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Static heterogeneity in metallic glasses

Tetsu Ichitsubo (Kyoto University, Japan)
Present (Apr 1, 2010-Mar 31, 2011):
University of Tennessee at Knoxville (Professor Takeshi Egami)

Collaborators
Hidemi Kato (Tohoku University)
Eiji Abe (University of Tokyo)
Shiro Biwa (Kyoto University)
Shinya Hosokawa (Hiroshima Tech.)
Kazuhiro Matsuda (Kyoto Univ.)
Junji Saida (Tohoku University)
Alfred Q.R. Baron (RIKEN, SPring-8)
Eiichiro Matsubara (Kyoto University)

Present study:

1. Beta relaxation (detected by ultrasound) leading to crystallization (Stochastic resonance)

2. Static heterogeneity of glasses, inferred from (1)

3. Phonon behavior of some metallic glasses, to reveal the static heterogeneity of (2)

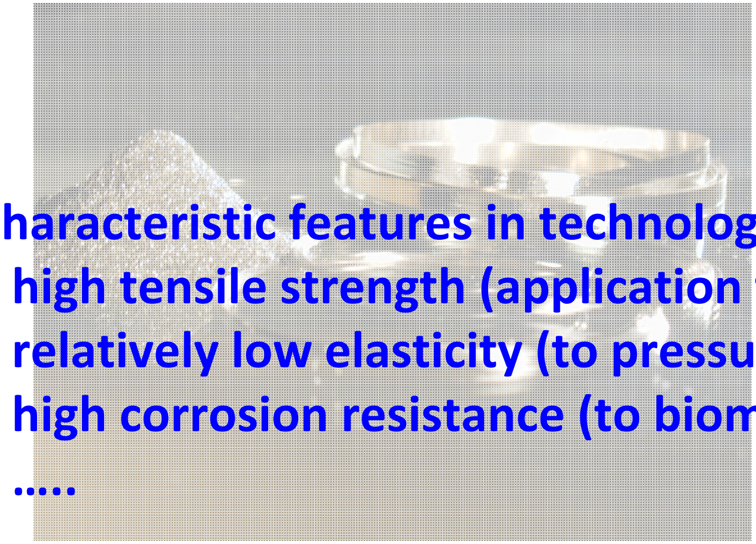
4. Structural view of glass transition

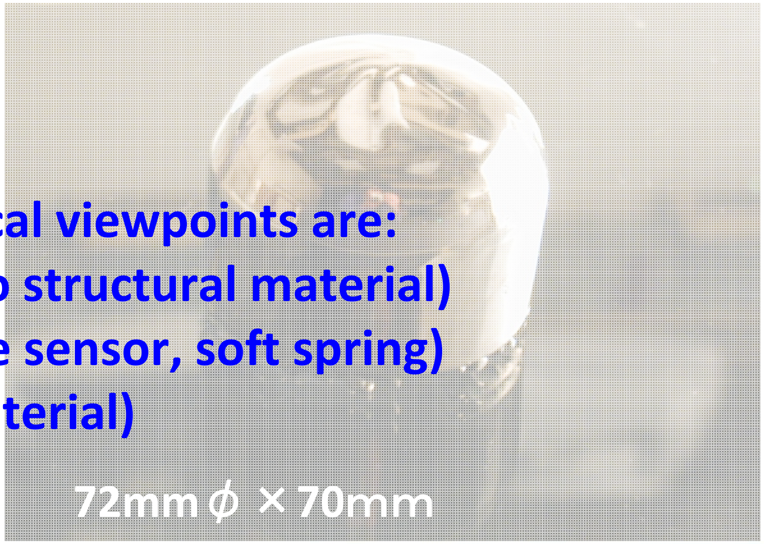
5. The recent results from the others

6. I’d like to have some theoretical idea from YOU!

What is Metallic Glass (MG) ?

Metallic glasses (MGs) are defined as
“amorphous alloys that exhibit the reversible glass transition”.



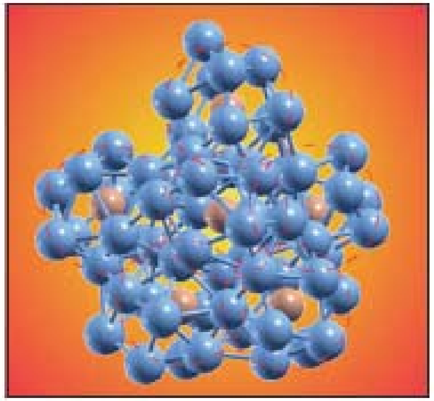


Characteristic features in technological viewpoints are:

- high tensile strength (application to structural material)
- relatively low elasticity (to pressure sensor, soft spring)
- high corrosion resistance (to biomaterial)
- …..

Attractive features in scientific view are:

- Why MGs are so stabilized?
  Kinetically and thermodynamically…..
- How is the structure of MGs?
  Homogeneous or inhomogeneous?



E. Ma et al, Nature.

Complicated Relaxation Processes in Glasses

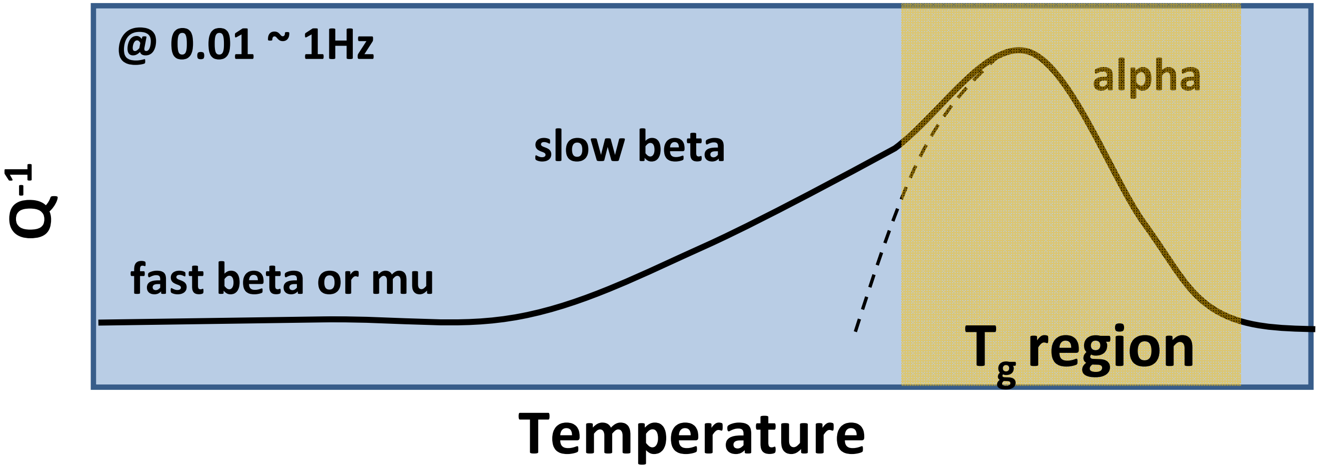
Several kinds of relaxation processes in glasses….

- **So-called “α relaxation” meaning**
  the dynamic glass transition
- **Slow β Relaxation (or JG) relaxation**
  Still unsolved and ill-understood…..
  Homogeneous relaxation mode or local relaxation mode?
- **Fast β Relaxation (μ relaxation) in mode coupling theory (MCT)**
  Rattling motion in a transient cage

$$\eta = G\tau$$

$$\tau\,(\mathrm{at\ T_g}) \sim 1\text{-}100\,\mathrm{s}$$

$$\Rightarrow\ f \sim 0.01\text{-}1\,\mathrm{Hz}$$



Objective: We try to investigate the correlation between the glass structure and relaxation processes.

Elastic constants and Viscosity in metallic glasses (MGs)

Materials Transactions, JIM, Vol. 36, No. 7 (1995), pp. 890 to 895
Hisamichi Kimura*, Michio Kishida**, Takejiro Kaneko*,
Akihisa Inoue* and Tsuyoshi Masumoto*

frequency: 300～600 Hz

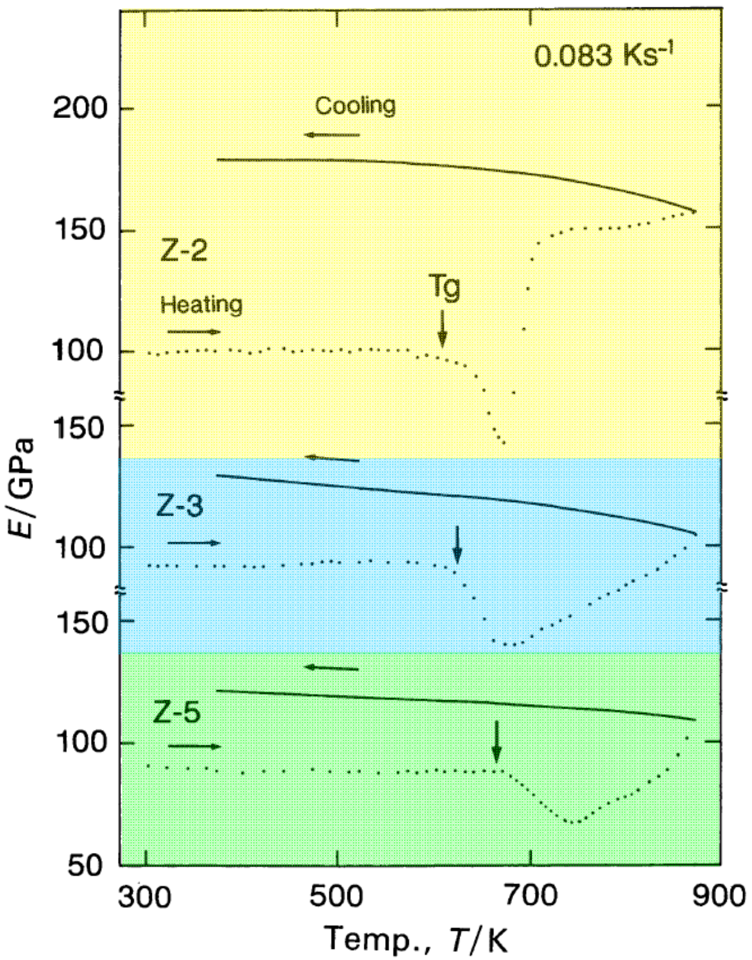
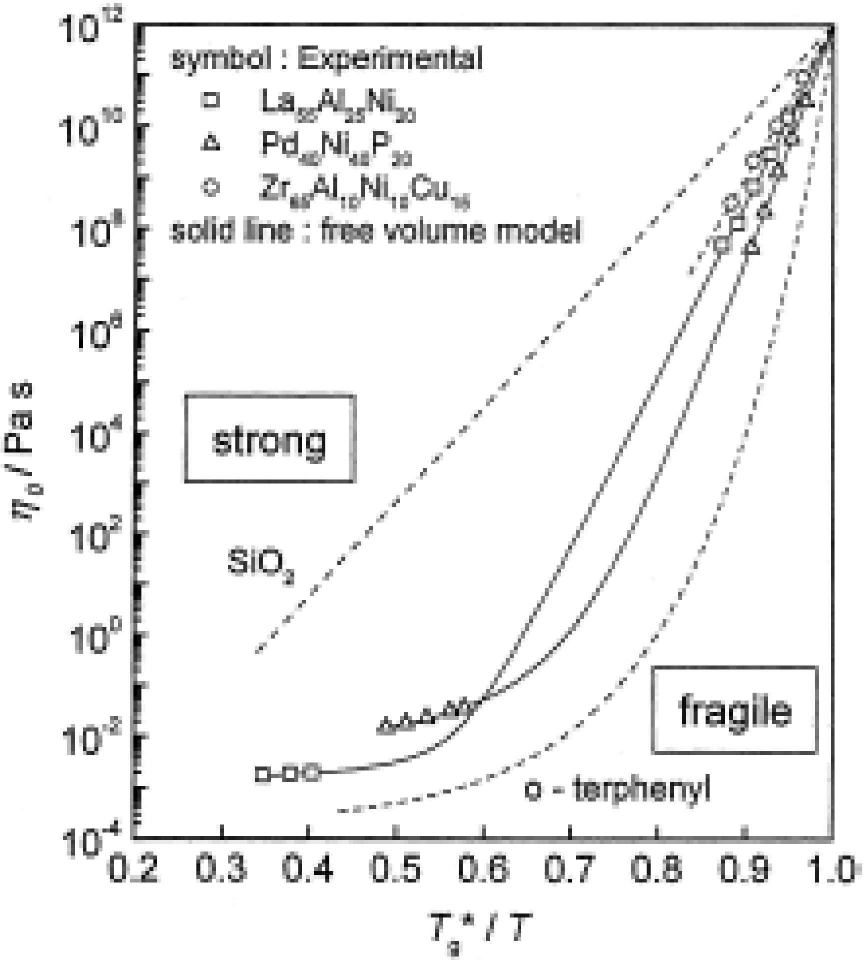


