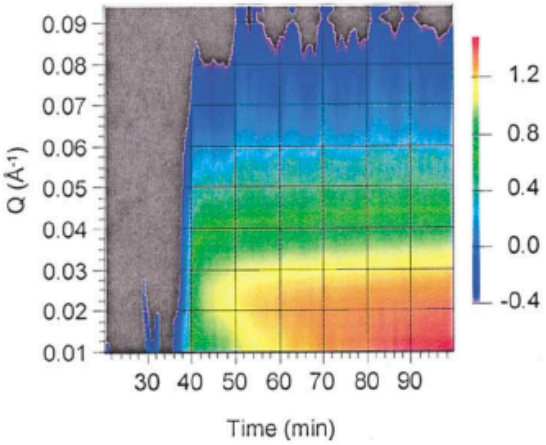
Experimental Setup for Simultaneous Diffraction and Small Angle Scattering Measurements

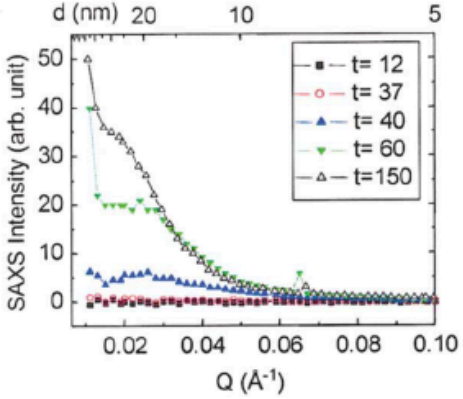


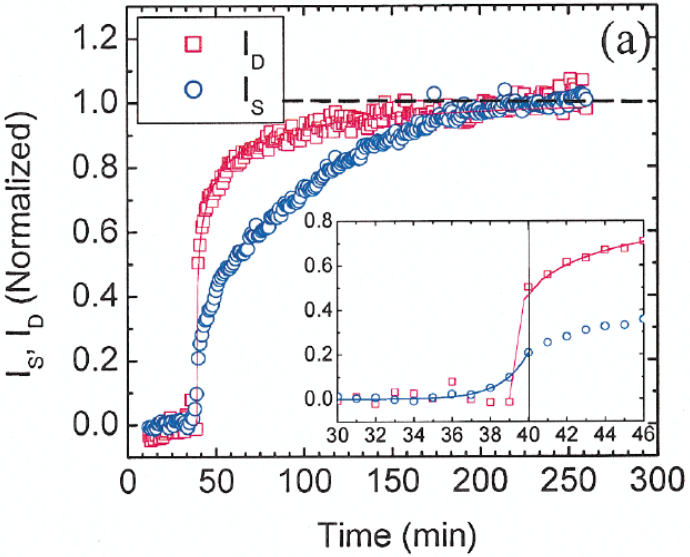
Phase separation proceeds before crystallization





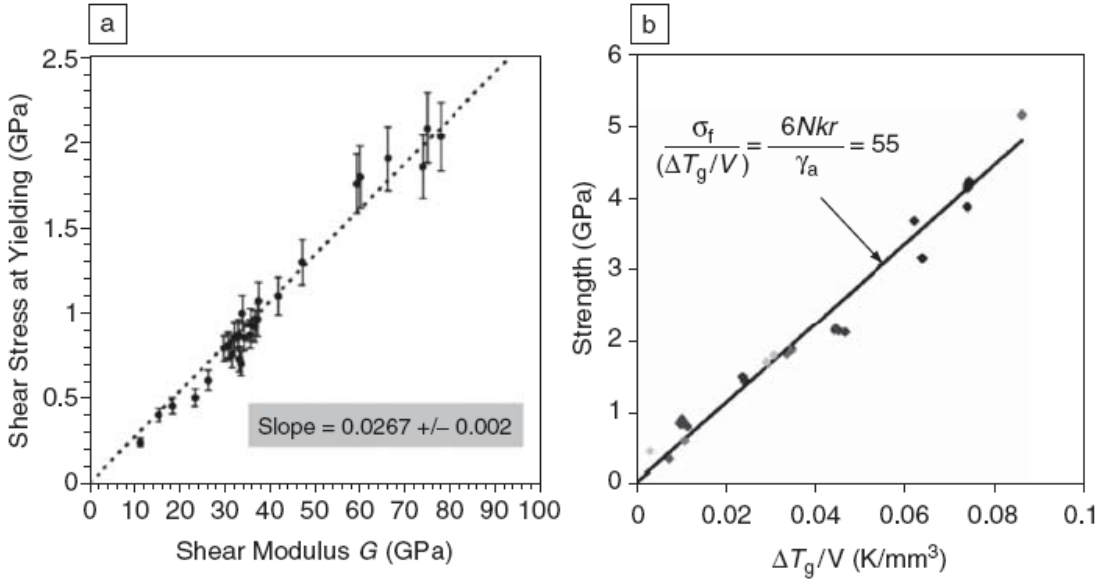






X.-L. Wang et al., PRL (2003)

Why metallic glasses are of interest from physics point of view?

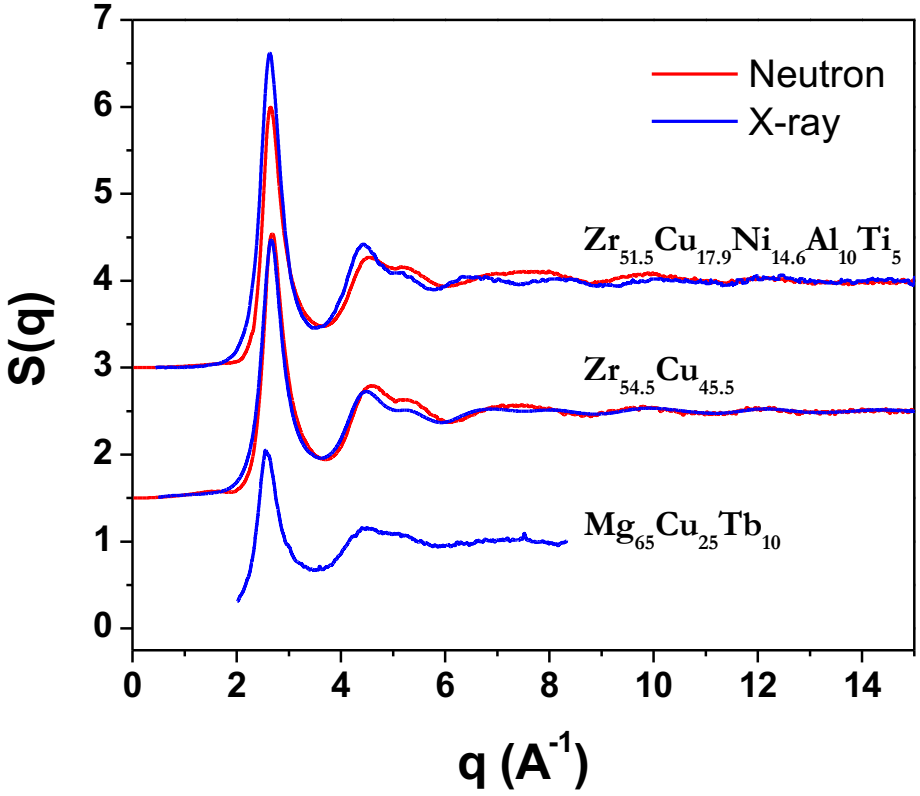


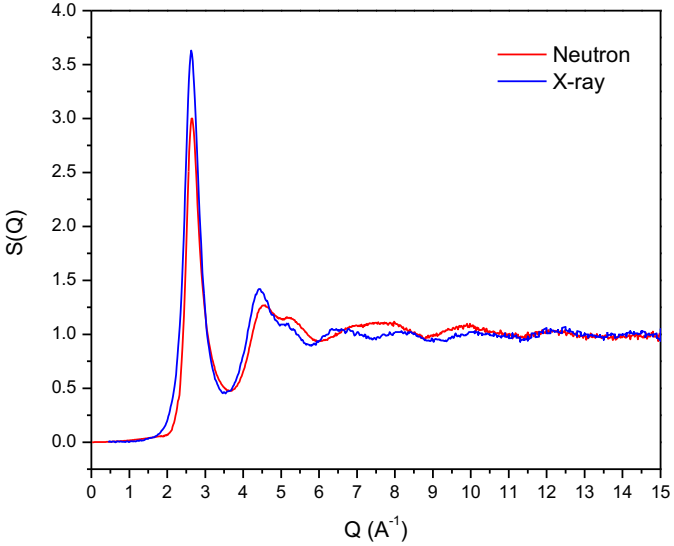
B. Yang, C.T. Liu, T.G. Nieh, *Appl. Phys. Lett.* **88**, 221911 (2006).

Apparently distinct properties of metallic glasses display striking, unexplained correlations with each other (from MRS Bulletin, August 2007)

As the structure determines the properties, is there a structural commonality?

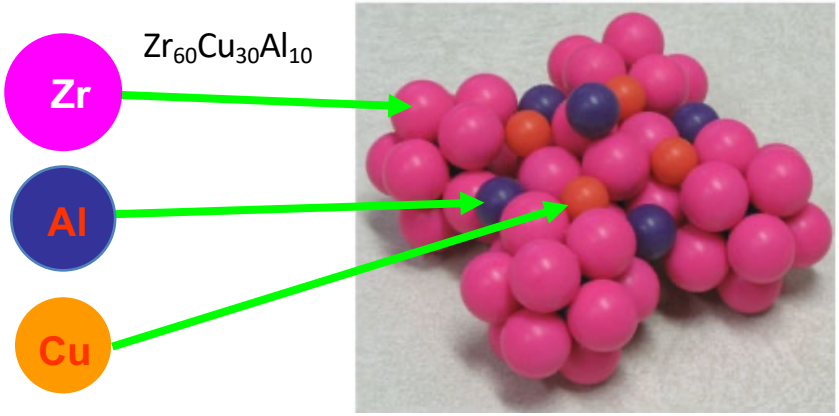
The diffraction data provided the clue - all diffraction data look much the same





- First peak is sharp, ~0.4-0.5 $Å^{-1}$
- High-Q peaks are broad, ~1.4-1.8 $Å^{-1}$

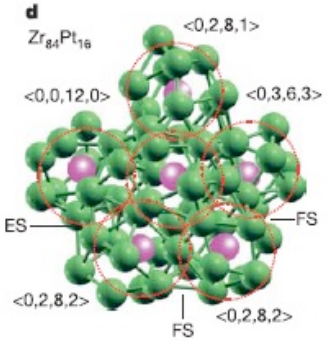
In metallic glasses the fundamental building blocks are solute-centered clusters



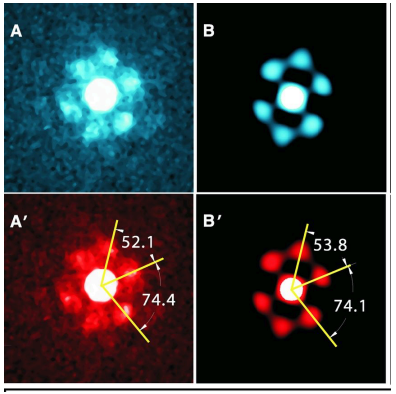
Dan Miracle: Nature Mater. 2004

This concept also applies to multi-component alloys, Ma et al., APL 2007

$Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$



Evan Ma: Nature, 2007

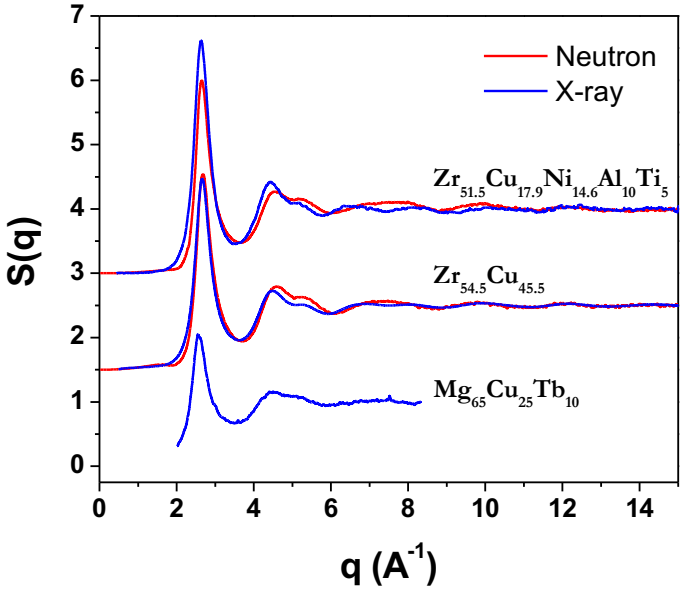


MW Chen, Science, 2013

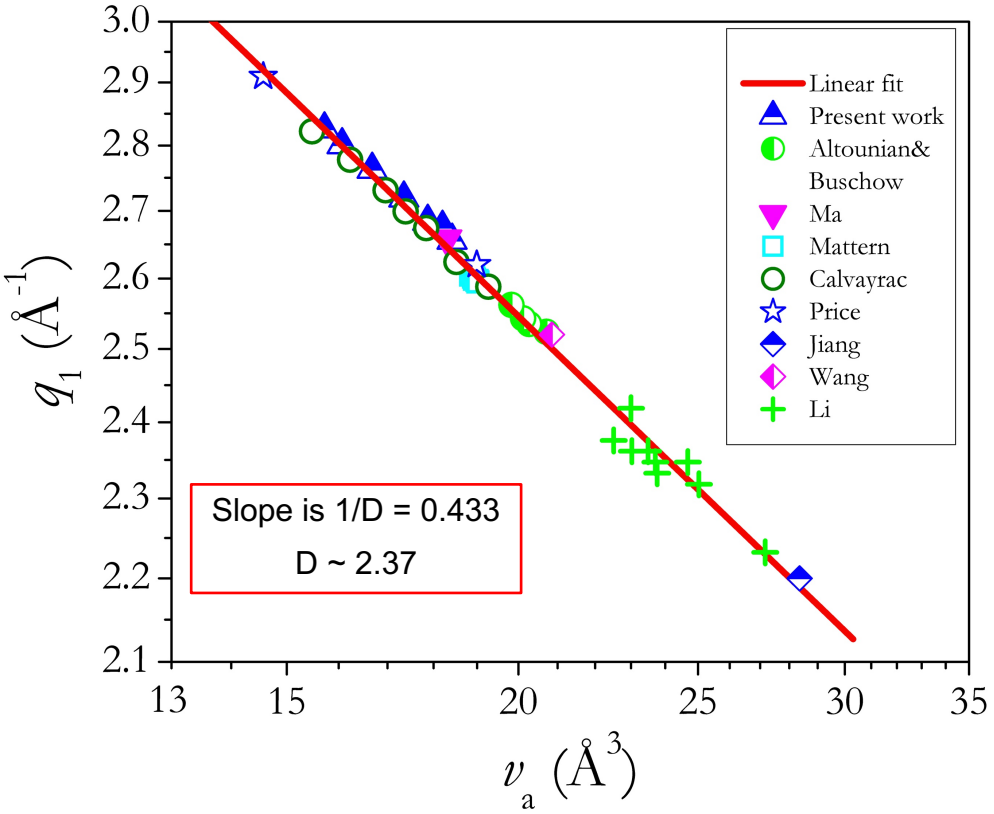
How are the clusters connected?