Fig. 10 Temperature dependence of Young's modulus (E) of $Zr_{67}Cu_{33}$ (Z-2), $Zr_{65}Al_{7.5}Cu_{27.5}$ (Z-3) and $Zr_{60}Al_{15}Co_{2.5}Ni_{7.5}Cu_{15}$ (Z-5).

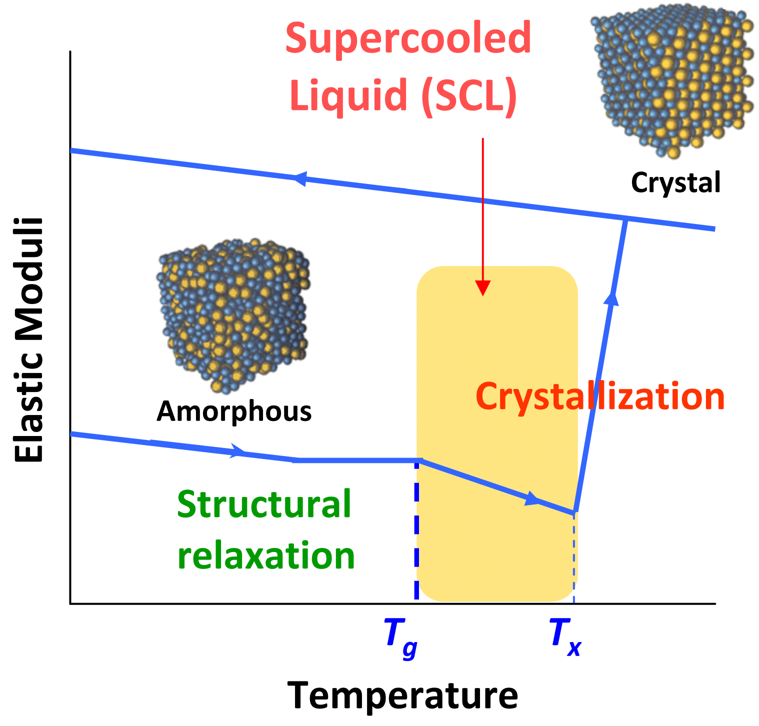


Ultrasound-induced instability

Recently, in the process of measuring the *T*-dependence of elastic moduli of some BMGs, we have found that crystallization is much accelerated around the glass transition temperature *Tg* under ultrasonic (US) perturbation.

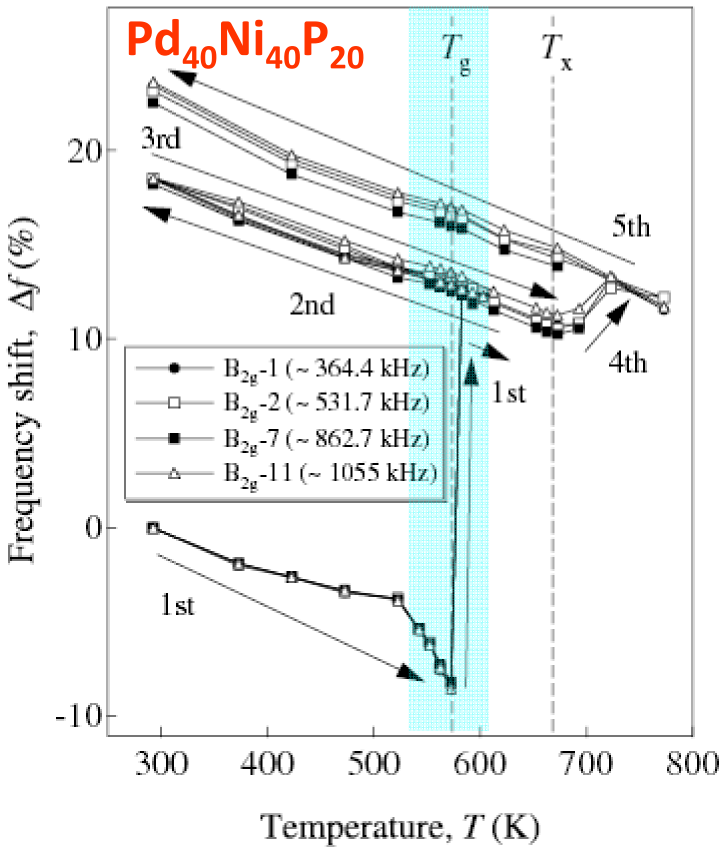
Normal heating without US

Normal temperature dependence of elastic moduli



Heating under US

Ichitsubo et al., Acta Materialia 52, 423 (2004).



Instability of amorphous structure by external vibrations

Kopcewicz et al. Appl. Phys. 23, 1 (1980), Nucl. Instrum. Methods Phys. Res. 199, 163 (1982). J. Mag. Mag. Mater. 40, 139 (1983).

Effects of radio-frequency (RF) magnetic field on crystallization of ferrous amorphous alloys, Ex.) $Fe_{40}Ni_{40}B_{20}$:

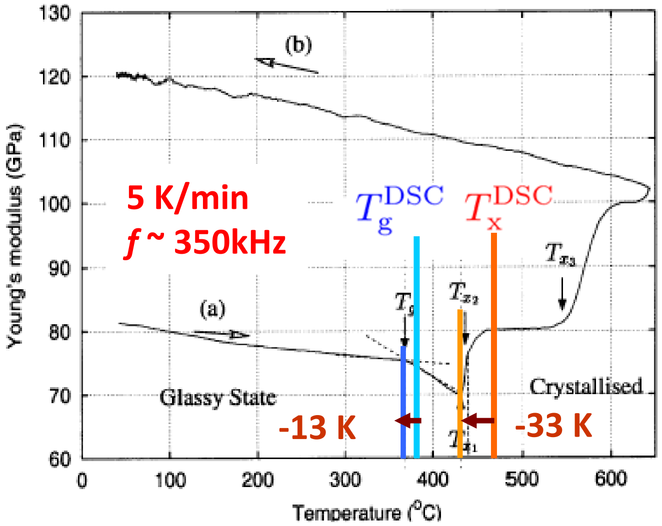
RF magnetostrictive vibration is responsible for the acceleration of crystallization.

Gupta et al. J. Mag. Mag. Mater. 44, 329 (1984).

Ultrasonic vibrations enhance the crystallization process of an Fe-Si-B-C amorphous alloy.

Keryvin et al. Intermetallics 10 (2002), 1289.

Significant reduction of T_g and T_x was observed during the ultrasonic pulse-echo measurements for a $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glass.



Mizubayashi et al.

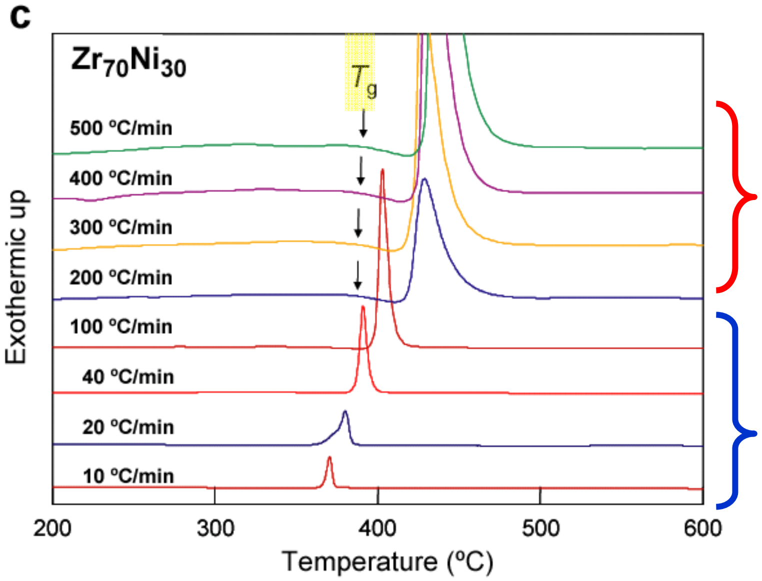
Electro-pulsing induced crystallization at very low temperature.

These phenomena indicate that the structural stability of metallic glasses is deteriorated under dynamic external fields even at relatively low temperature (below or around *Tg*).

$T_X < T_g$: Intriguing feature rarely observed in other types of glasses

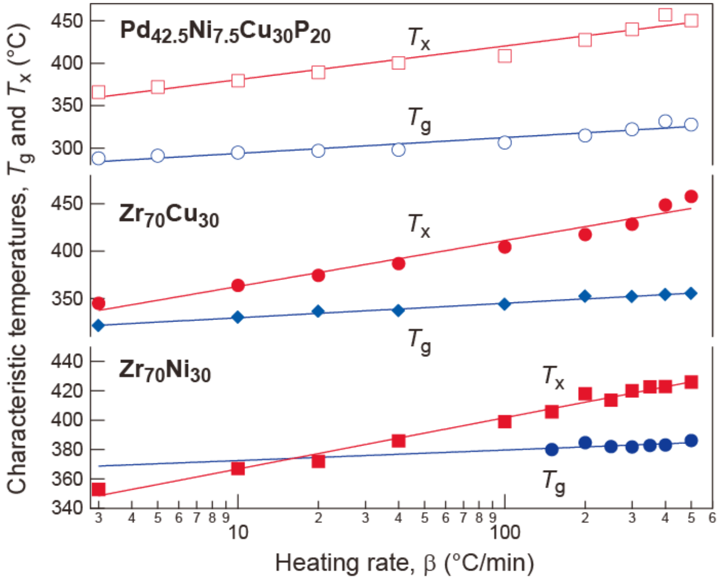
Some metallic glasses show Tx without Tg, i.e., Tx < Tg

Magnitude relation of Tg and Tx is reversed at a certain heating rate….



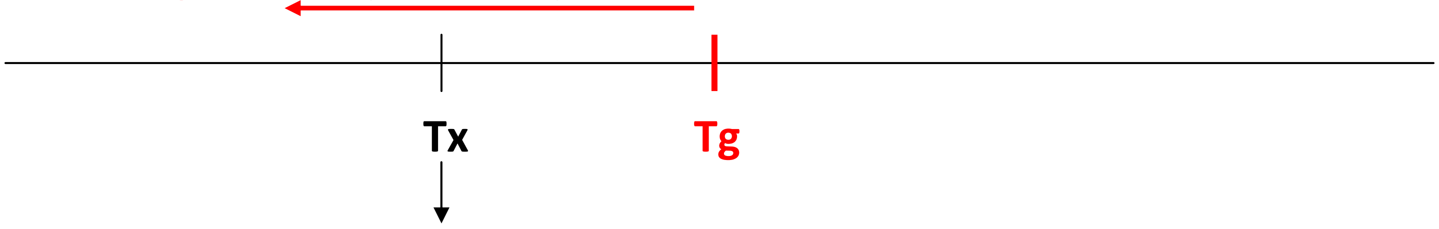
$T_g < T_x$
@ High
heating rate

$T_x < T_g$
@ Slow
heating rate



Crystallization below the kinetic freezing temperature Tg ???

Kinetic freezing with respect to alpha relaxation, but beta relaxation still alive



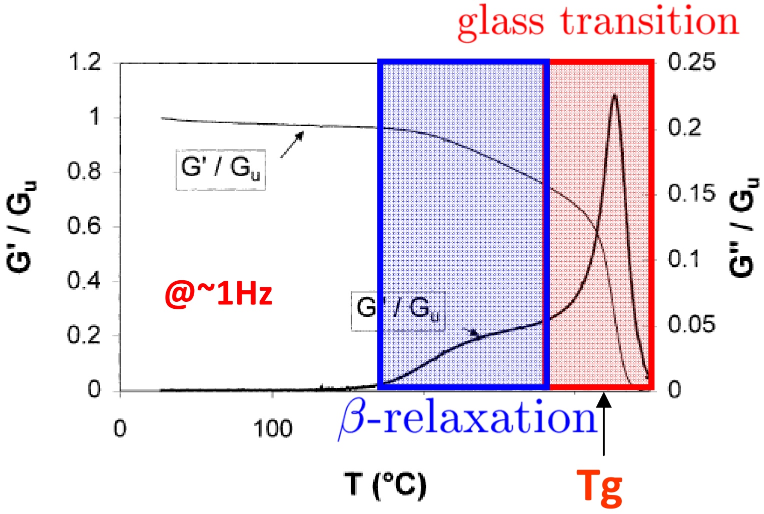
Diffusion is appreciably detected for less-stable metallic glasses around Tx.

Atomic motions associated with the crystallization below Tg
appears to be motions associated with the beta relaxation.

The β -relaxation frequently observed in fragile glasses

β-relaxation in $Pd_{43}Ni_{10}Cu_{27}P_{20}$

J.M. Pelletier et al.,
Mater. Sci. Eng. A336, 190 (2002).



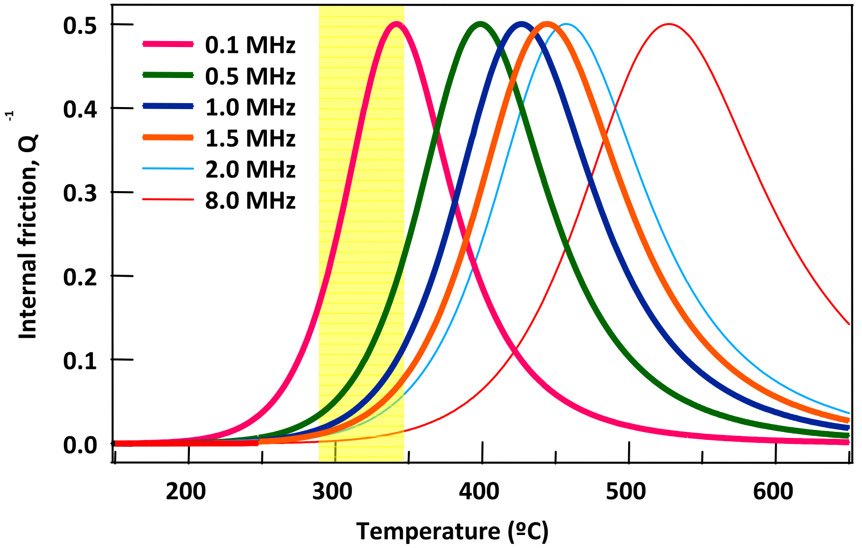
G_u = unreluxed shear modulus
G' = srorage modulus
G'' = loss modulus

$E \approx 1.0$ [eV], $\tau_0 \approx 1.0 \times 10^{-14}$ [s]

Internal friction (Debye relaxation)

$$\frac{Q^{-1}}{\Delta} = \frac{\omega\tau_0 \exp(E/RT)}{1+[\omega\tau_0 \exp(E/RT)]^2}$$

for MHz frequencies

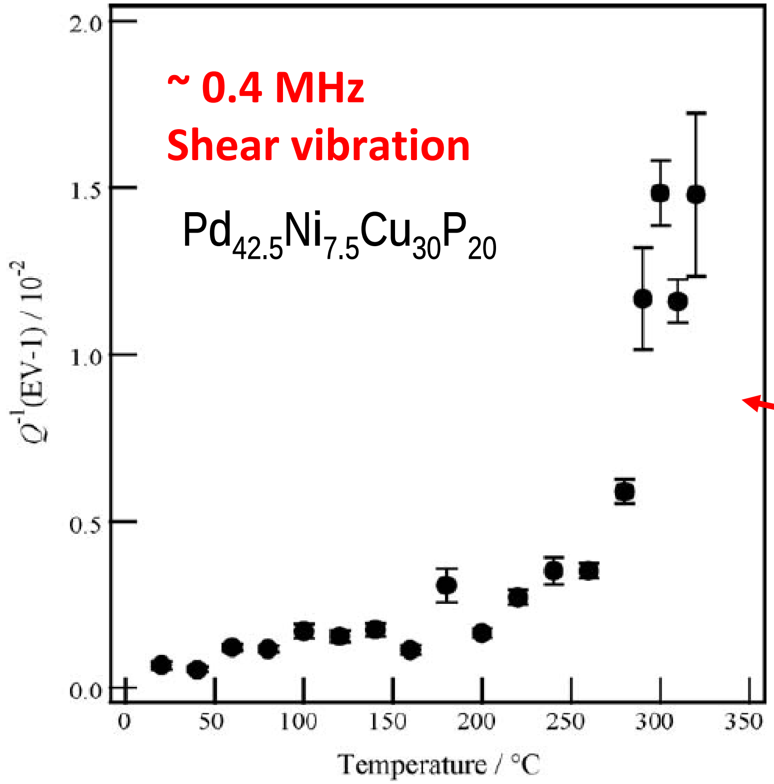


At about 1Hz (low frequency), the internal friction increases far below T_g.

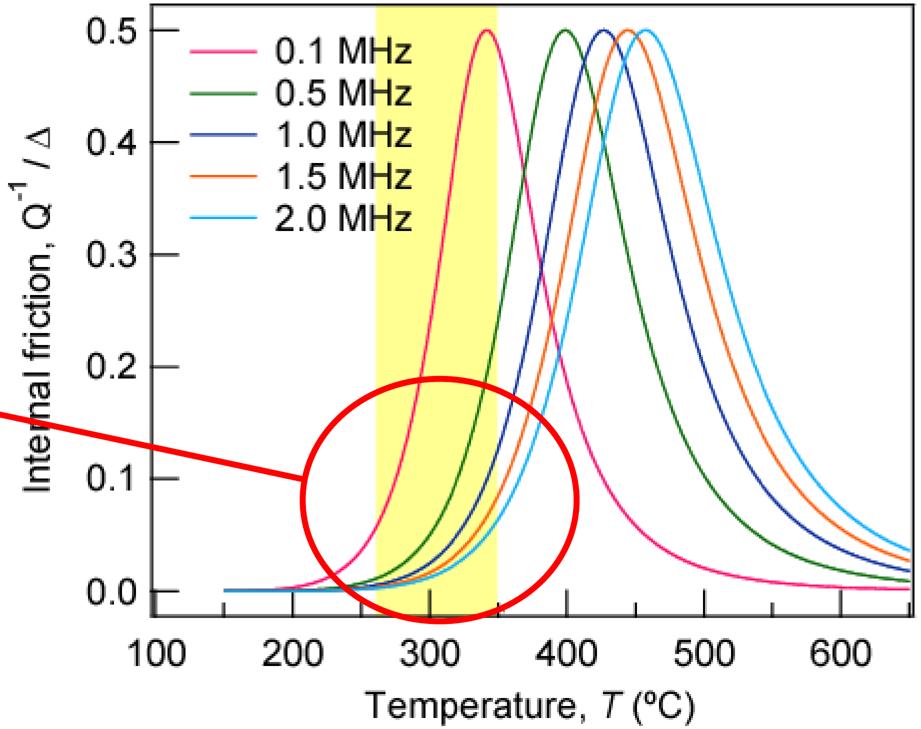
At MHz frequencies, the internal friction peak appears around T_g.