Scaling analysis of the first sharp diffraction peak indicates fractal behavior

D. Ma, A. D. Stoica, and X.-L. Wang, *Nature Materials*, 8, 30-34 (2009)

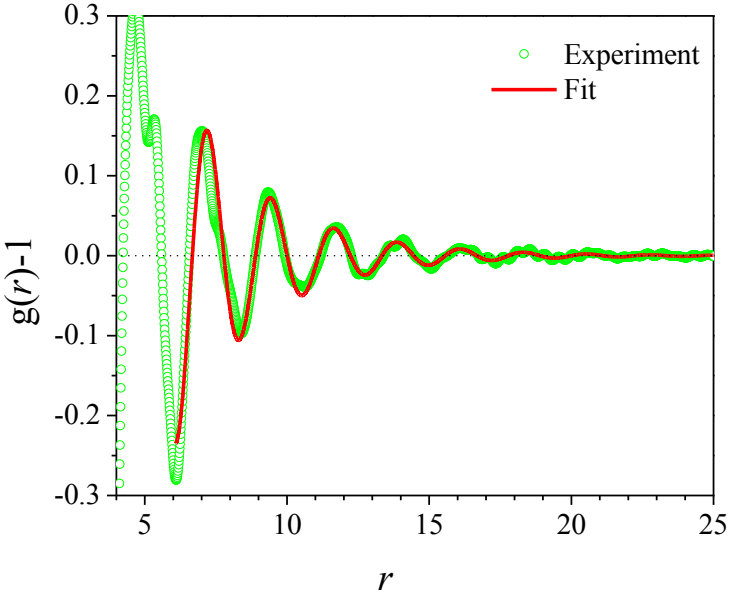


All diffraction data look much the same – an important clue



Experimental pair distribution function is well described by a power-law correlation function for a fractal network

$$C(r) = (A/r^{D-D_f})\exp(-r/\xi)\sin(q_1 r + \phi)$$

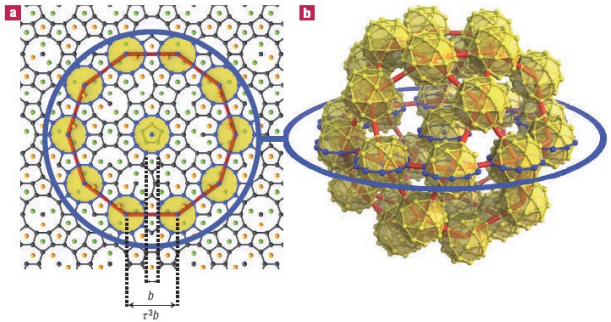


Following Sinha et al., PRB, 1985

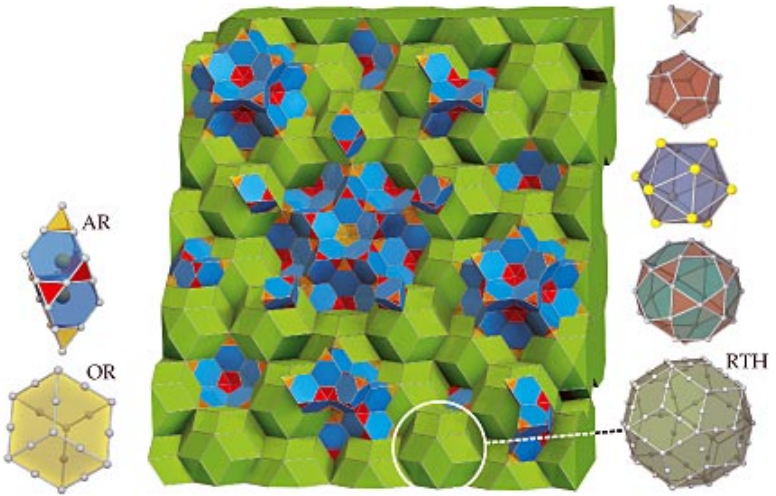
- **We propose fractal packing of atomic clusters**
- **Fractal structure breaks down at short-range length scale**
- **q_1 specifies the wavelength of the correlation function at medium-range length scale**

Understanding the fractal aspect from the space filling perspective: quasicrystals

Takakura et al., Nature Materials, 2007



YbCd $_{5.7}$



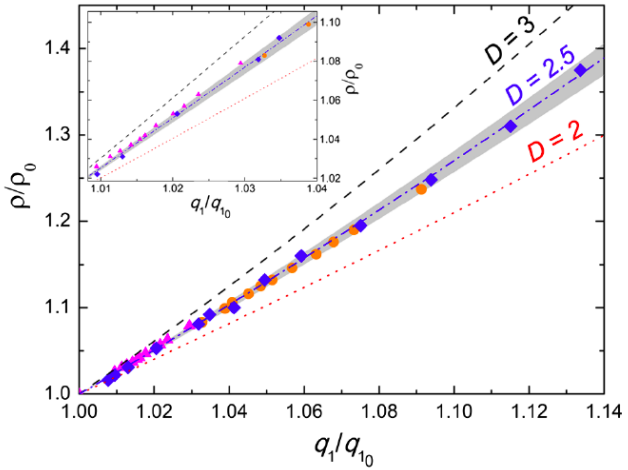
- D=2.7
- Basic building blocks are RTH
- RTH cannot completely fill the space due to five-fold symmetry
- AR and OR fill in the gaps to connect RTH

The fractional power law is confirmed by subsequent studies

PRL 112, 185502 (2014) PHYSICAL REVIEW LETTERS week ending 9 MAY 2014

Universal Fractional Noncubic Power Law for Density of Metallic Glasses

Qiaoshi Zeng,[1,2,4,5,*] Yoshio Kono,[3] Yu Lin,[1] Zhidan Zeng,[1,2,4,5] Junyue Wang,[4,5] Stanislav V. Sinogeikin,[3] Changyong Park,[3] Yue Meng,[3] Wenge Yang,[4,5] Ho-Kwang Mao,[4,5] and Wendy L. Mao[1,2]
[1]*Geological and Environmental Sciences, Stanford University, Stanford, California 94305, USA*

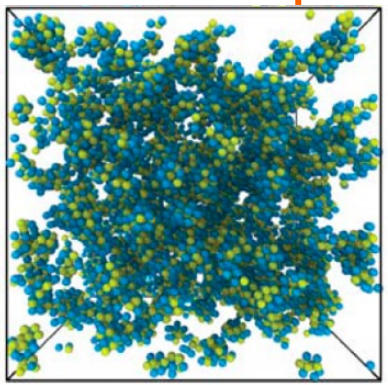


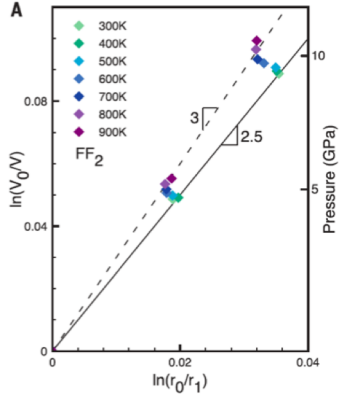
REPORTS
METALLIC GLASSES

Fractal atomic-level percolation in metallic glasses

David Z. Chen,[1*] Crystal Y. Shi,[2†] Qi An,[3†] Qiaoshi
William A. Goddard III,[3] Julia R. Greer[1,7]

D. Z. Chen, Science, 349, 6154 (2015)

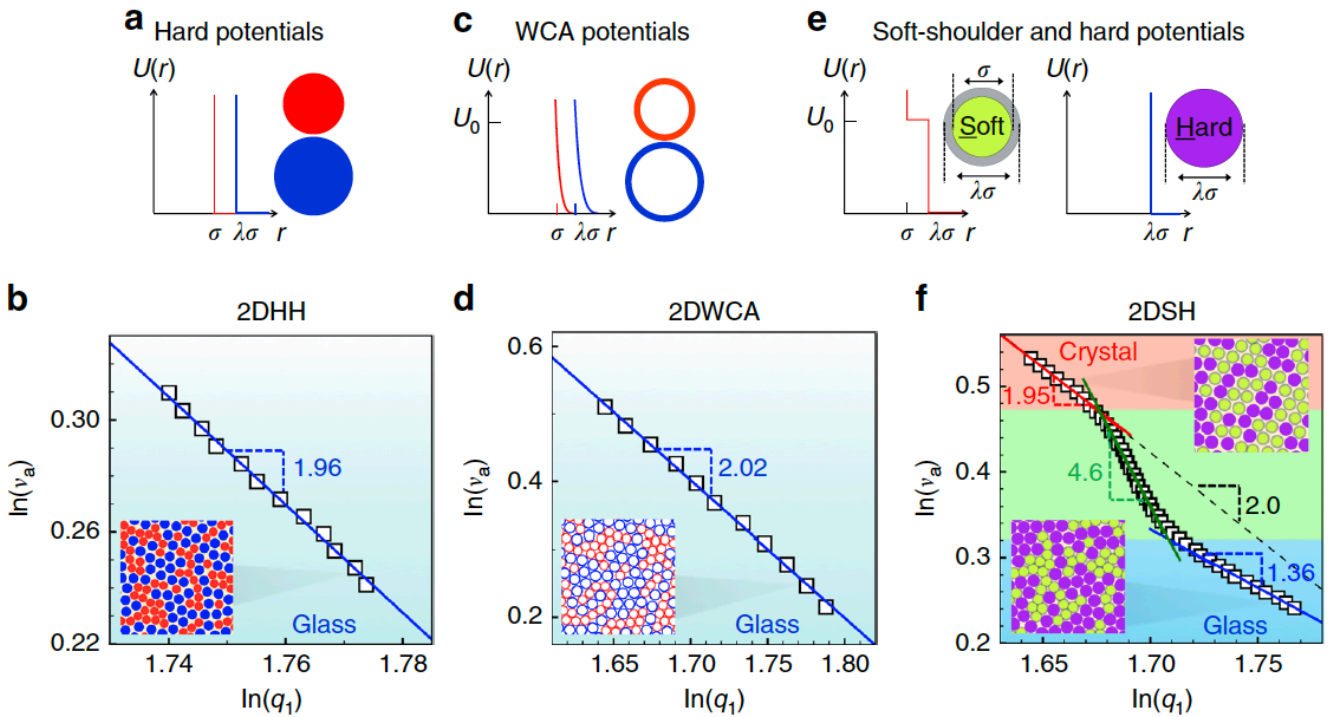




nature COMMUNICATIONS

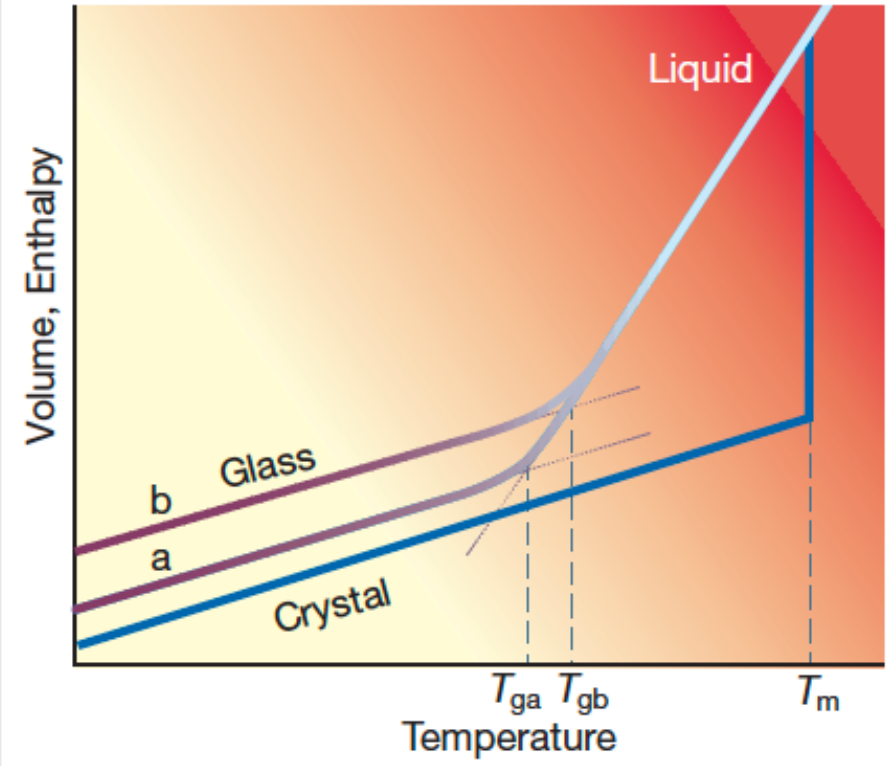
H. J. Zhang, K. Y. Qiao, and Y. L. Han, 11, 2005 (2020)

Power laws in pressure-induced structural change of glasses



Effect of two-length scales, i.e., the softness

Jagla, *J. Chem. Phys.* **111**, 8980–8986 (1999)



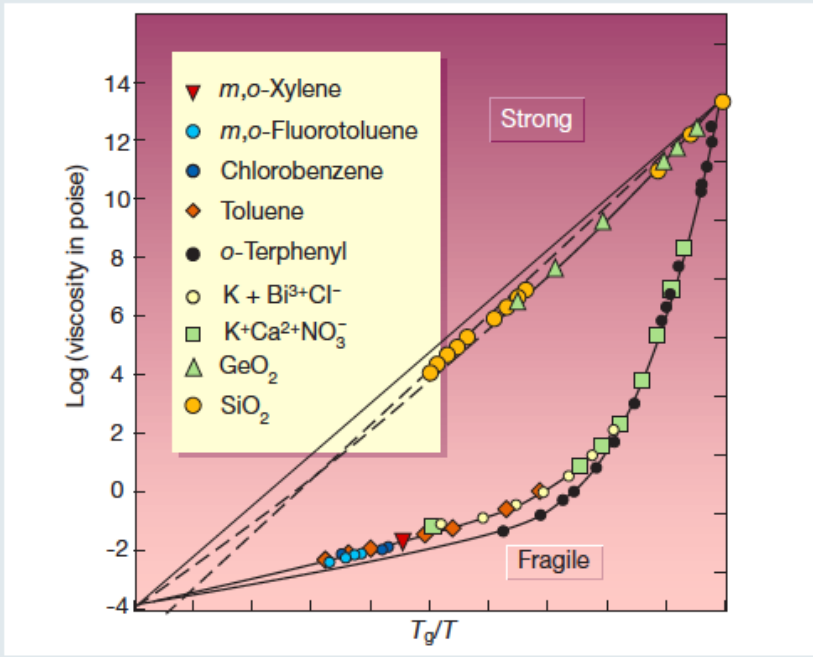


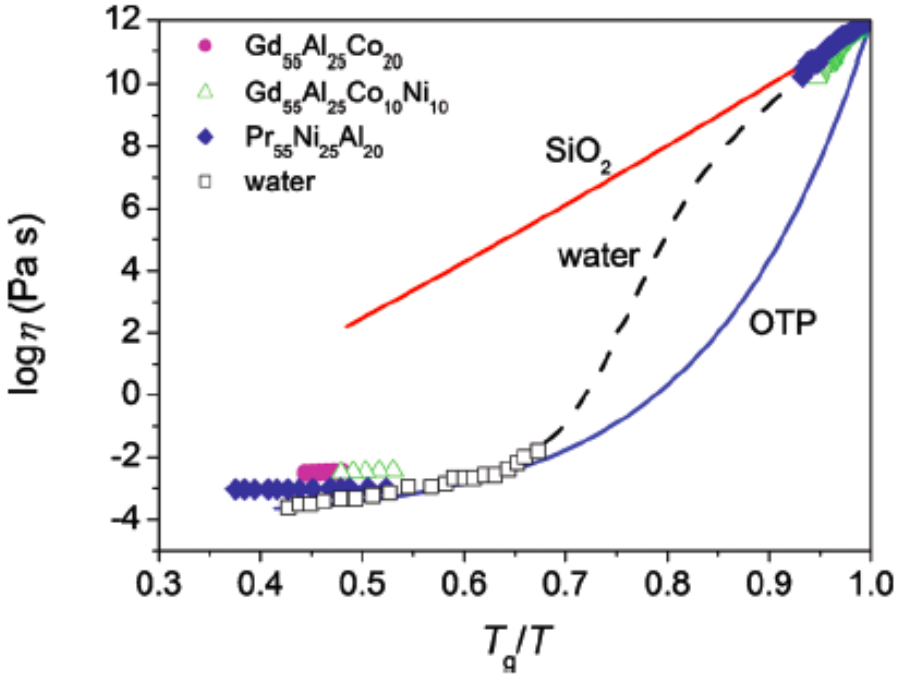
Figure 2 T_g-scaled Arrhenius representation of liquid viscosities showing Angell's strong–fragile pattern. Strong liquids exhibit approximate linearity (Arrhenius behaviour), indicative of a temperature-independent activation energy $E = d\ln\eta/d(1/T) \approx$ const. Fragile liquids exhibit super-Arrhenius behaviour, their effective activation energy increasing as temperature decreases. (Adapted from refs 9 and 11.)

Debenedetti & Stillinger, Nature, 2001

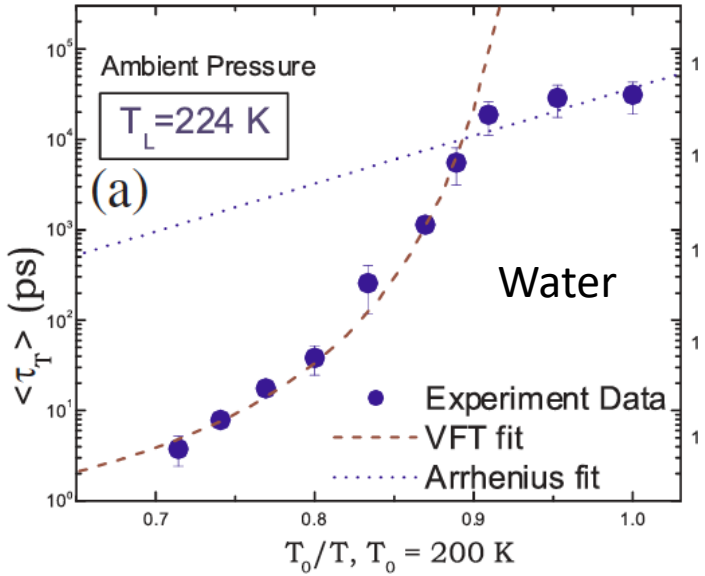
THE JOURNAL OF CHEMICAL PHYSICS 133, 014508 (2010)

Fragile-to-strong transition in metallic glass-forming liquids

Chunzhi Zhang,[1] Lina Hu,[1] Yuanzheng Yue,[1,2,a)] and John C. Mauro[3]
[1]*Key Laboratory for Liquid-Solid Structural Evolution & Processing of Materials, Shandong University, Jinan 250061, China*
[2]*Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark*
[3]*Science and Technology Division, Corning Incorporated, Corning, New York, USA*



Phase transition in no-man's Land?

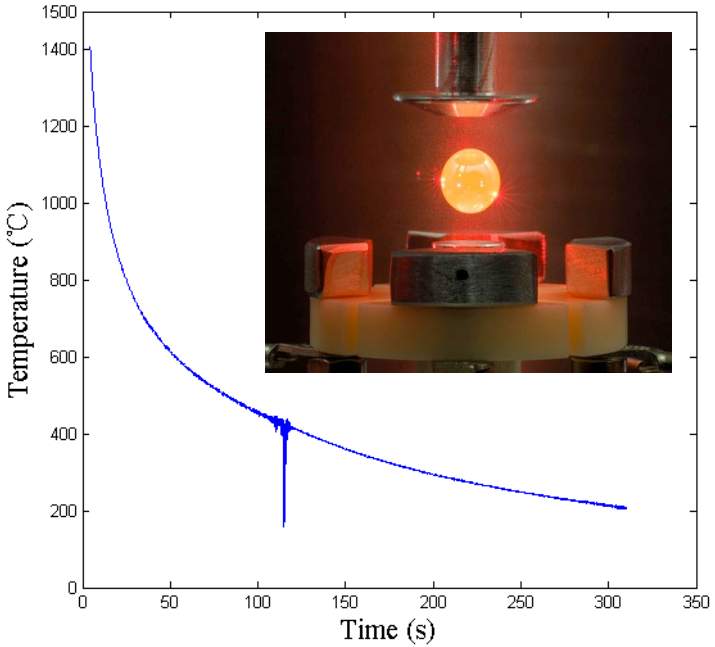


L. Liu, S.-H. Chen et al., PRL, 2005

APPLIED PHYSICS LETTERS **108**, 211907 (2016)

Structural crossover in a supercooled metallic liquid and the link to a liquid-to-liquid phase transition

Si Lan[1], Matthew Blodgett[2], Ken Kelton[2], J. L. Ma, J. Fan, and Xun-Li Wang[1]
[1]Department of Physics and Mat. Sci., City University of Hong Kong
[2]Department of Physics, Washington University at St. Louis



nature COMMUNICATIONS

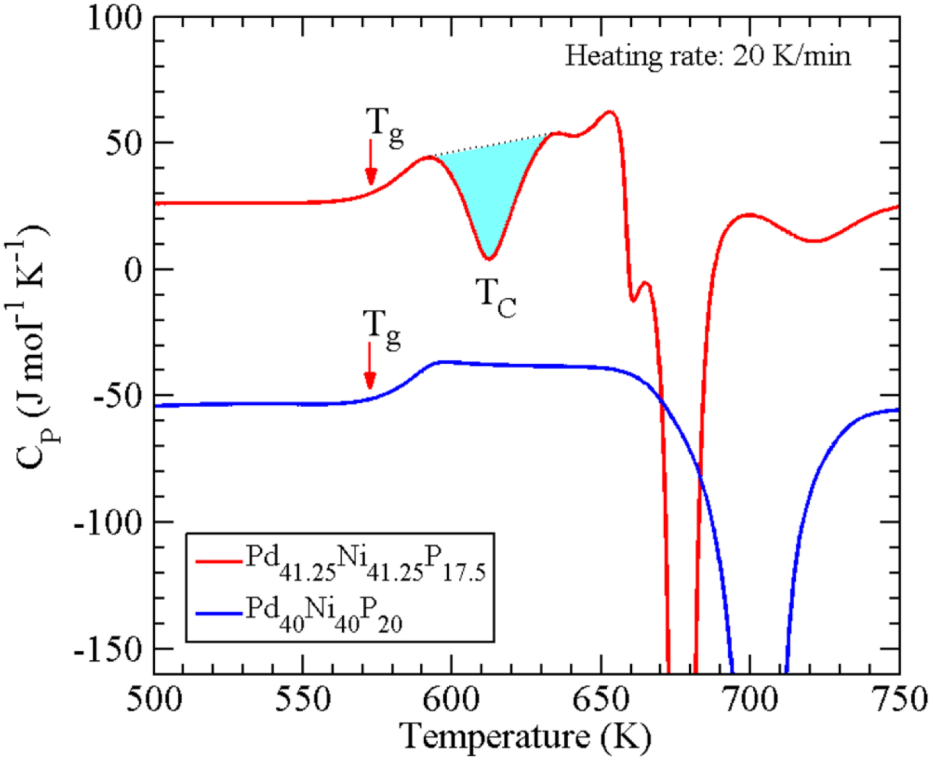
Hidden amorphous phase and reentrant supercooled liquid in Pd-Ni-P metallic glass

S. Lan[1,2], Y. Ren[3], X. Y. Wei[2], B. Wang[2], E. P. Gilbert[4], T. Shibayama[5], S. Watanabe[5], M. Ohnuma[3], and X.-L. Wang[3]

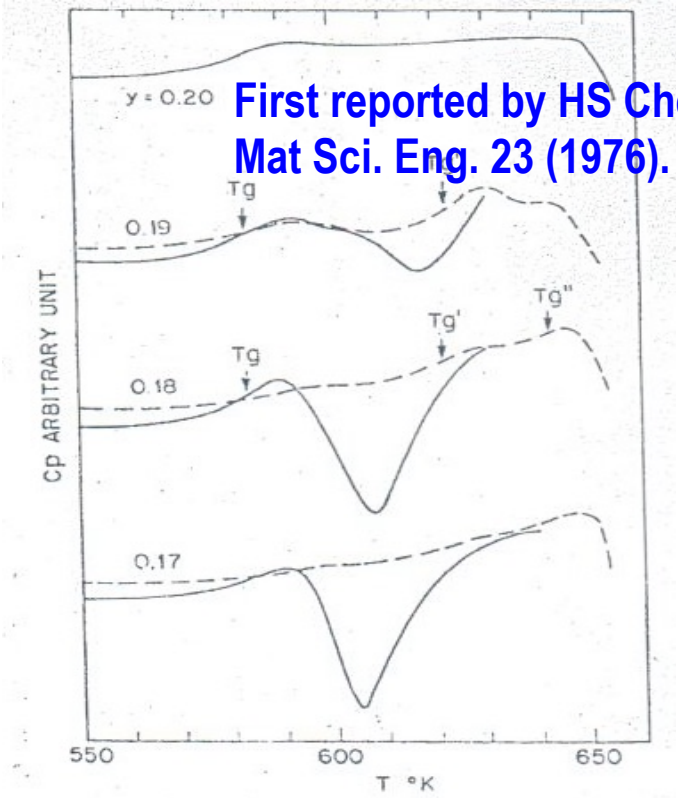
[1]Nanjing University of Science and Technology, China
[2]City University of Hong Kong
[3]Advanced Photon Source, Argonne National Laboratory, USA
[4]Australia Centre for Neutron Scattering, Australia
[5]Hokkaido University, Japan

Nature communications, 8, 14679 (2017)

DSC scan for $Pd_{41.25}Ni_{41.25}P_{17.5}$ reveals a pronounced anomalous exothermal peak



$(Pd_{0.5}Ni_{0.5})_{100-x}P_x$ glassy ribbons



First reported by HS Chen, Mat Sci. Eng. 23 (1976).

The DSC anomaly has been reported in many other metallic glass alloys

- Zr-Be-X (X=Ti, Nb)
- Zr-Ti-Cu-Ni-Be
- Gd–Zr–Al–Ni
- Ni–Zr–Nb–Al–Ta
- Cu-Zr–Al–Y
- Mg–Cu–Ag–Gd

- Fe–M–Y–B (M= Mo, W, Nb)
- $(Fe_{0.9}Co_{0.1})_{67.5}Nb_4Gd_{3.5}B_{25}$
- $(Fe_{0.75-x}Dy_xB_{0.2}Si_{0.05})_{96}Nb_4$
- $(Fe_{0.76-x}Dy_xB_{0.24})_{96}Nb_4$ (x =0-0.07)

- *BMGs with the DSC anomaly tend to have better glass forming ability*
- *Is it universal? Do they have the same structural origin?*

The structural origin has been a subject of debate

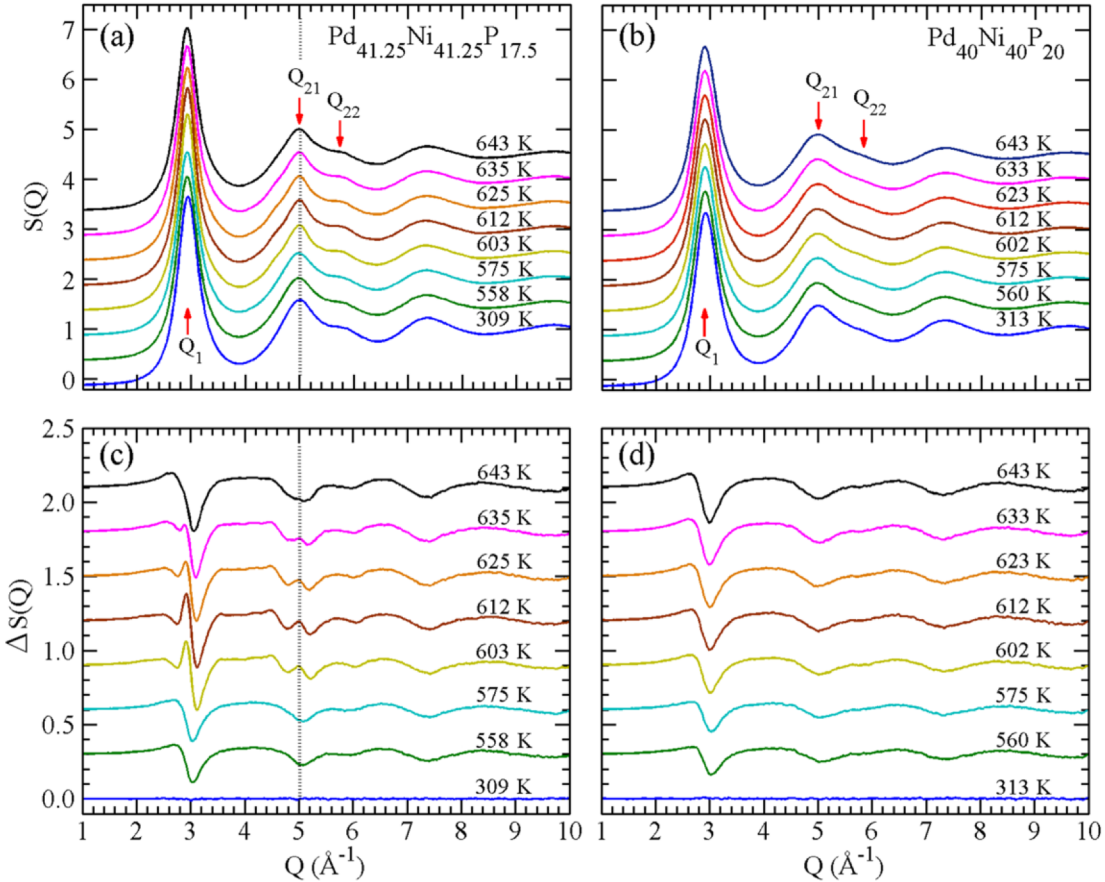
Mostly negative conclusions

- **Crystallization (HS Chen)**
- **Phase separation (HS Chen, Yavari)**
- **Short-range ordering (Yavari, Kumar, Jiang)**
- **“Cluster motion” (Zheng et al.)**
- **Two glass transitions (Shen & Inoue)**

We have therefore decided to take a comprehensive approach to look into the problem

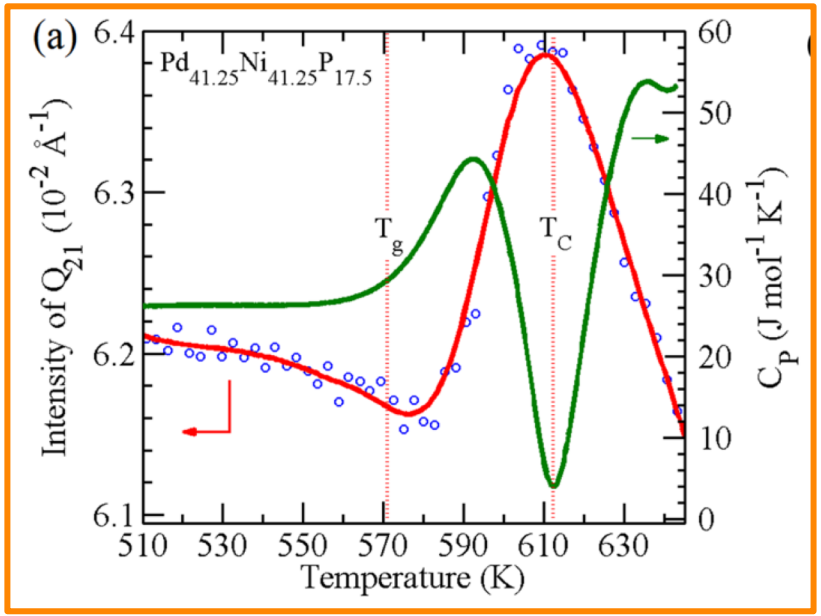
with In-situ synchrotron diffraction, small angle neutron scattering, TEM

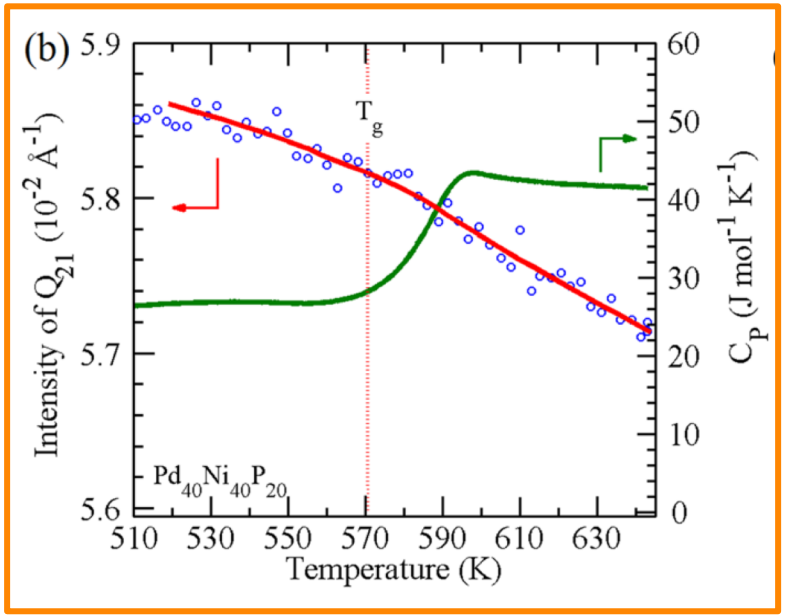
In-situ synchrotron diffraction has been used to study structure evolution