The β -relaxation frequently observed in fragile glasses

Actual observation of high frequency internal friction around Tg



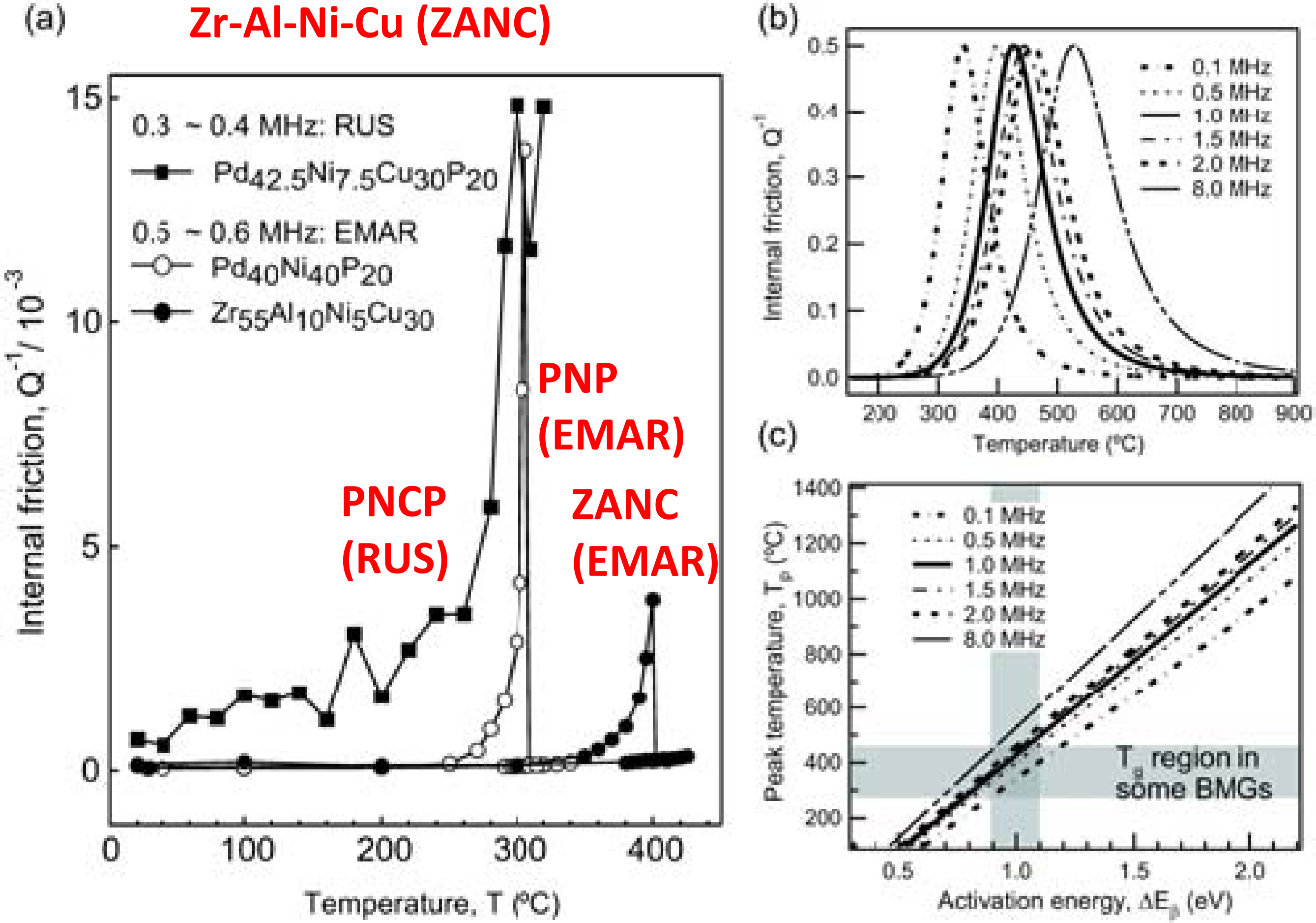
Calculated internal friction



The increase of the internal friction means that the periodic ultrasonic strain is resonant with atomic motion. Thus, it is considered that the atomic motions of the beta relaxation can be responsible for the US-induced crystallization of bulk metallic glasses.

Temperature dependence of internal friction of some metallic glasses

Pd-Ni-Cu-P glass (PNCP)
Pd-Ni-P (PNP)
Zr-Al-Ni-Cu (ZANC)



PNP (EMAR)

PNCP (RUS)

ZANC (EMAR)

$$Q_\beta^{-1} = \Delta \frac{\omega\tau}{1+(\omega\tau)^2}$$

$$\tau = \tau_0 \exp\left(\frac{\Delta E_\beta}{kT}\right)$$

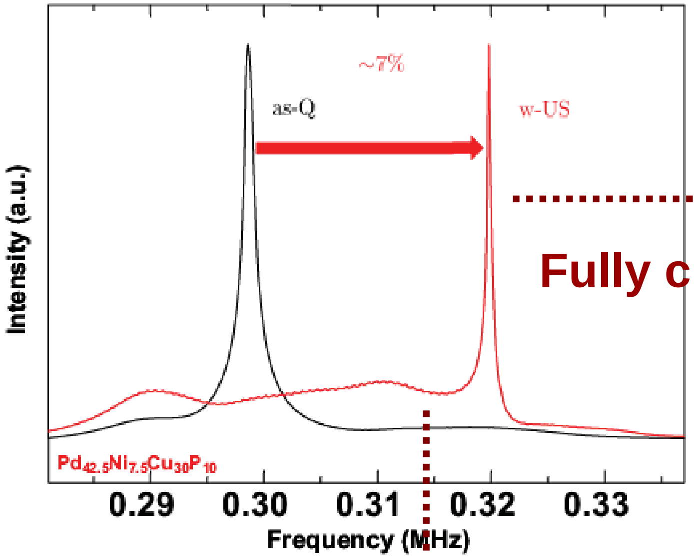
Peak temperature

$$T_P = -\frac{\Delta E_\beta}{k \ln \omega\tau_0}$$

ΔE of the beta relaxation is about 1 eV for most of BMGs. (By H.S. Chen et al.)
In the range of MHz frequencies, the beta relaxation can be observed around Tg of MGs.

Annealed under US just below Tg (290ºC < Tg = 300ºC, 18h, ~0.35MHz)

Resonant Ultrasound Spectrum

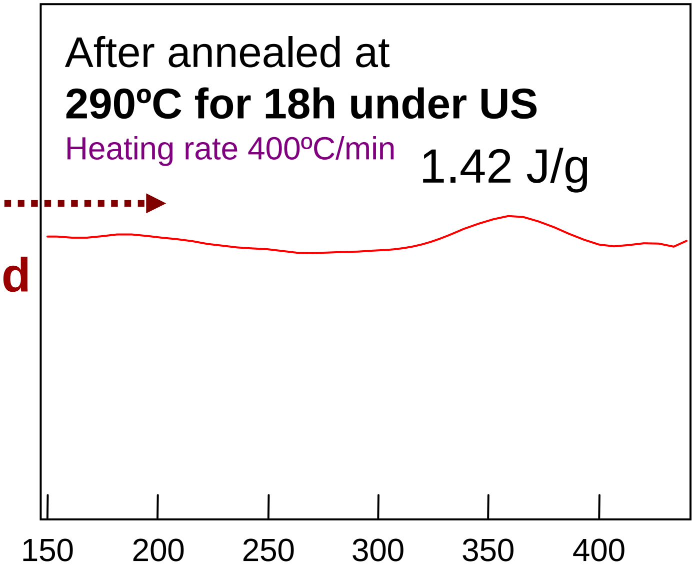


Fully crystallized

DSC profile

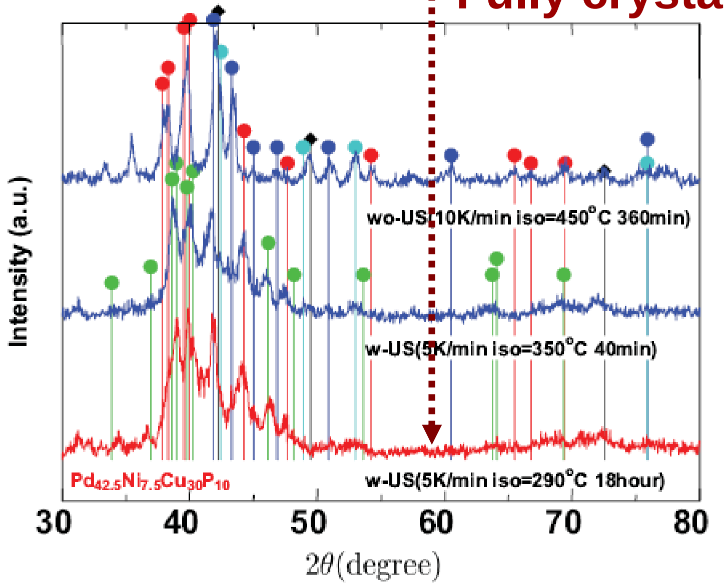
$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$

After annealed at
290ºC for 18h under US
Heating rate 400ºC/min



XRD profile

Fully crystallized

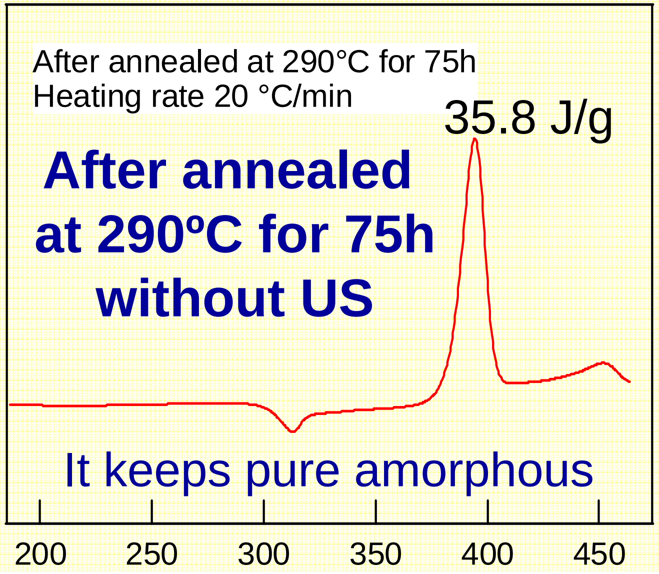


c.f.