- No crystallization peaks
- Diffraction peaks (e.g., Q_{21}) first sharpens and then broadens
- A transition is identified at T~612 K

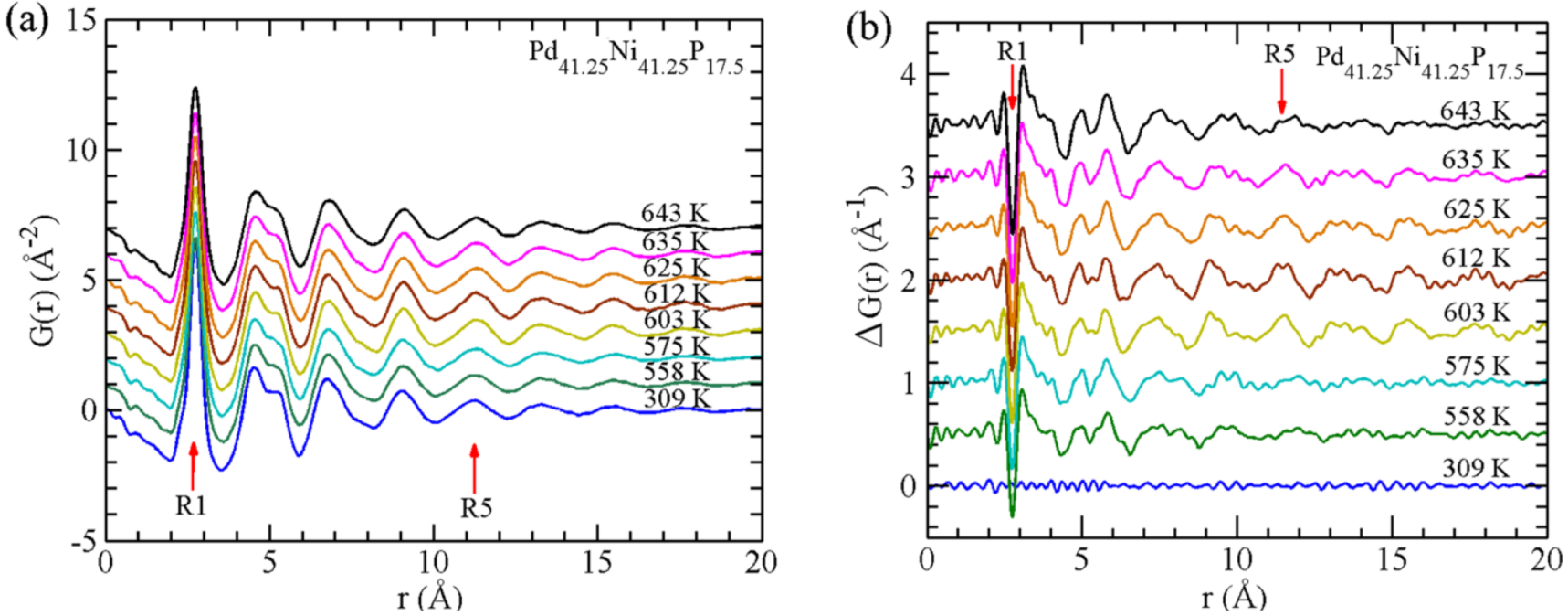
Synchrotron X-ray intensity data show a perfect correlation with Cp





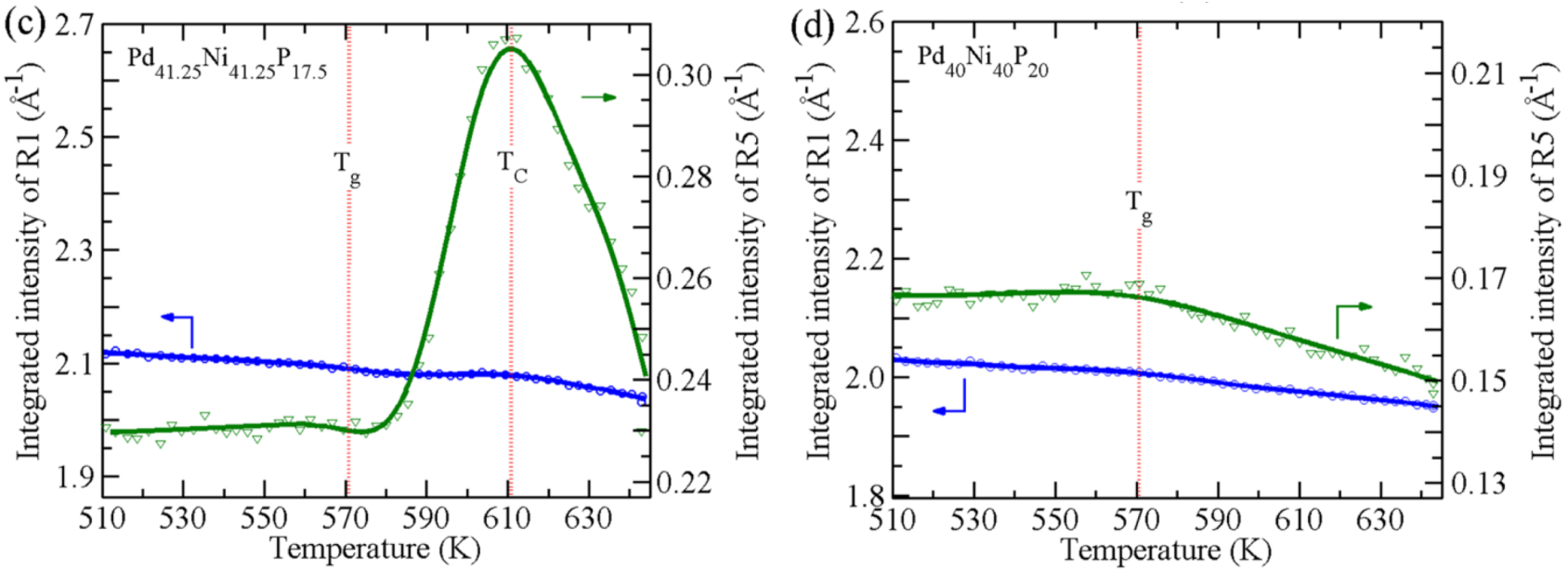
- P20 sample shows a single transition, at T_g
- An additional transition is observed in P17.5, at T_C=612 K

Real space analysis reveals significant changes at medium-range order



- Little change is seen in nearest-neighbor or short-range order (R1)
- A significant rise and fall is observed in higher order shells (e.g., R5)

Liquid-to-liquid phase transition at Tc is driven by medium-range order

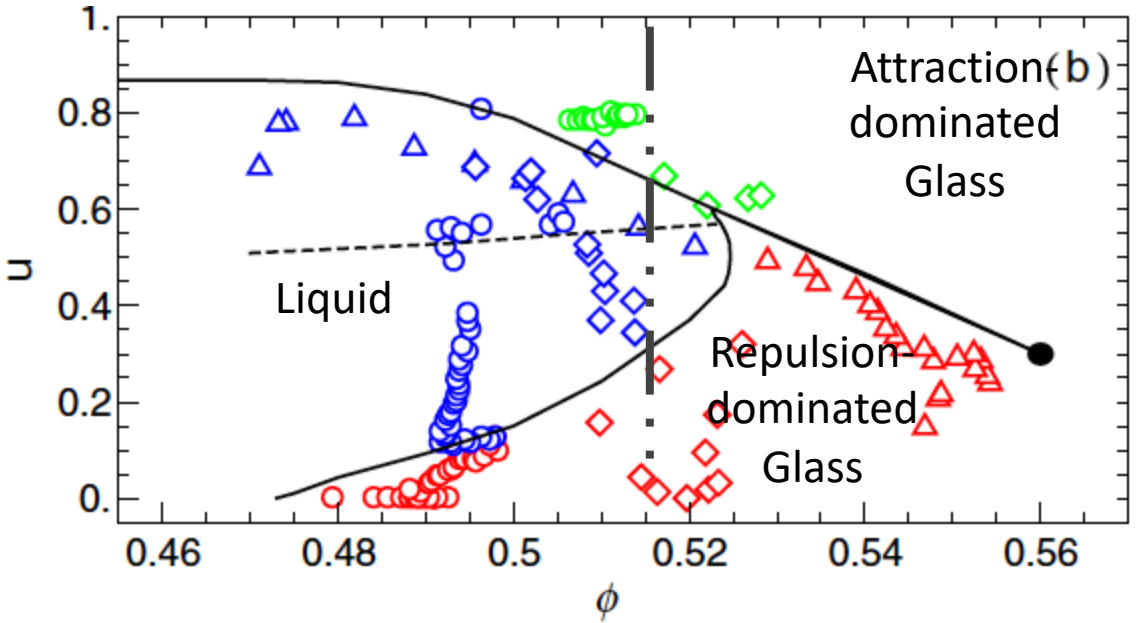


- Little change is seen in nearest-neighbor or short-range order (R1)
- A significant rise and fall observed in higher order shells (e.g., R5)
- $Pd_{40}Ni_{40}P_{20}$ sample shows smooth decline beyond Tg

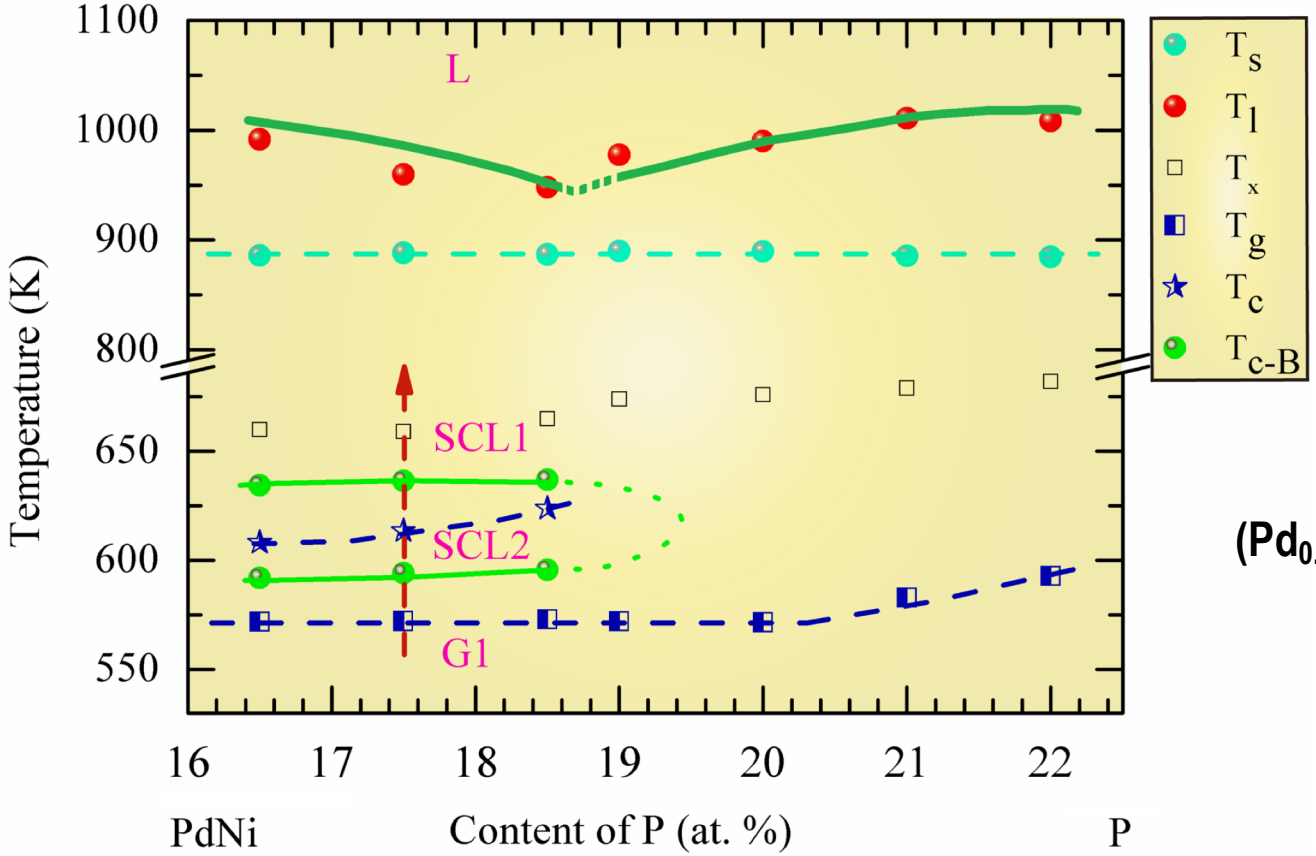
How a Liquid Becomes a Glass Both on Cooling and on Heating

Xinhui Lu,[1] S. G. J. Mochrie,[1,2] S. Narayanan,[3] A. R. Sandy,[3] and M. Sprung[3]
[1]*Department of Physics, Yale University, New Haven, Connecticut 06511, USA*
[2]*Department of Applied Physics, Yale University, New Haven, Connecticut 06511, USA*
[3]*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*

Reentrant glass in a colloid system

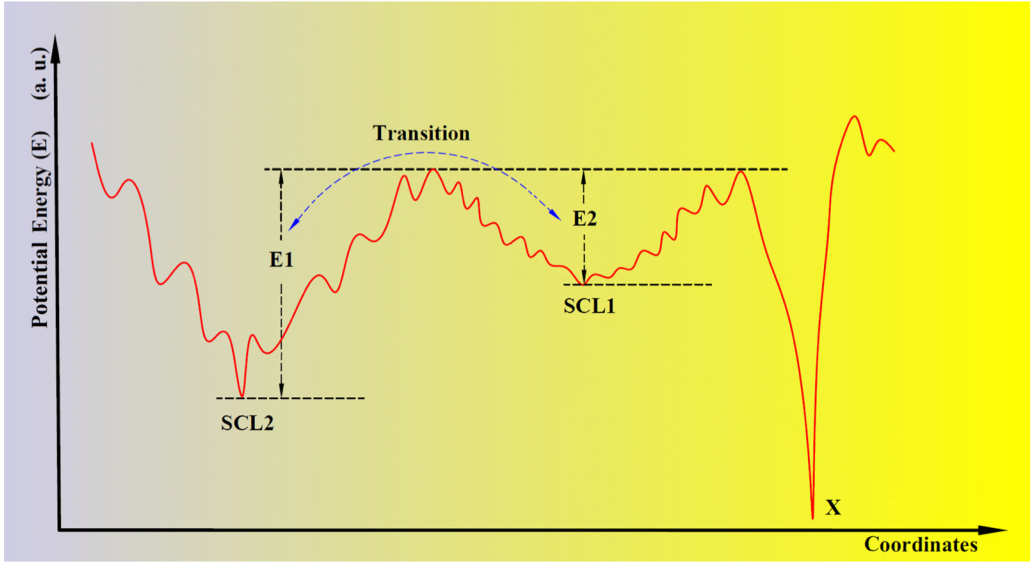


Composition dependence and sequence of transition



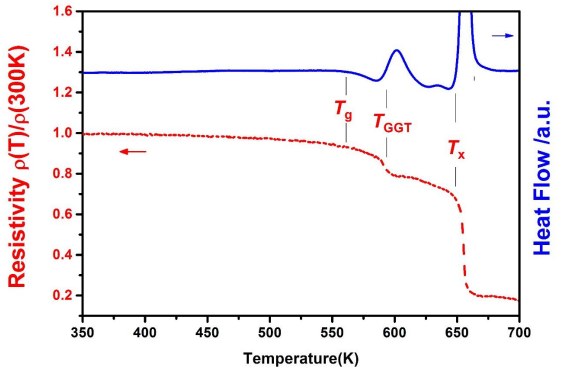
$(Pd_{0.5}Ni_{0.5})_{100-x}P_x$

Understanding the LLPT from the potential energy landscape perspective



- Three minima: crystalline phase X, SCL1, SCL2
- SCL2 is a more ordered state
- Quenched samples are in SCL1 at room temperature
- SCL1 is stabilized by entropy at high temperatures

Courtesy of Zhaoping Lu
University of Science and Technology Beijing



A sudden drop staring at 600 K indicates an ordering change in the glass structure.

Q. Du et al. & Z. P. Lu, "Reentrant glass transition leading to ultrastable metallic glass," Mat. Today, 34, 66-77 (2020).

APPLIED PHYSICS LETTERS **108**, 211907 (2016)

Structural crossover in a supercooled metallic liquid and the link to a liquid-to-liquid phase transition

Si Lan[1], Matthew Blodgett[2], Ken Kelton[2], J. L. Ma, J. Fan, and Xun-Li Wang[1]
[1]Department of Physics and Mat. Sci., City University of Hong Kong
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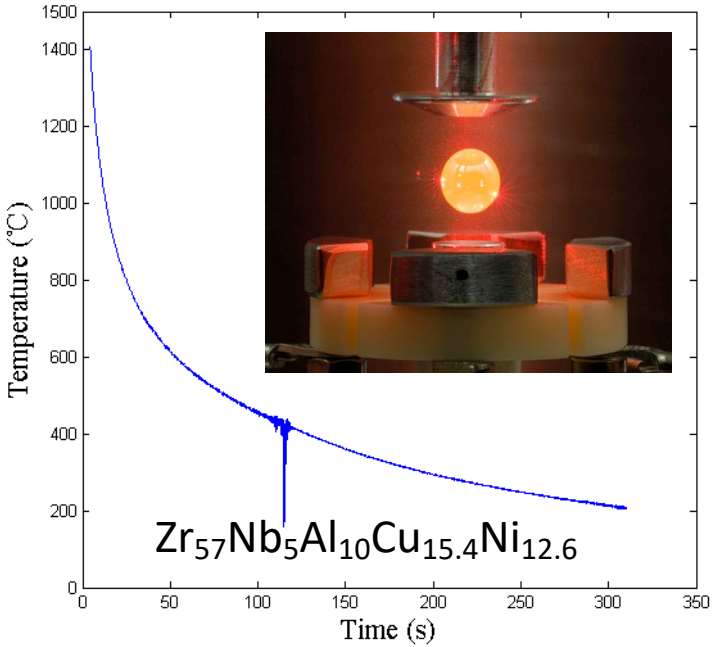
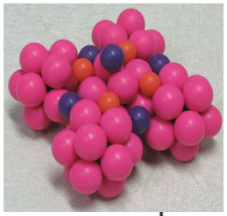
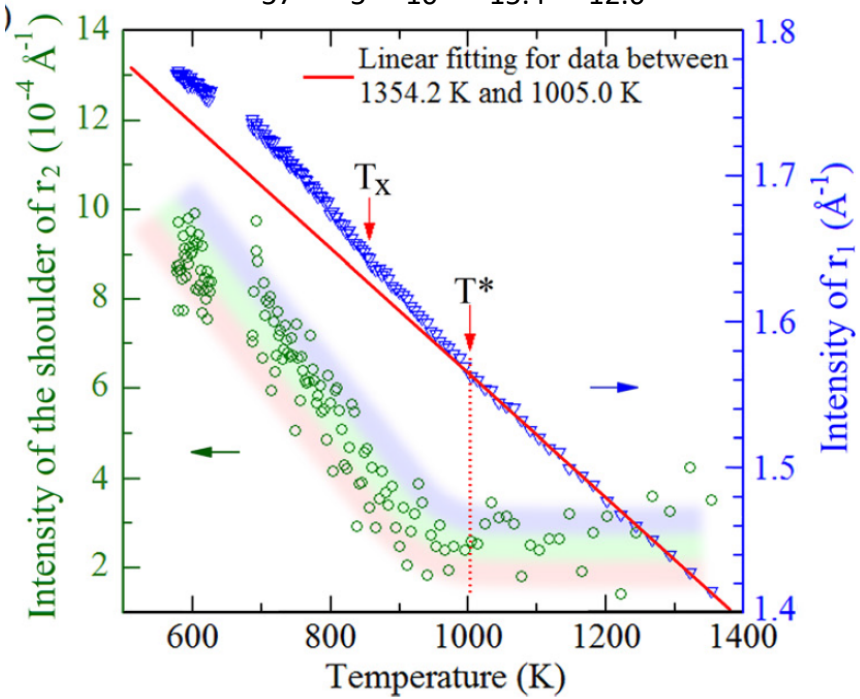


Structure cross-over during cooling by levitation



$Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$



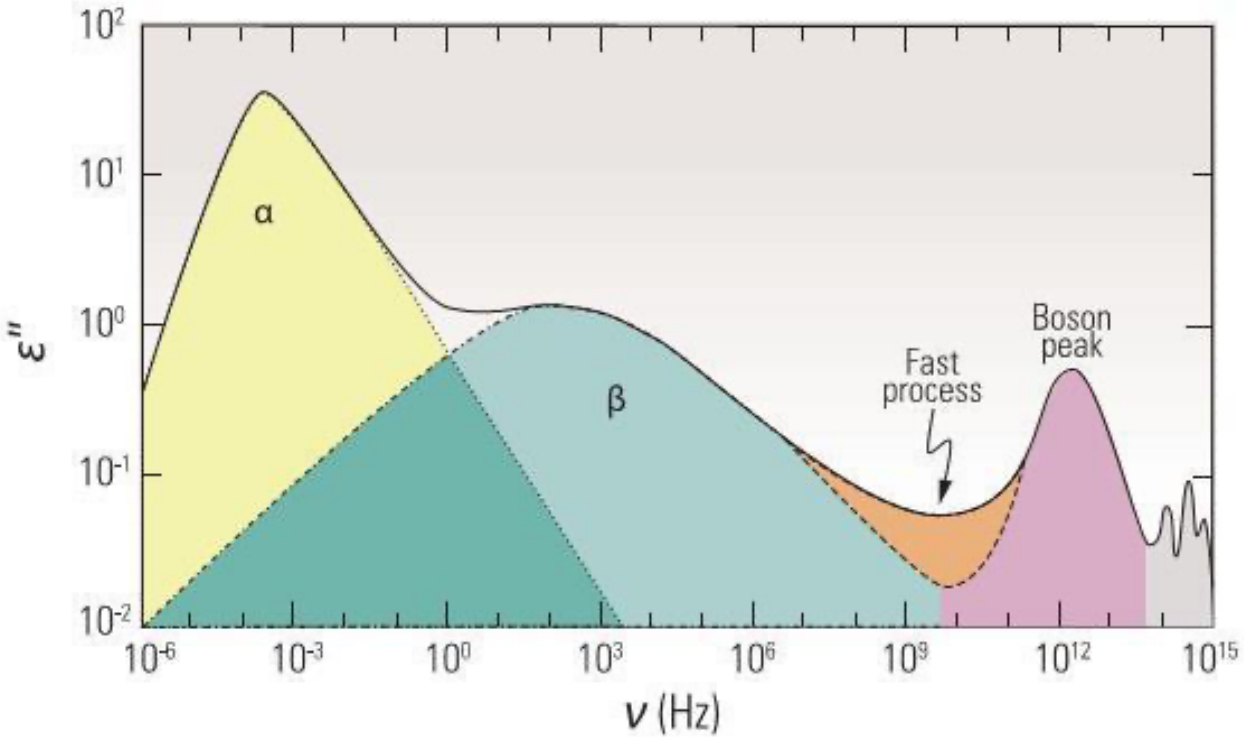
Molecular dynamics simulation suggests the rise in 2nd shoulder is due to correlations by solute atoms

Connectivity of building blocks is the key to link amorphous and crystalline states

"A medium-range structure motif linking amorphous and crystalline states"

Si Lan et al., Nature Materials, accepted

The glass dynamics are rich and diverse

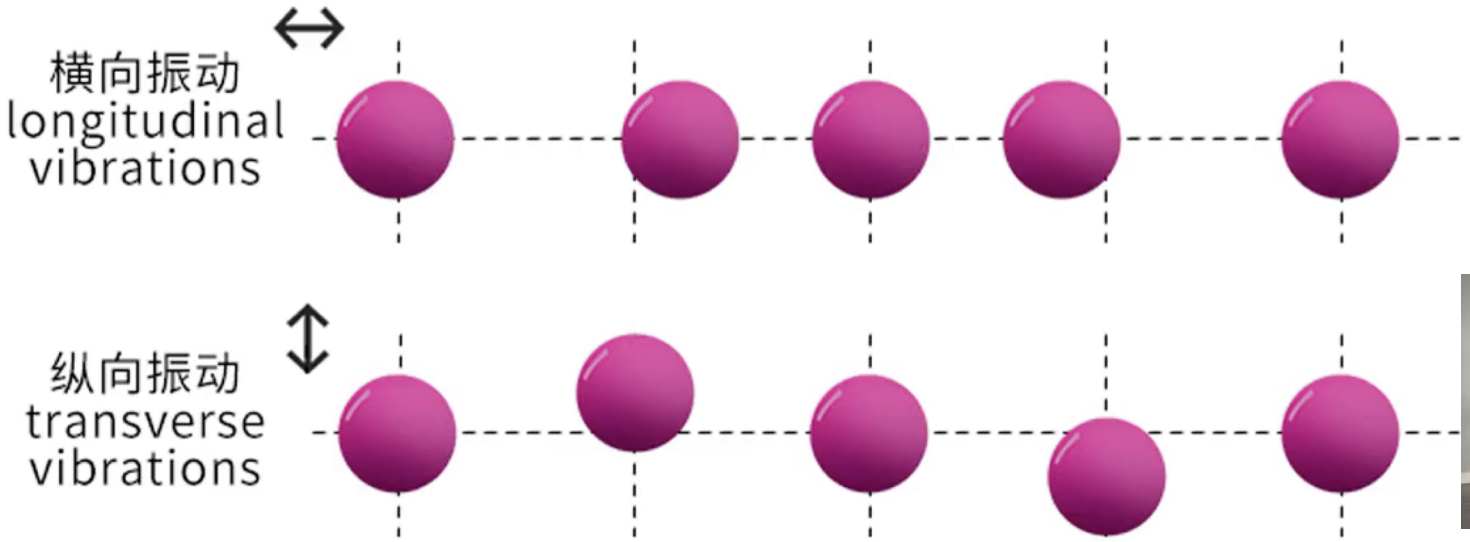


Three distinct modes

- **Primary relaxation**
- **Slow relaxation**
- **Phonons**

Schematic illustration of dielectric loss as a function of the frequency in glassy materials. (Lunkenheimer)

Physical picture – the nature of longitudinal and transverse acoustic phonons



The longitudinal excitation is closely related to the density of materials, while the transverse excitation is more sensitive to the structures of materials.

Phonon measurement by inelastic neutron scattering (INS) for crystalline materials

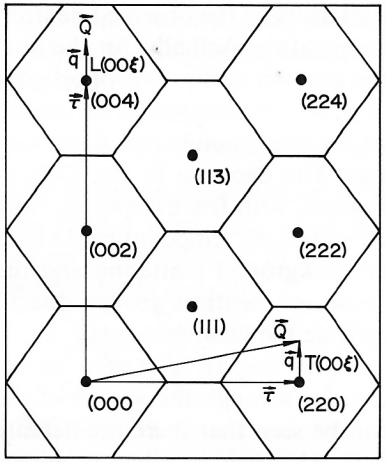


FIG. 6. Typical scattering geometries for the detection of longitudinal and transverse [100] modes [in the $(1\bar{1}0)$ scattering plane] of an fcc crystal.

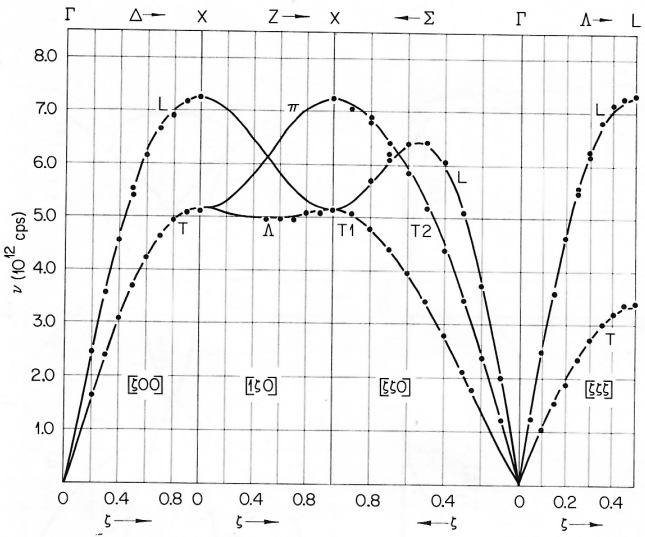


FIG. 7. The phonon dispersion curves of Cu along the major symmetry directions at 49 K; ν represents frequency $\omega/2\pi$. The solid lines were obtained by fitting the data to a sixth-nearest-neighbor axially symmetric Born–von Kármán model. (From Nicklow *et al.*[99])

Phonon measurement by inelastic neutron scattering (INS) for crystalline materials

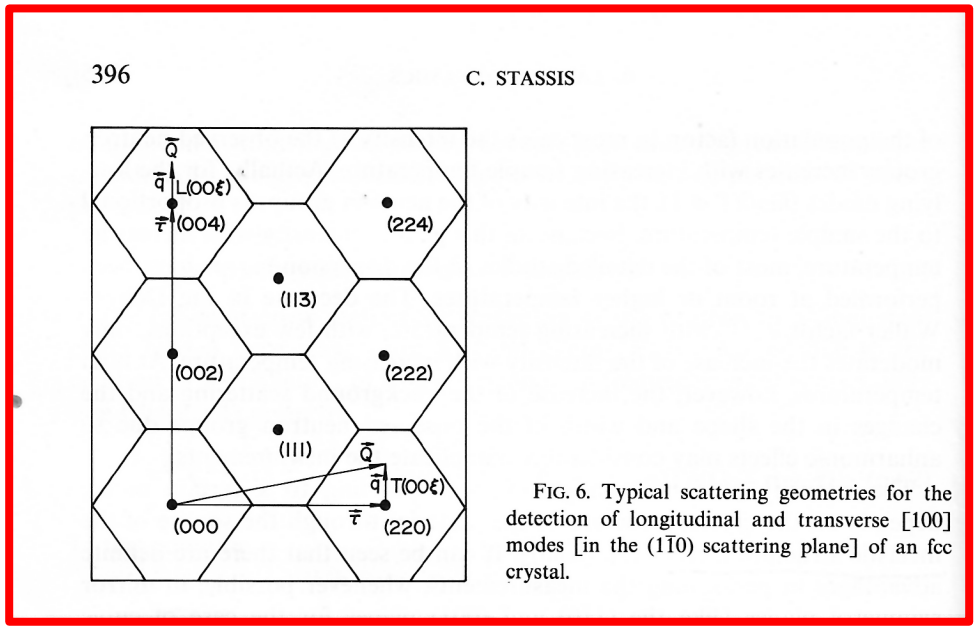
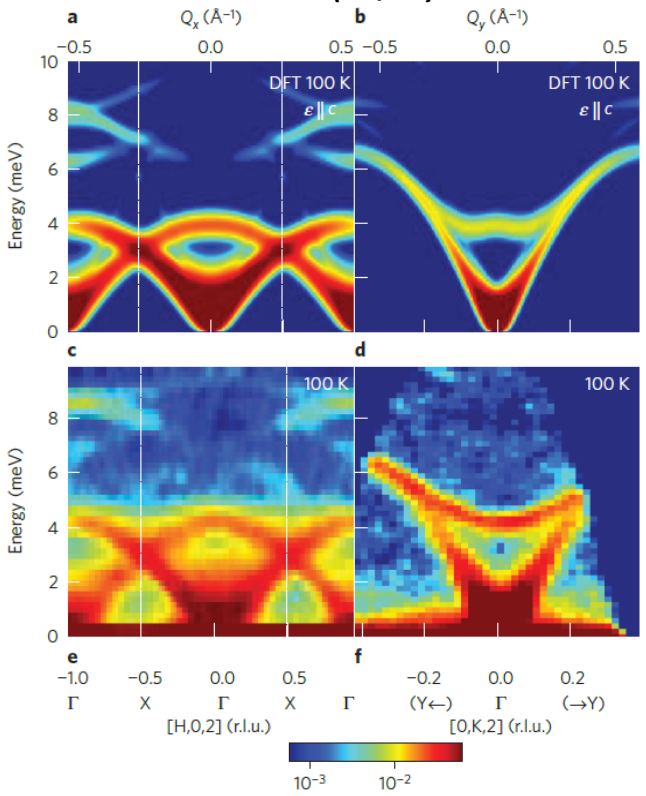


FIG. 6. Typical scattering geometries for the detection of longitudinal and transverse [100] modes [in the (1$\bar{1}$0) scattering plane] of an fcc crystal.