After annealed at 290°C for 75h
Heating rate 20 °C/min

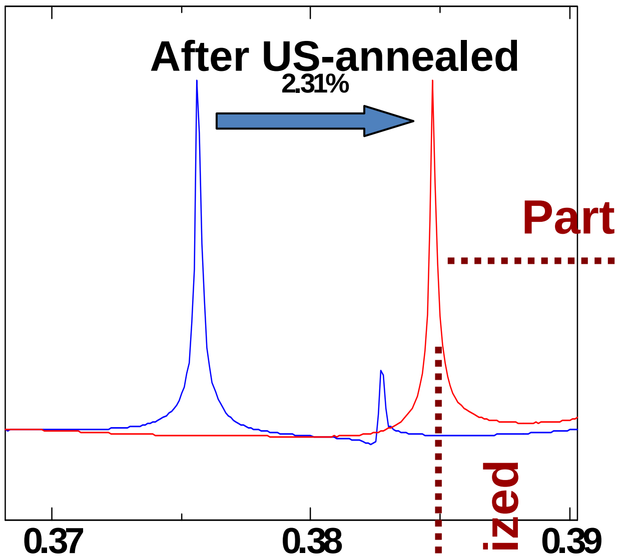
After annealed at 290ºC for 75h without US

It keeps pure amorphous



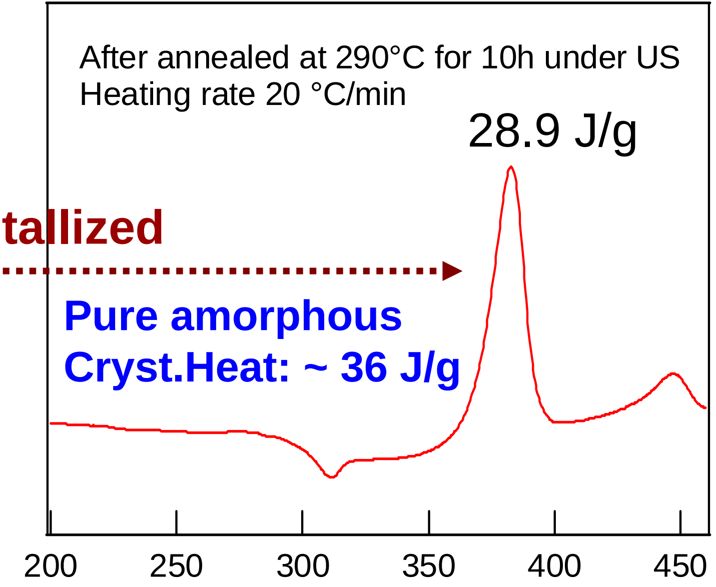
Annealed under US just below Tg (290ºC, 10h, ~0.35MHz)

Resonant Ultrasound Spectrum



DSC profile

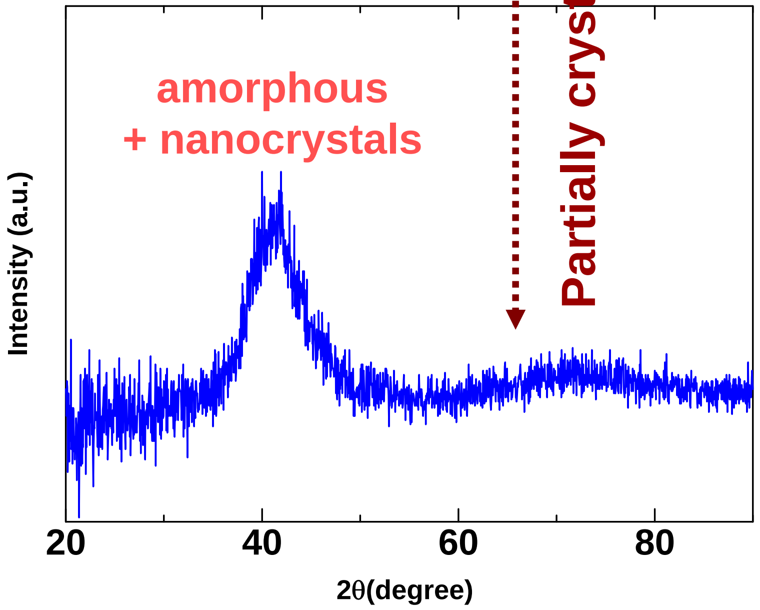
$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$



Partially crystallized

Pure amorphous
Cryst.Heat: ~ 36 J/g

XRD profile



amorphous
+ nanocrystals

Partially crystallized

Which parts in amorphous matrix are crystallized under US vibrations?

ure after annealed under US

300ºC) , 10h, 0.35MHz

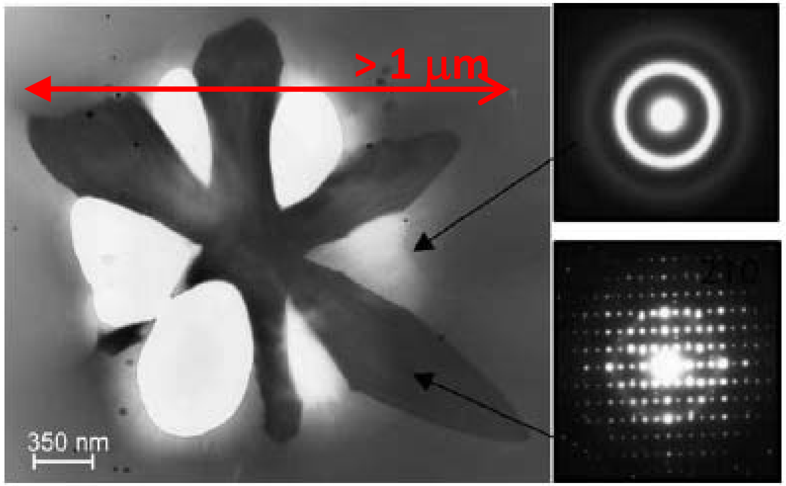
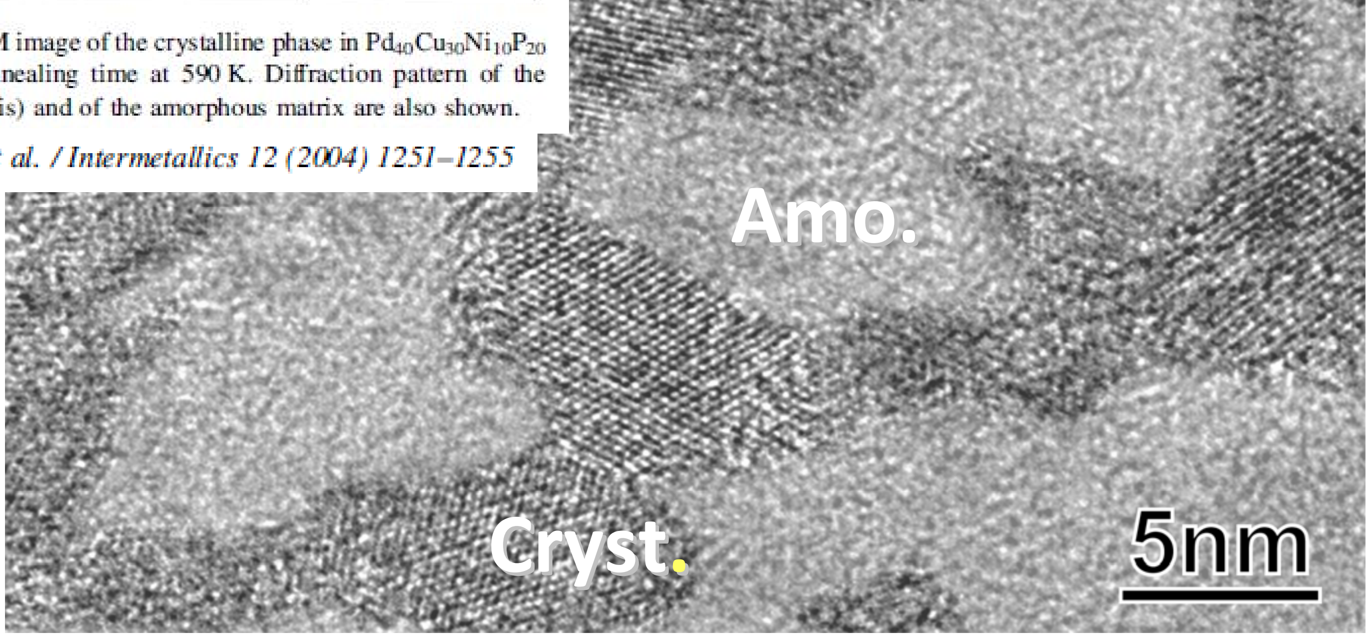


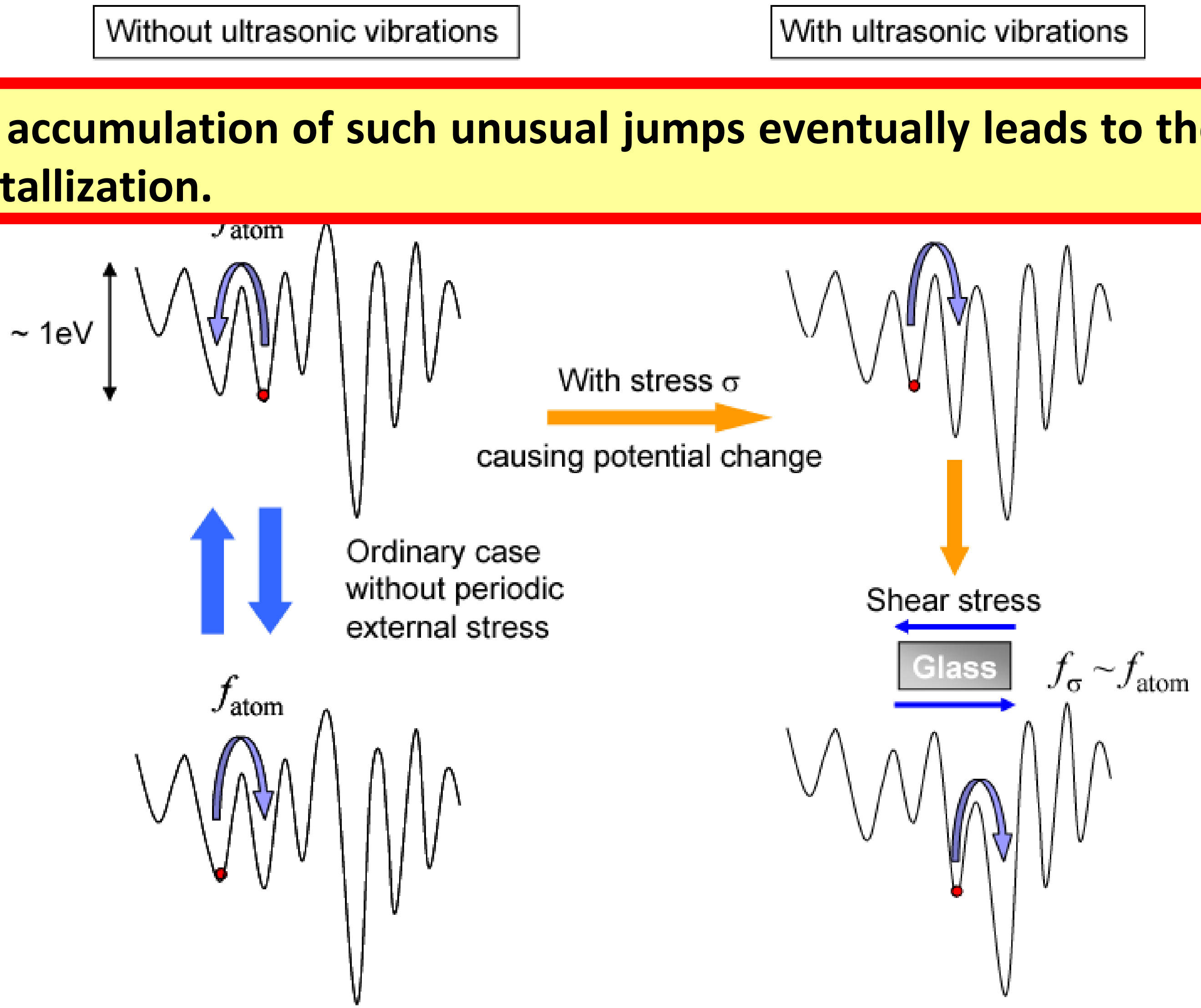
Fig. 3. Bright field TEM image of the crystalline phase in $Pd_{40}Cu_{30}Ni_{10}P_{20}$ observed after 30 h annealing time at 590 K. Diffraction pattern of the crystal ([2 1 0] zone axis) and of the amorphous matrix are also shown.

M. Wollgarten et al. / Intermetallics 12 (2004) 1251–1255



The isolated amorphous islands are surrounded by the crystallized region, although usually an isolated crystalline particle is formed in the amorphous matrix. (Amorphous-like regions are colored gray.)

The energy landscape, atomic jumps and its resonant motion



The accumulation of such unusual jumps eventually leads to the rapid crystallization.

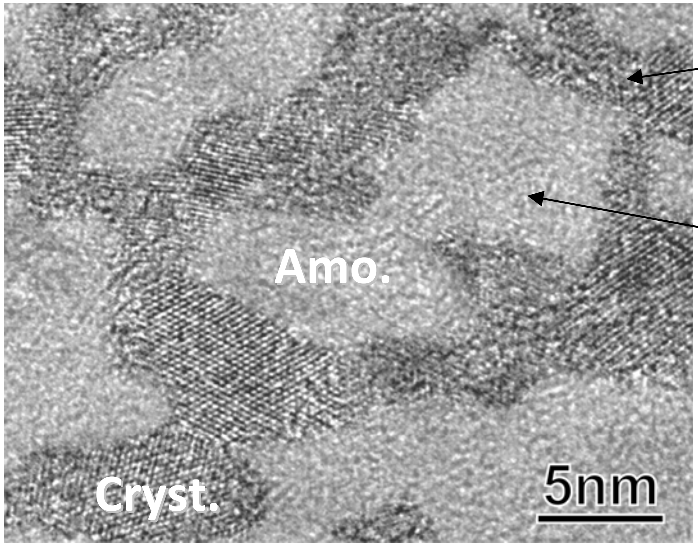
In the absence of US strain, atomic jumps occur repeatedly at the same sites.

Under the US strains, the landscape potential changes with the US strains, unusual jumps take place.

Structural model of amorphous & supercooled liquid

It is considered that crystallization at such a low temperature (below Tg) is strongly related with the β relaxation, where the atomic motions are stochastically resonant with the US vibrations. In the regions where the crystallization occurs, intrinsically, the atomic mobility is high, density is low, and elasticity is soft. From this viewpoint, we infer a structural model as shown below…

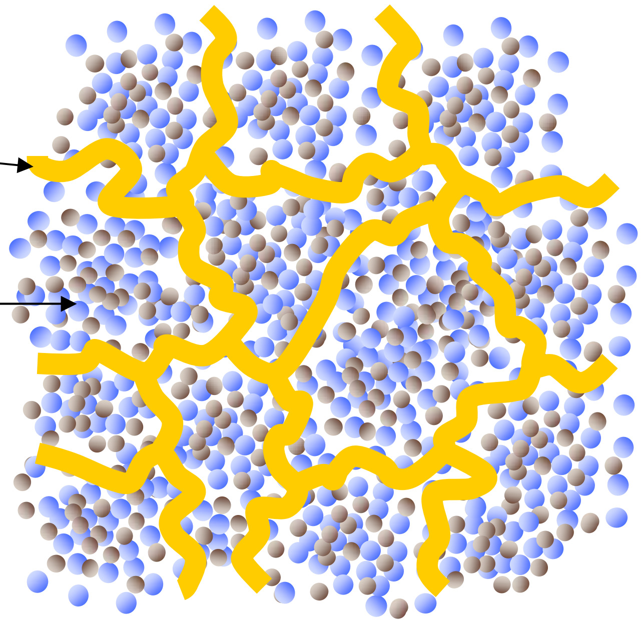
Nanoscale microstructure



Ichitsubo et al., Phys. Rev. Lett. 95, 245501 (2005).

Weakly-bonded region (WBR)

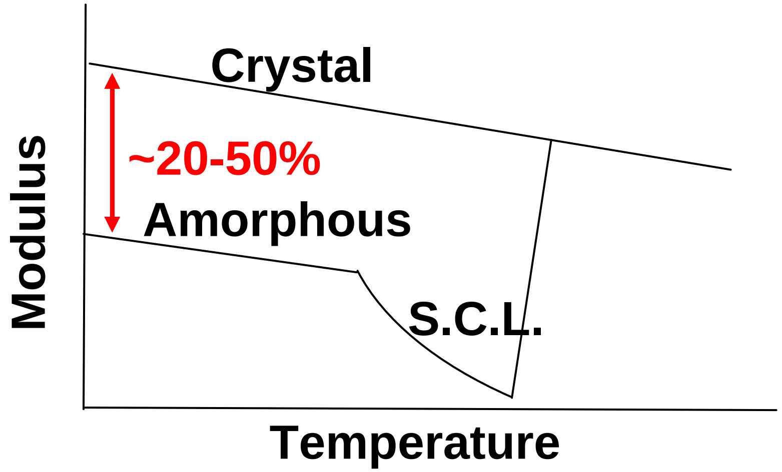
Strongly bonded region (SBR)



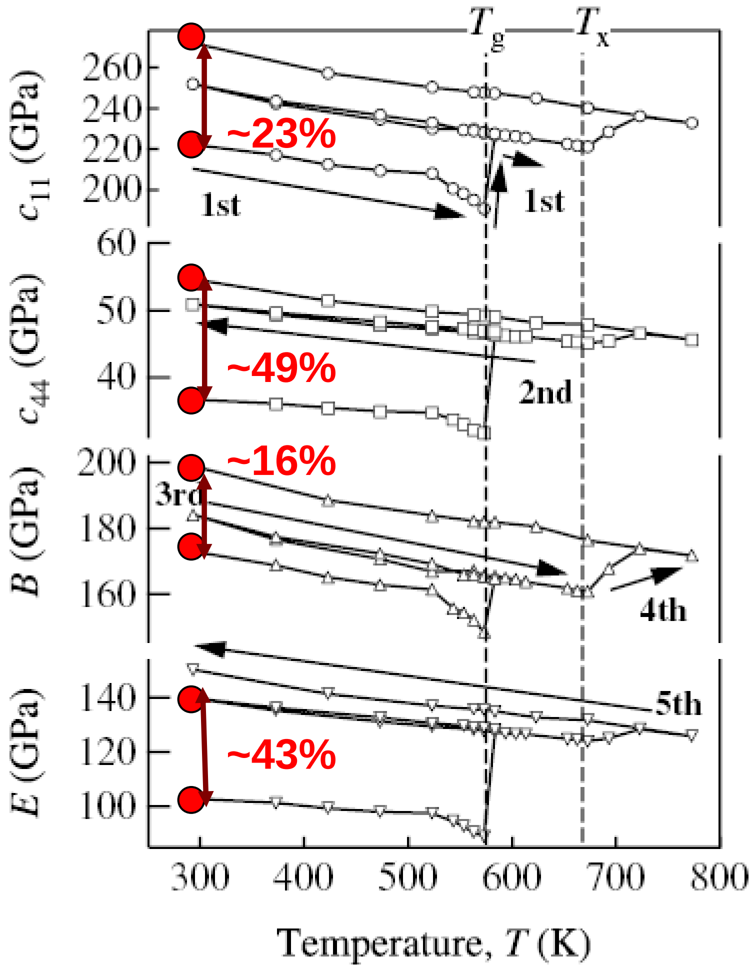
SBRs are surrounded by WBR matrix.

Marked change in the elastic constants accompanied by crystallization despite quite small change of mass density

PdNiP	Amorphous	Crystals	Change
c11	222	272	23%
c44	36.7	54.7	49%
ZrAlNiCu	Amorphous	Crystals	Change
c11	153	194	27%
c44	32.3	47.6	47%



But, density change after crystallization ~ 1-2% !