S(Q, E)



Strong dispersion anisotropy in SnSe C. Li, *et al.* Nat. Phys. **11**, 1 (2015)

Inelastic neutron scattering spectrum for polycrystalline and glassy materials

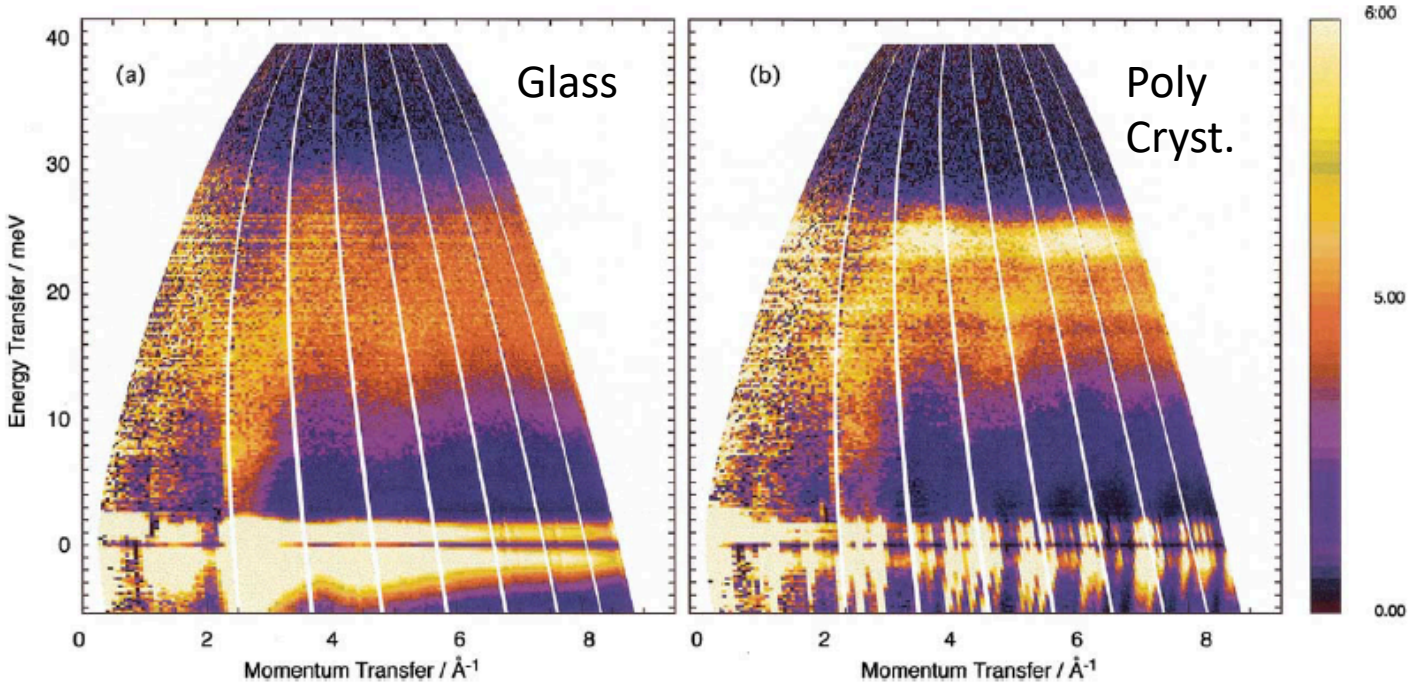


Fig. 3. $G(Q,E)$ of $Ni_{33}Zr_{67}$ alloy: (a) metallic glass and (b) crystallized sample.

Otomo et al., *J . non-cryst. Solids,* 312-314, 599-602 (2000)

Universal link between the boson peak and transverse phonons in glass

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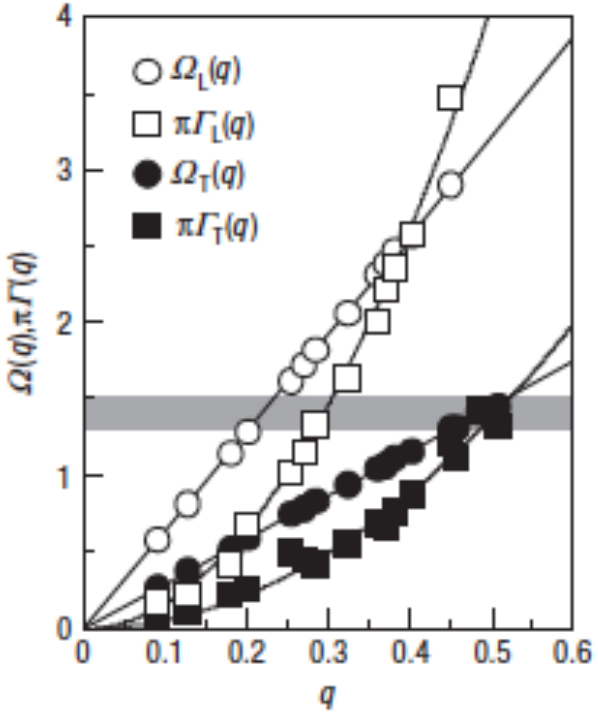
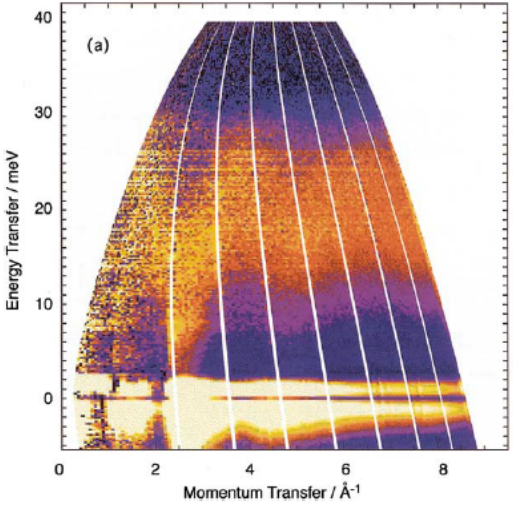
*e-mail: tanaka@iis.u-tokyo.ac.jp

- **Phonon peak width $\pi\Gamma \approx \omega$ at Boson peak energy for transverse phonons.**
- **This is the Ioffe-Regel limit above which transverse phonons are short-lived and thought to cease to propagate**
- **Are there high-frequency transverse phonons?**

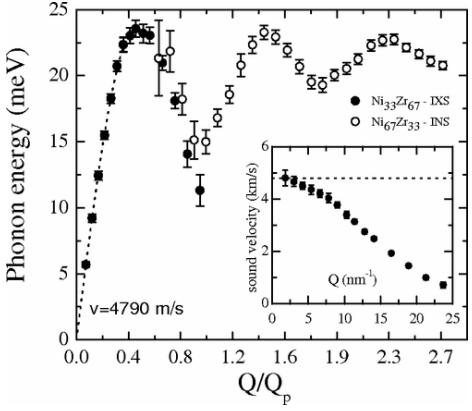


Transverse phonons are difficult to measure



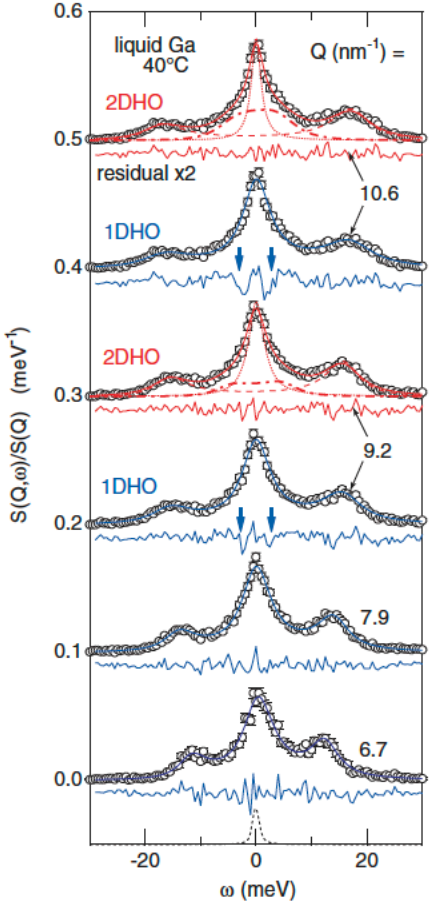
Otomo et al.,
J . non-cryst. Solids
312-314, 599-602 (2000)

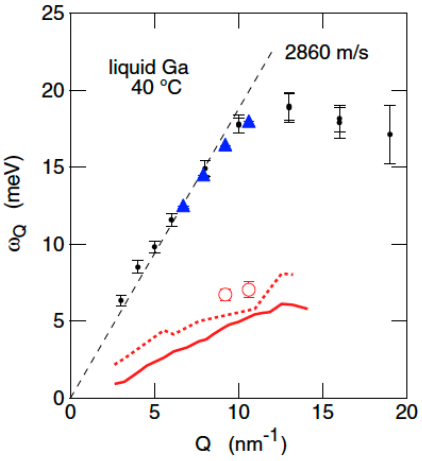
$Zr_{67}Ni_{33}$@MARI



T. Scopigno, *et al.*
"High-Frequency Dynamics in Metallic Glasses,"
PRL. ***96***, 135501 (2006)

$Zr_{67}Ni_{33}$



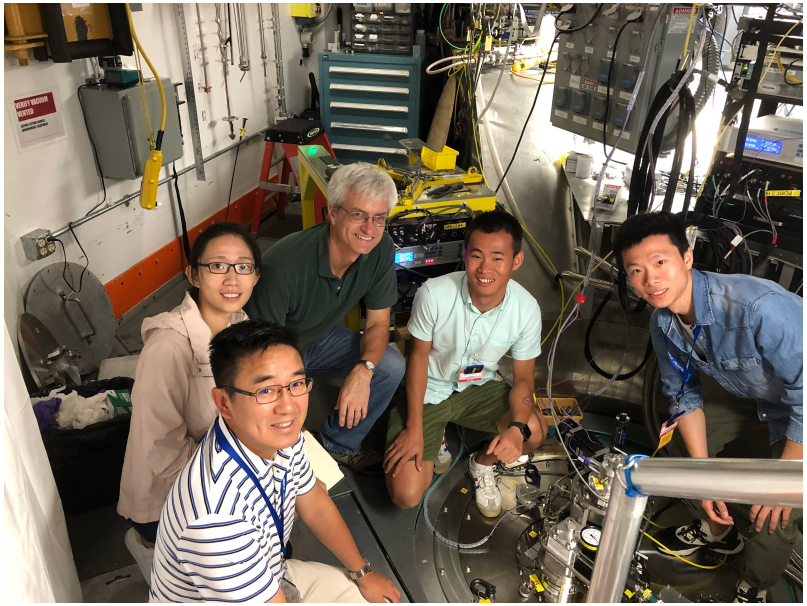


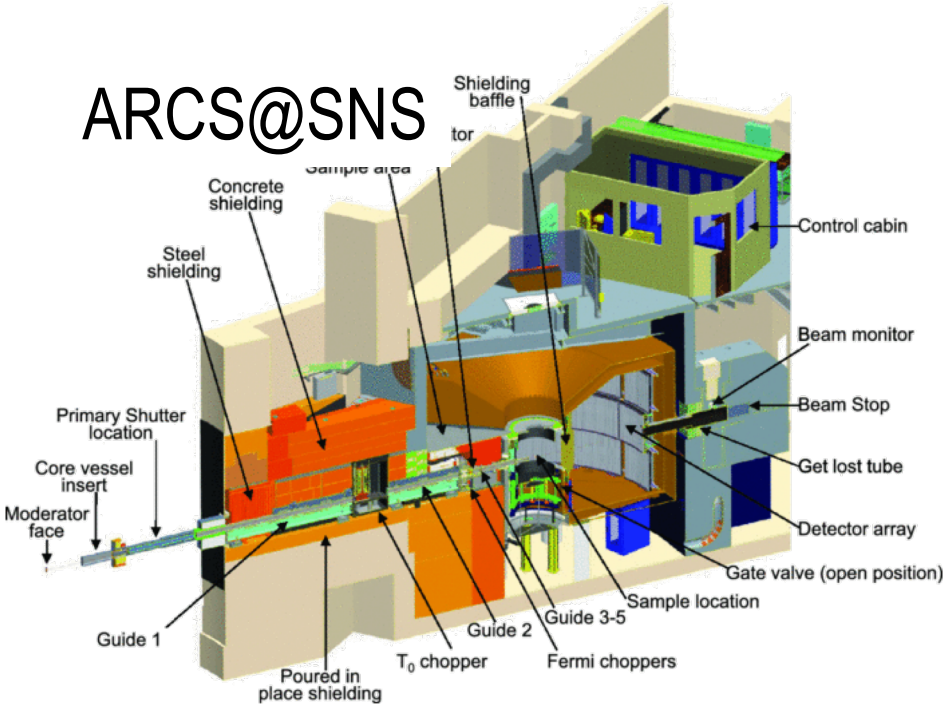
Hosokawa et al.,
PRL 102, 105502 (2009)

PHYSICAL REVIEW LETTERS **124,** 225902 (2020)

Observation of High-Frequency Transverse Phonons in Metallic Glasses

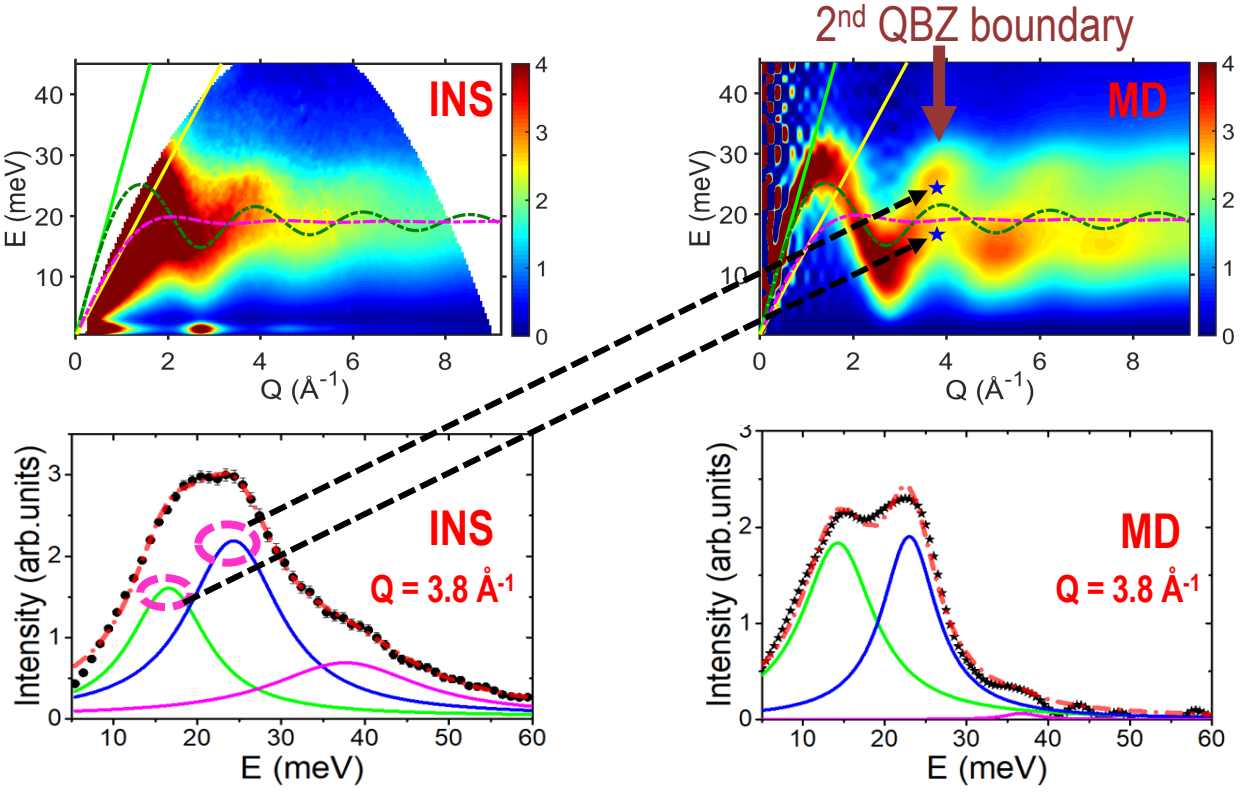
X. Y. Li,[1,2,3,*] H. P. Zhang,[4,*] S. Lan,[1,5,*] D. L. Abernathy,[6] T. Otomo,[7] F. W. Wang,[2,3,8] Y. Ren,[9] M. Z. Li,[4,†] and X.-L. Wang[1,10,‡]





GDOS : $G(\boldsymbol{Q},E)=\left[1-e^{-\frac{E}{k_BT}}\right]\frac{E}{Q^2}S(\boldsymbol{Q},E)$

INS data are analyzed through Generalized Density of States (GDOS) and compared with MD simulations



$Zr_{46}Cu_{46}Al_8$

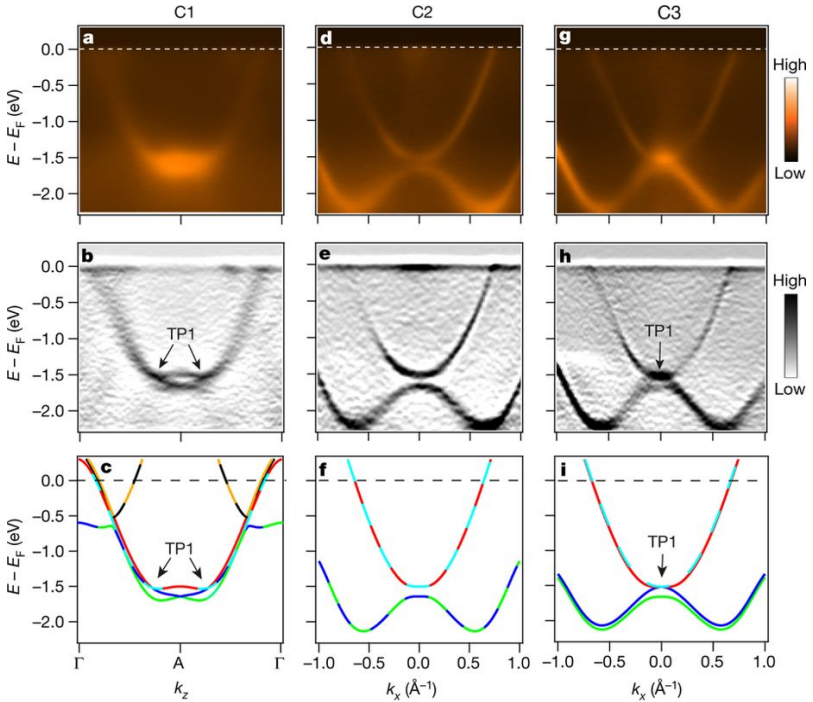
- A characteristic phonon dispersion
- Phonon spectrum significantly broadened
- Phonon spectrum dominated by acoustic modes

MD method:
van Hove correlation function with atoms neutron weighting factor

LA/TA separation at 2nd quasi Brillouin zone (QBZ) boundary

The 2nd derivative method was adopted from the ARPES community

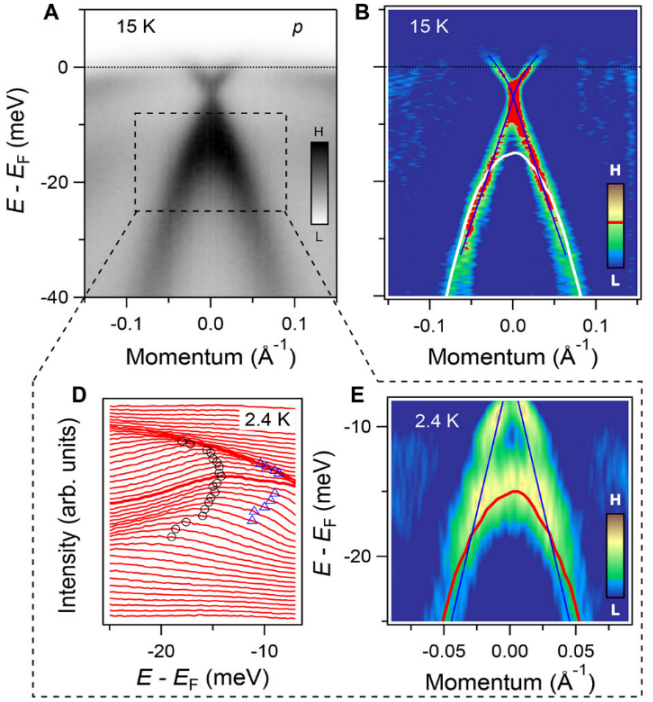
Topological semimetal MoP



Three-component fermions

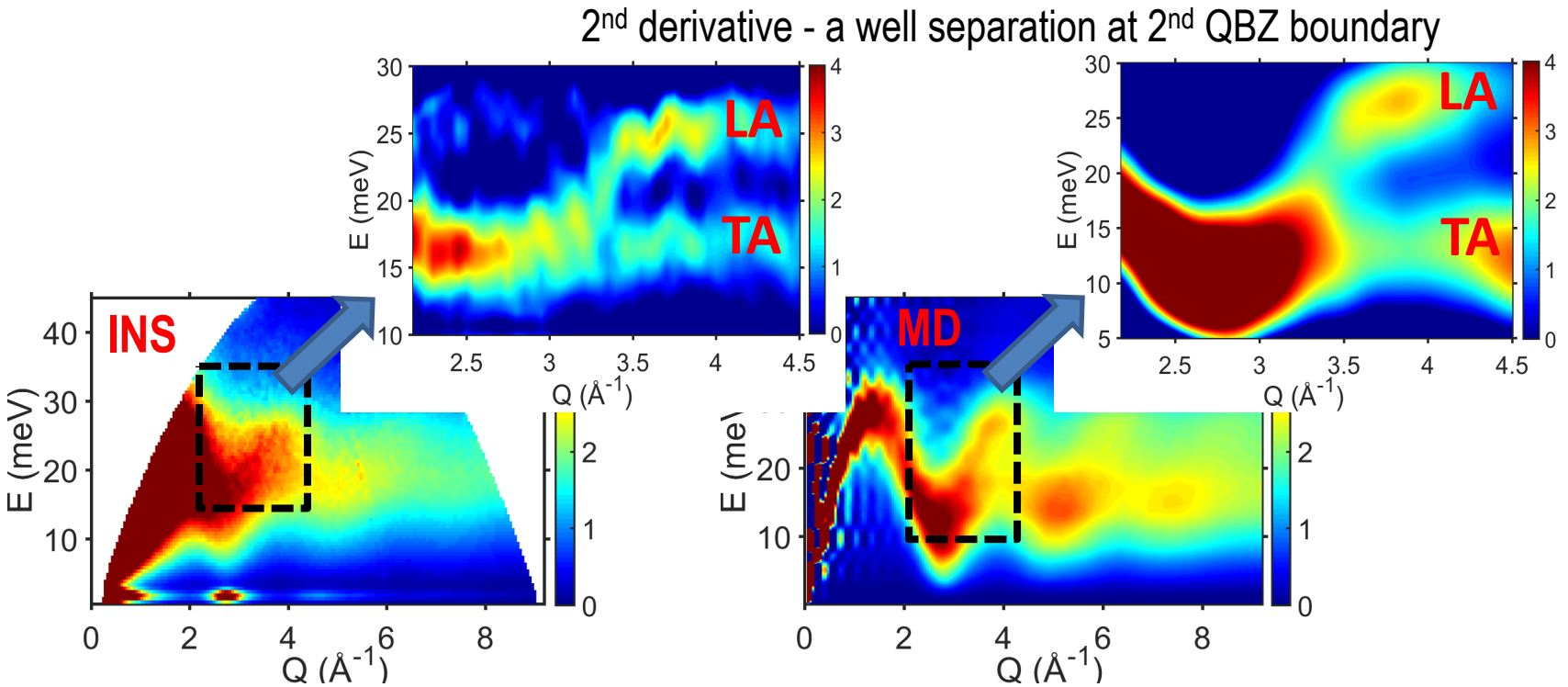
B. Lv, *et al.* Nature **546,** 627 (2017)

Topological superconductor $FeTe_{0.5}Se_{0.5}$



P. Zhang, *et al.* Science **360,** 182 (2018)

Two branches are separated by the 2nd derivative method – longitudinal vs. transverse phonons

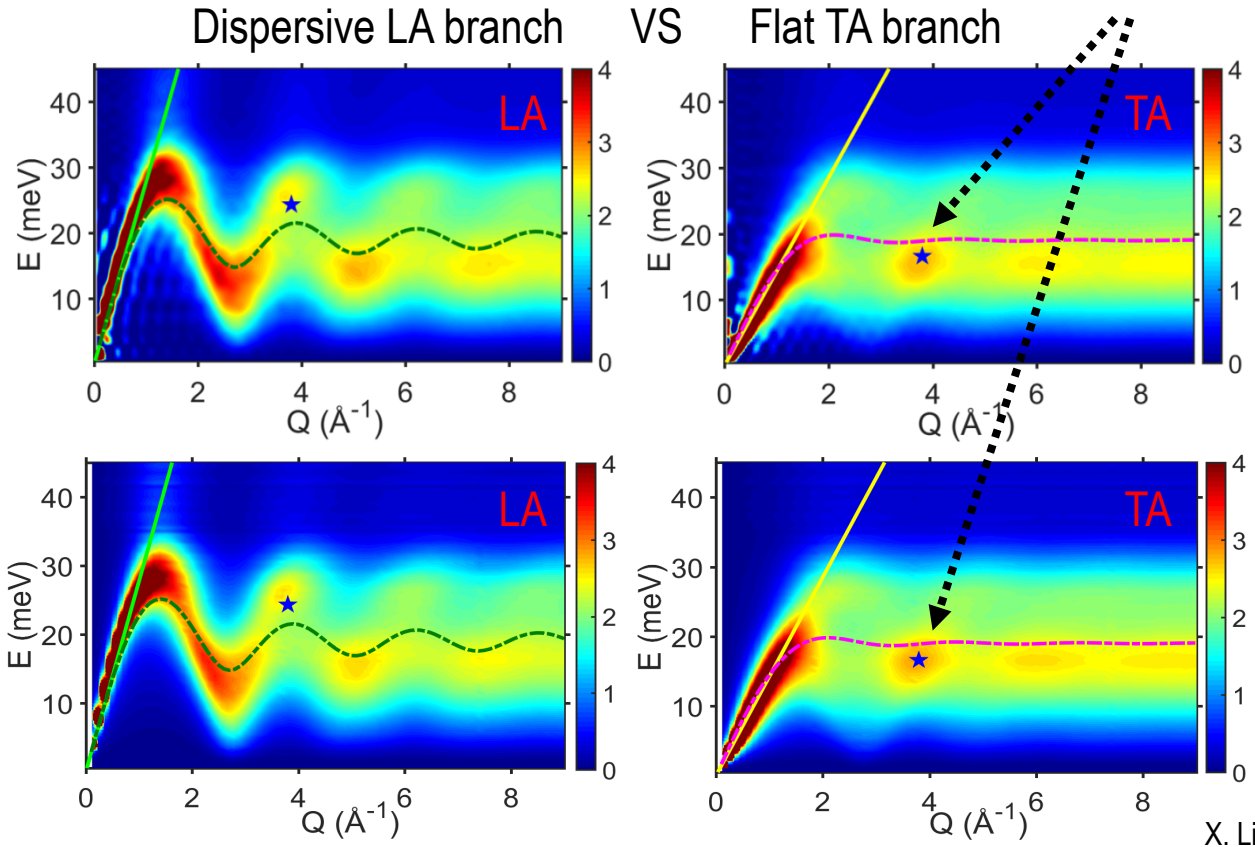


1st time the 2nd derivative applied to INS data analysis.

X. Li, *et al*, ***Phys. Rev. Lett.*** **124**, 225902 (2020)

Experimental findings are further confirmed by MD simulations

Strong intensities at 2nd QBZ boundary



Dynamic matrix method

$$\boldsymbol{e}_{\lambda,L}(\boldsymbol{Q}) = [\boldsymbol{e}_{\lambda}(\boldsymbol{Q}) \cdot \hat{\boldsymbol{Q}}]\hat{\boldsymbol{Q}}$$

$$\boldsymbol{e}_{\lambda,T}(\boldsymbol{Q}) = \boldsymbol{e}_{\lambda}(\boldsymbol{Q}) - \boldsymbol{e}_{\lambda,L}(\boldsymbol{Q})$$

Velocity correlation function method

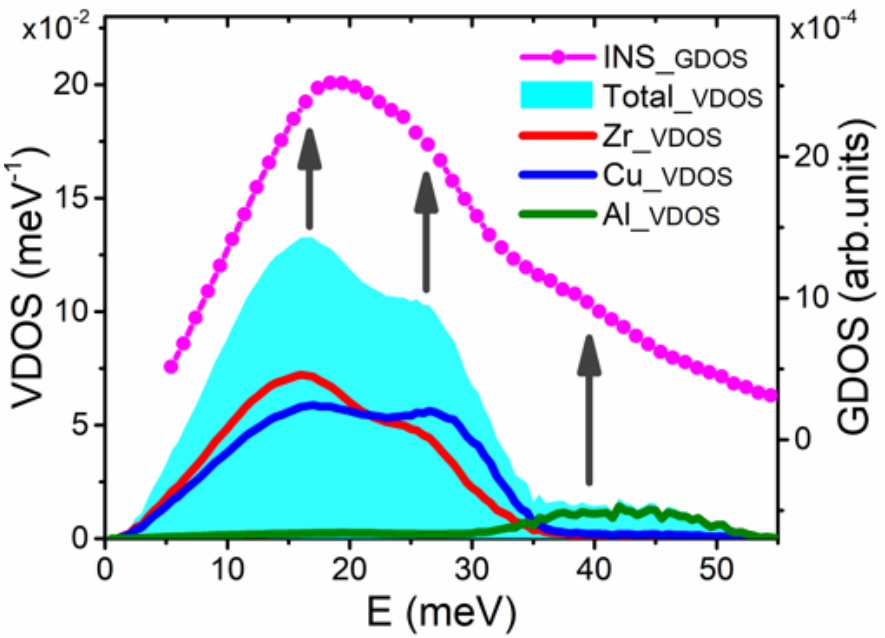
$$\boldsymbol{j}_{L}(\boldsymbol{Q},t) = [\boldsymbol{j}(\boldsymbol{Q},t) \cdot \hat{\boldsymbol{Q}}]\hat{\boldsymbol{Q}}$$

$$\boldsymbol{j}_{T}(\boldsymbol{Q},t) = \boldsymbol{j}(\boldsymbol{Q},t) - \boldsymbol{j}_{L}(\boldsymbol{Q},t)$$

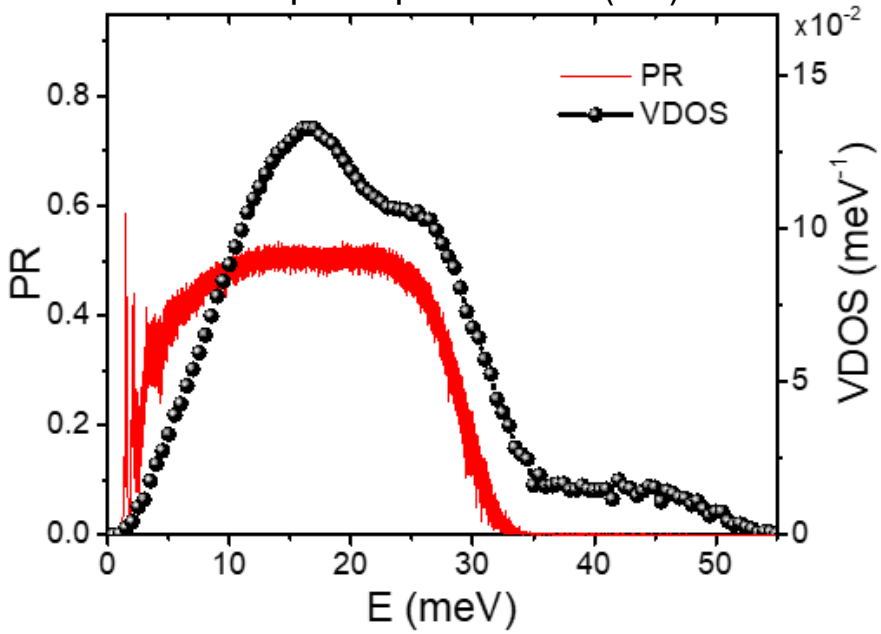
X. Li, *et al*, ***Phys. Rev. Lett.*** **124**, 225902 (2020)

MD simulations provided further insights

MD vs. Exp.