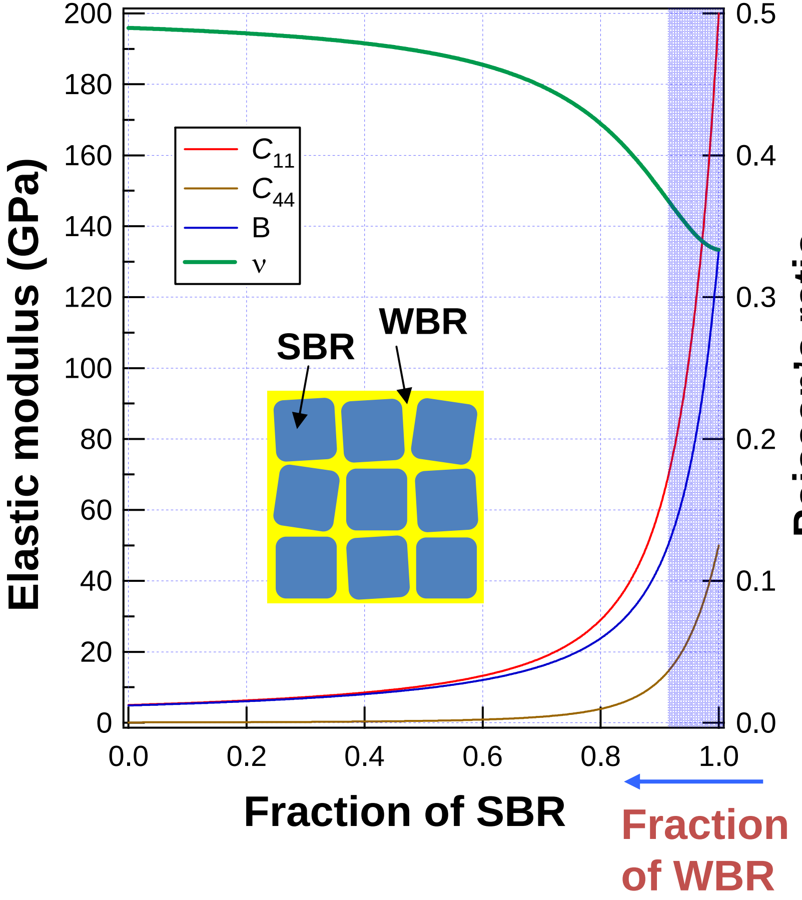
$Pd_{40}Ni_{40}P_{20}$

Macroscopic Elastic Constants by Effective-Mean-Field Method

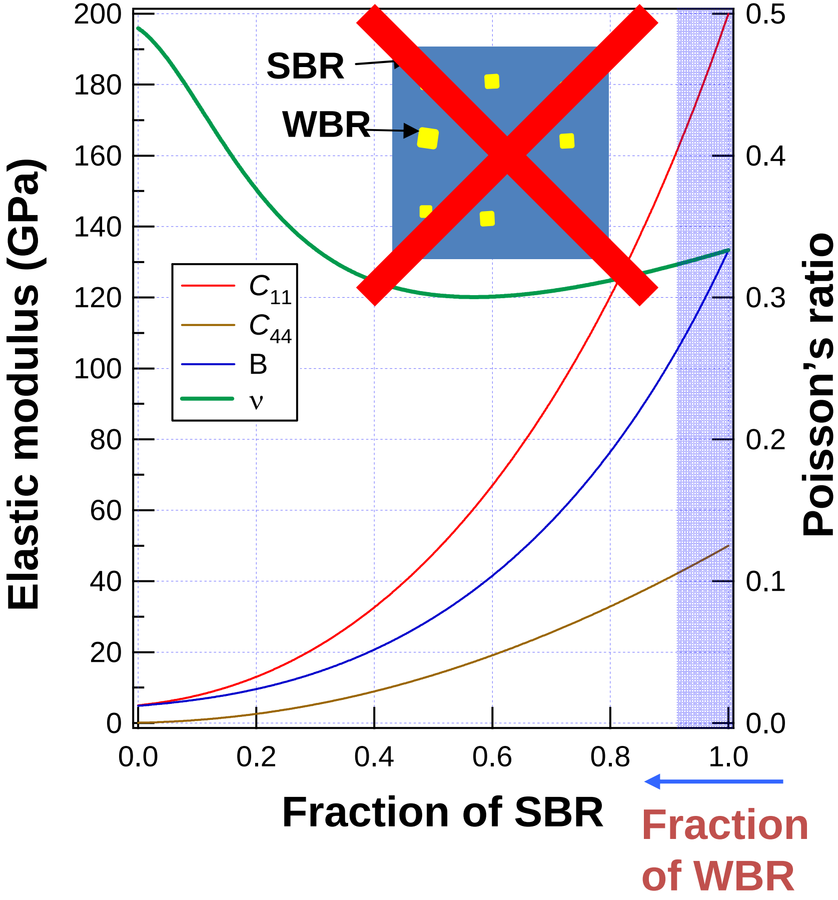
Weakly-bonded region (WBR): c_{11} = 5 GPa, c_{12} = 4.8 GPa

Strongly-bonded region (SBR): c_{11} = 200 GPa, c_{12} = 100 GPa (ν = 0.33)

SBRs in WBR Matrix



WBRs in SBR Matrix

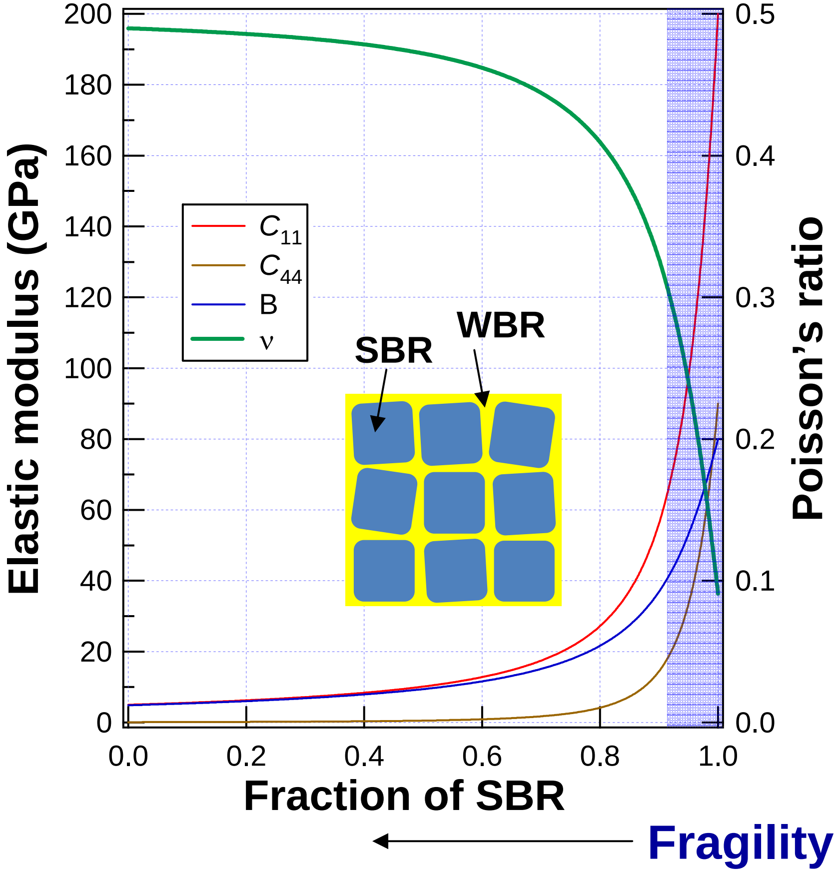


In the case where SBRs have small Poisson ratio like covalently bonded clusters

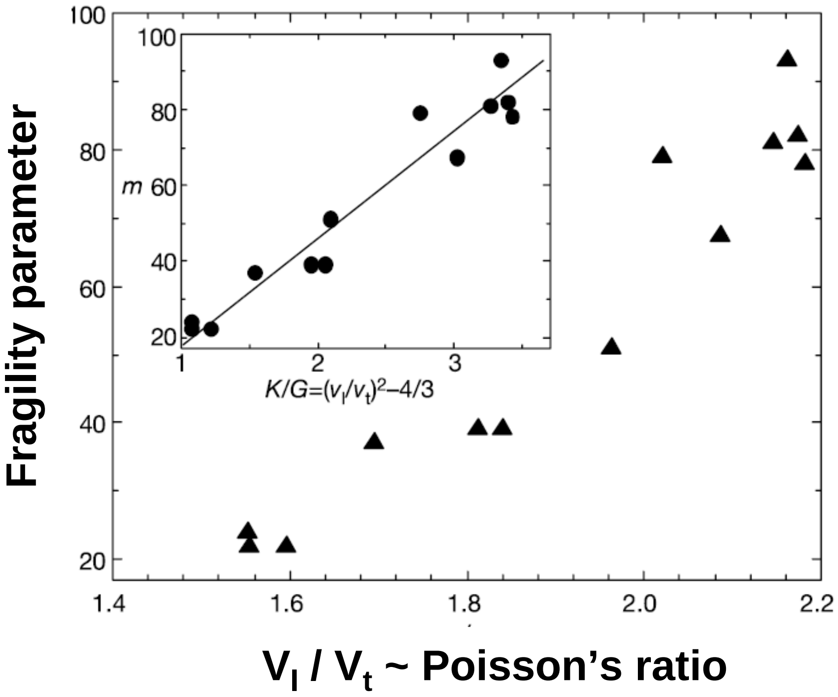
Weakly-bonded region (WBR): c_{11} = 5 GPa, c_{12} = 4.8 GPa

Strongly-bonded region (SBR): c_{11} = 200 GPa, c_{12} = 20 GPa: $\nu = 0.09$

SBRs in WBR Matrix



V.N. Novikov & A.P. Sokolov, Nature 431, 961 (2004)



Macroscopic Elastic Constants by Effective-Mean-Field Method

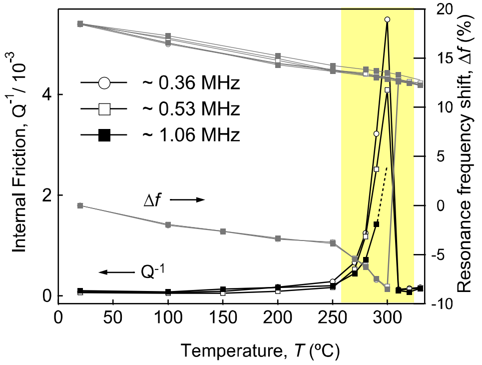
Summary of US-induced instability

Crystallization of metallic glasses is accelerated by ultrasonic vibrations even at relatively low temperatures (around the glass transition temperature). Here we discussed the mechanism of the structural instability of metallic glasses under ultrasonic perturbation.