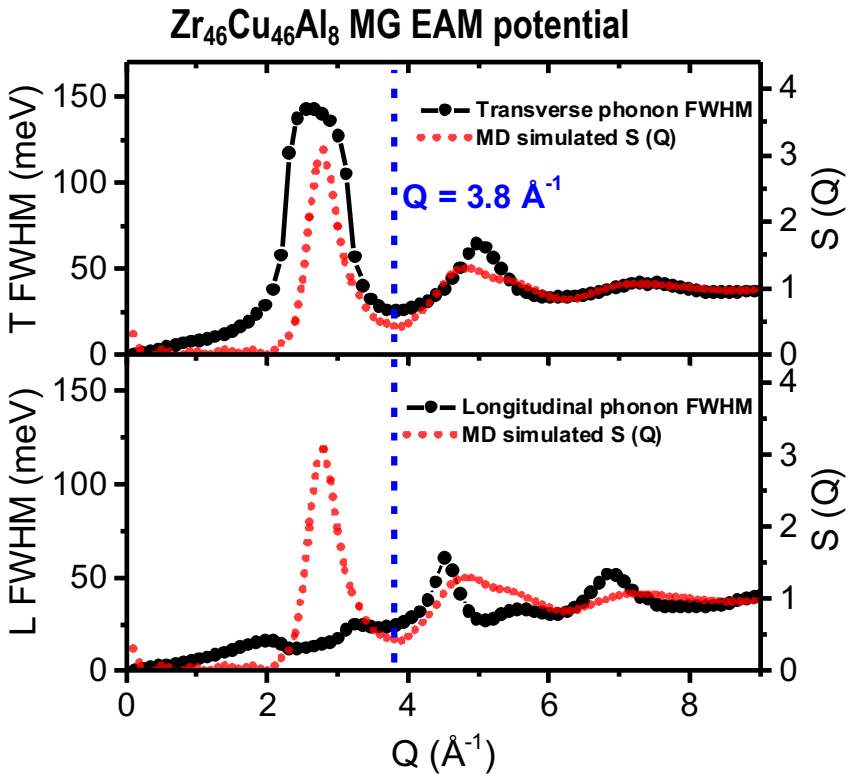
MD participation ratio (PR)

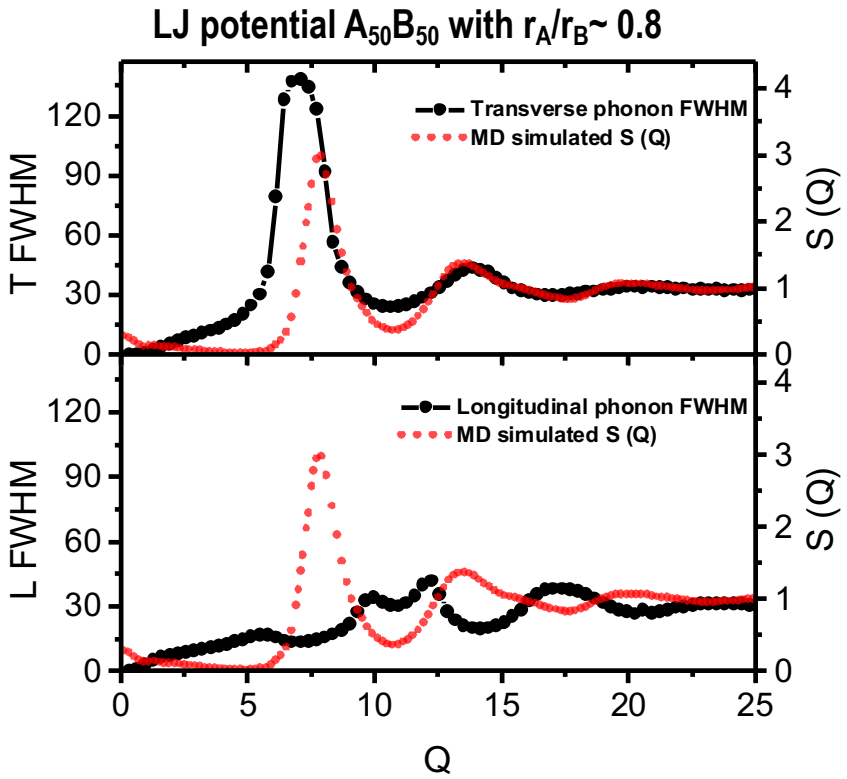


~17 & 26 meV peaks: contributions from Zr and Cu atoms, spatially extended modes

~40 meV peak: contributions dominated by Al atoms, spatially localized modes

Apparent peak width of transverse phonons follows S(Q)





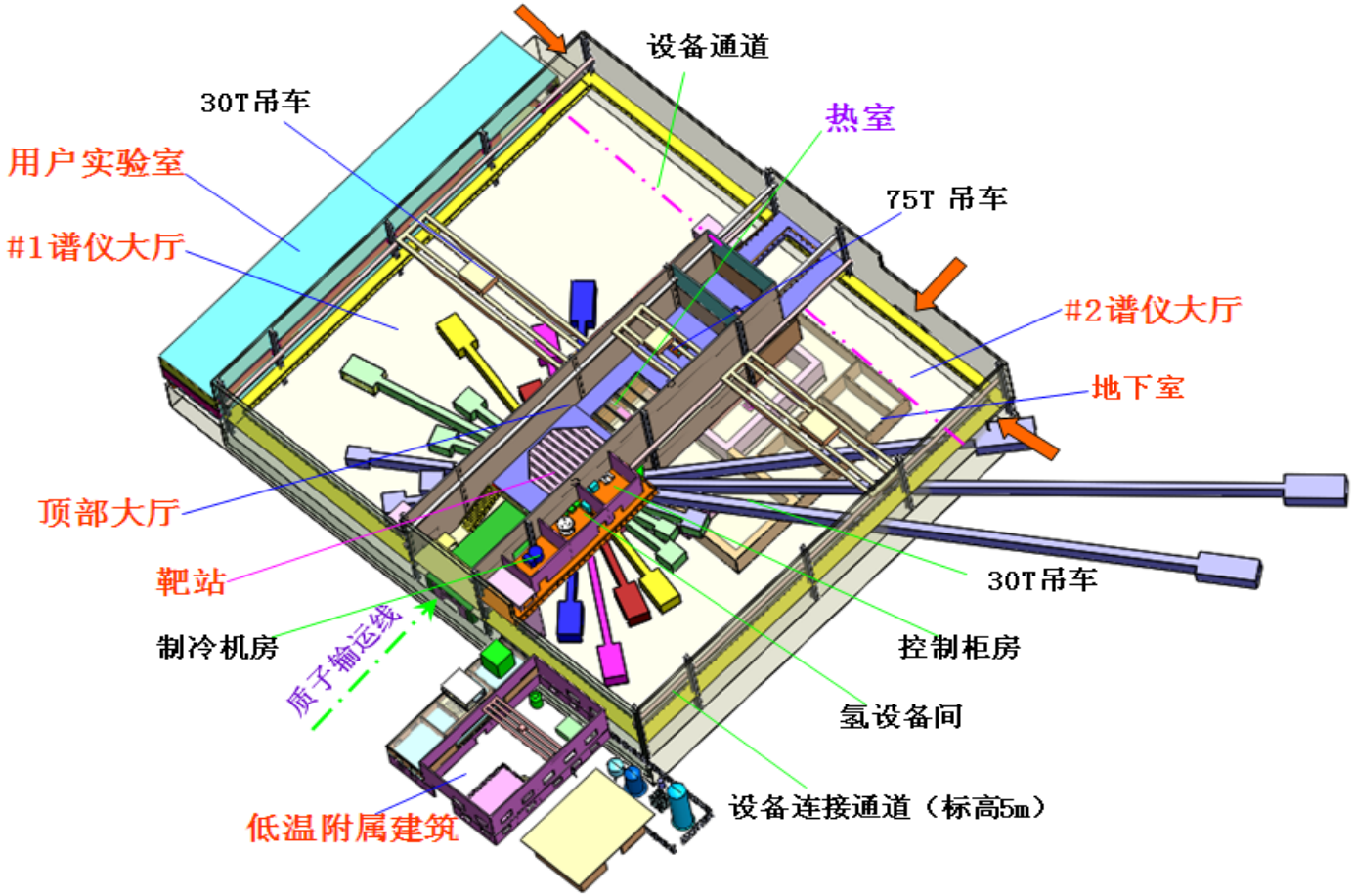
No correlation for longitudinal phonons

X. Li, *et al*, ***Phys. Rev. Lett.*** **124**, 225902 (2020)

The commission of CSNS has caused an international sensation

With a construction cost of 2.3 billion RMB, CSNS is destined to become an international hub for materials research

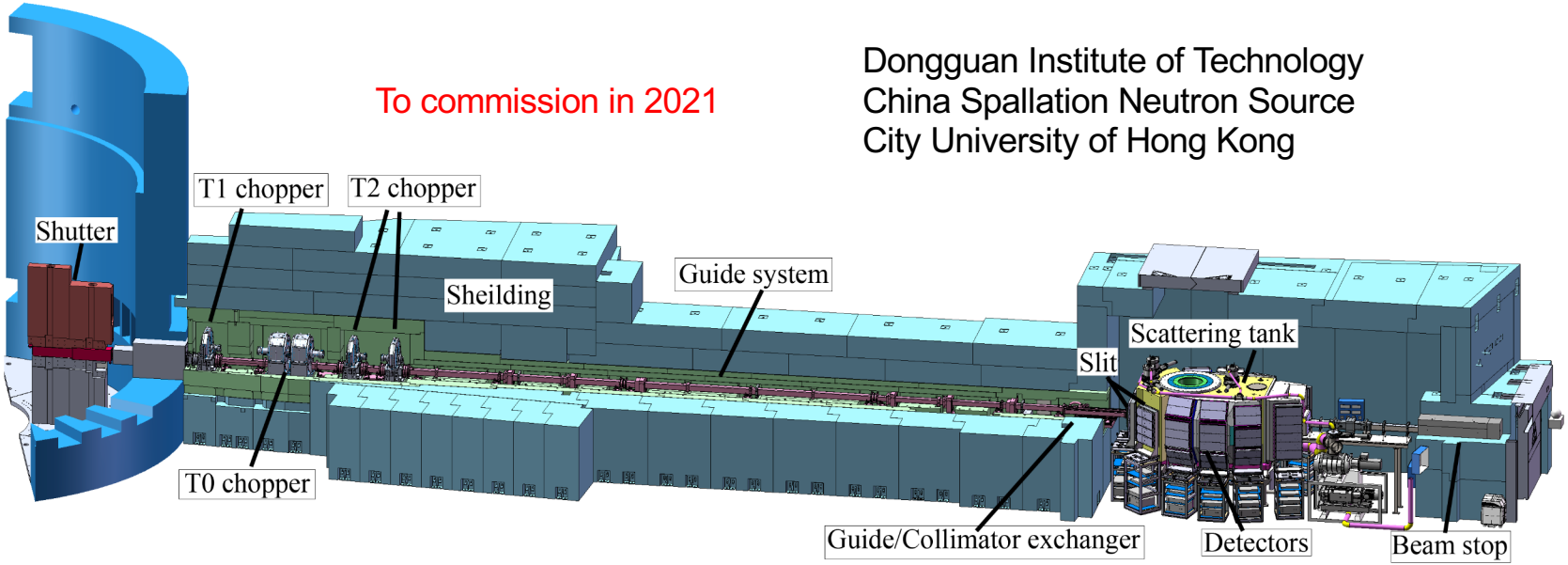
Experimental hall layout



CityU is a partner of the Multi Physics Instrument (MPI)

To commission in 2021

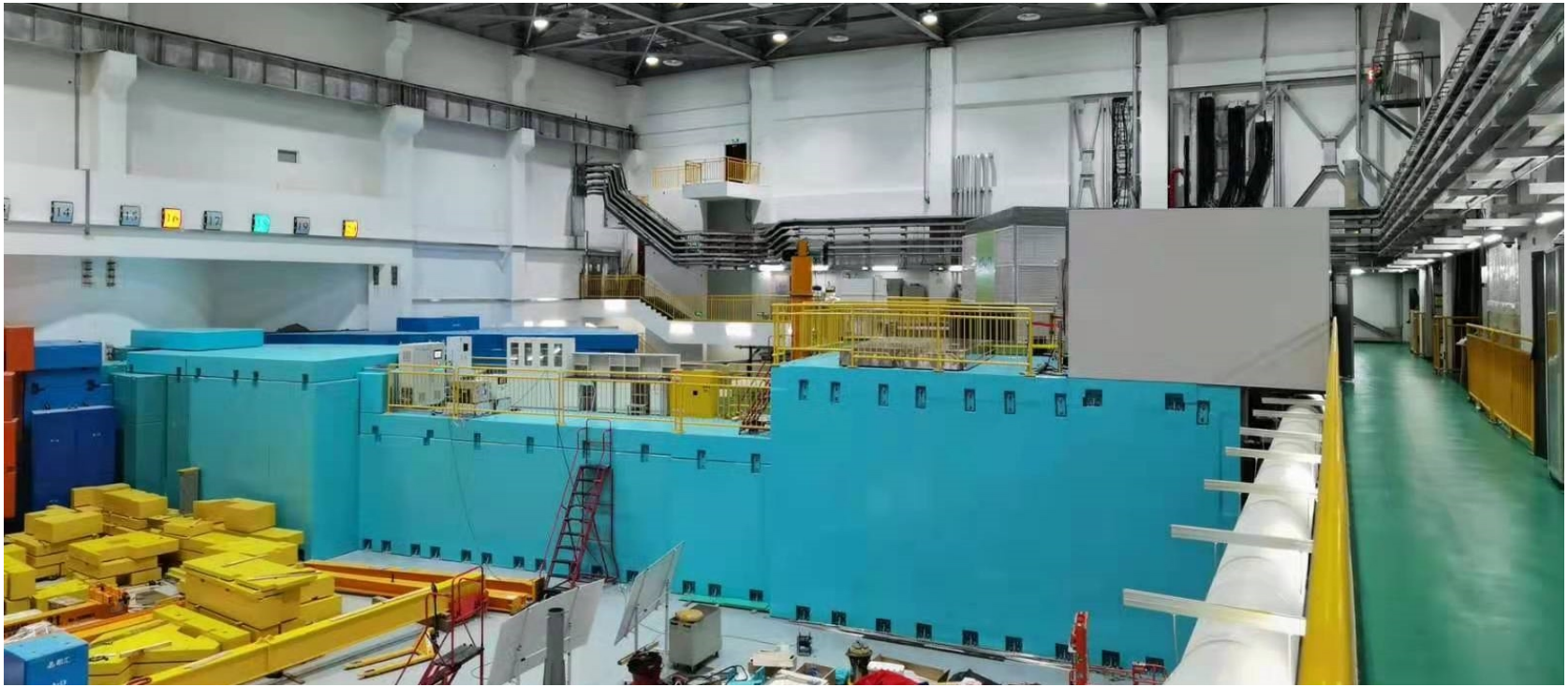
Dongguan Institute of Technology
China Spallation Neutron Source
City University of Hong Kong



- Beam line No.16
- Moderator: Decoupled Water
- Sample to moderator: 30 m
- Sample to detector: 1~3 m
- Accessible Q range: up to 50 $Å^{-1}$
- Q Resolution: $\Delta Q/Q \sim 0.3\%$

- High-pressure 3He detectors
- Flux on sample： ~10^7 n/s/cm^2
- Time resolution: ~ 2-5 min / data set

Commissioning of MPI



多物理谱仪是东莞理工学院、香港城市大学依托中国散裂中子源建设的全散射谱仪

Concluding remarks and outlook

- Scattering are powerful techniques to elucidate the structure and dynamics of glass materials
- Structure of glass can be visualized
  - Fundamental building blocks (maybe much larger than short-range order)
  - Connectivity of the building blocks
- Dynamics are important and maybe linked to the structure
- Medium-range and longer range ordering are the key

There is plenty room at the top