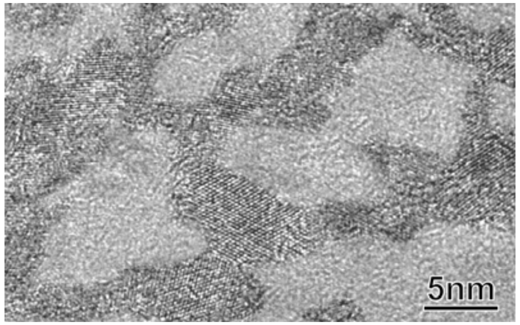
1. The US-induced crystallization at low temperatures is related to atomic motions in the β-relaxation, which was found from the frequency analysis.

2. It is reasonable to consider that the β-relaxation and US-induced crystallization are caused in an inhomogeneous microstructure of amorphous matrix.

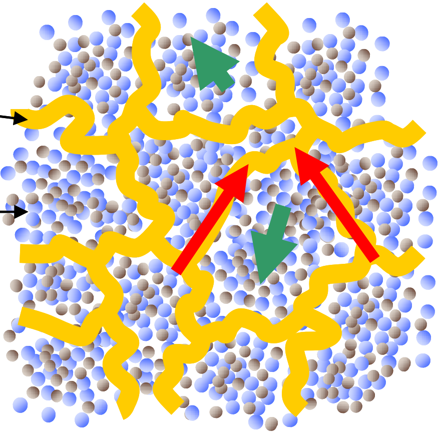
3. We proposed a plausible microstructural model for fragile metallic glasses; the model can explain well the physical property, such as marked increase in elastic moduli.



MHz internal friction = β relaxation



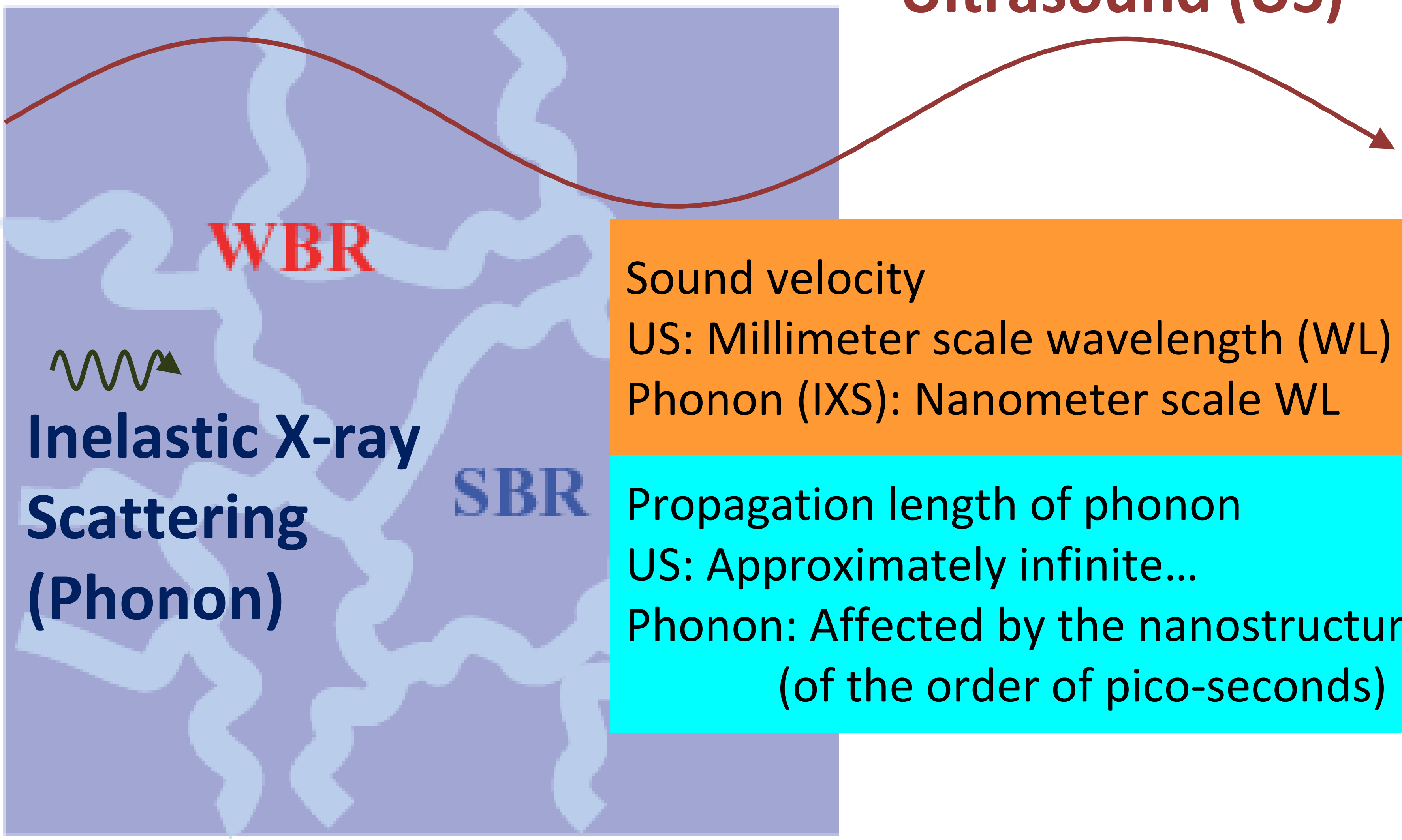
Partially crystallized structure with US just below Tg



Weakly-bonded region

Strongly bonded region

Two techniques for measuring the sound velocity of mm and nm scales



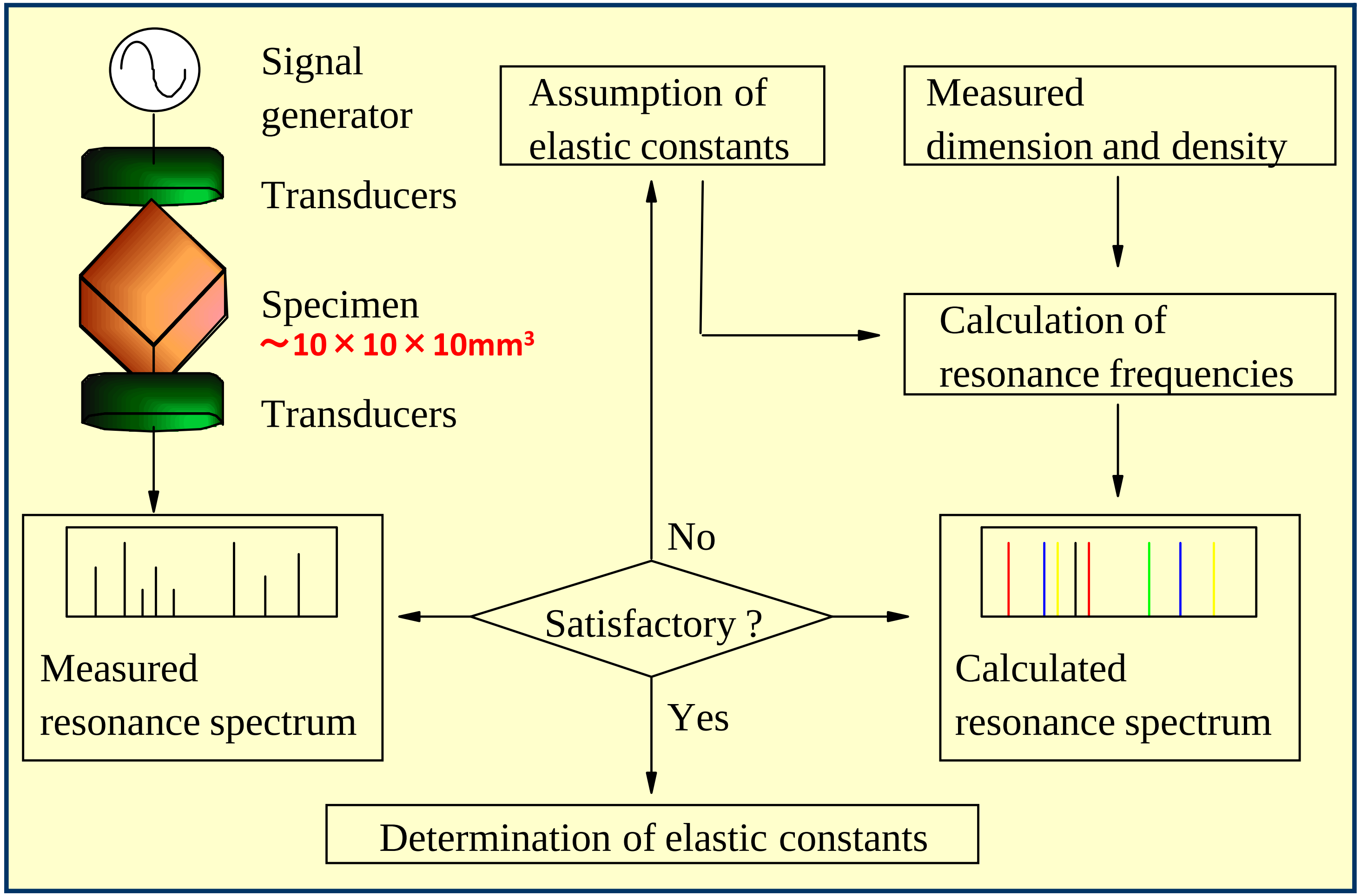
Ultrasound (US)

Inelastic X-ray Scattering (Phonon)

Sound velocity
US: Millimeter scale wavelength (WL)
Phonon (IXS): Nanometer scale WL

Propagation length of phonon
US: Approximately infinite…
Phonon: Affected by the nanostructure
(of the order of pico-seconds)

US Velocity from Resonant Ultrasound Spectroscopy (RUS)



Merit: All independent elastic constants can be obtained with only one sample, when using the RUS technique.

RUS spectrum of Pd-Ni-Cu-P (PNCP) at RT

$$0 = \delta\int_{t_1}^{t_2}\int_V\left[\frac{1}{2}\rho\dot{U}_i\dot{U}_j\delta_{ij} - \frac{1}{8}C_{ijkl}\left(\frac{\partial U_i}{\partial x_j}+\frac{\partial U_j}{\partial x_i}\right)\left(\frac{\partial U_k}{\partial x_l}+\frac{\partial U_l}{\partial x_k}\right)\right]dV\,dt$$

H.H. Demarest, 1971
I. Ohno, 1976

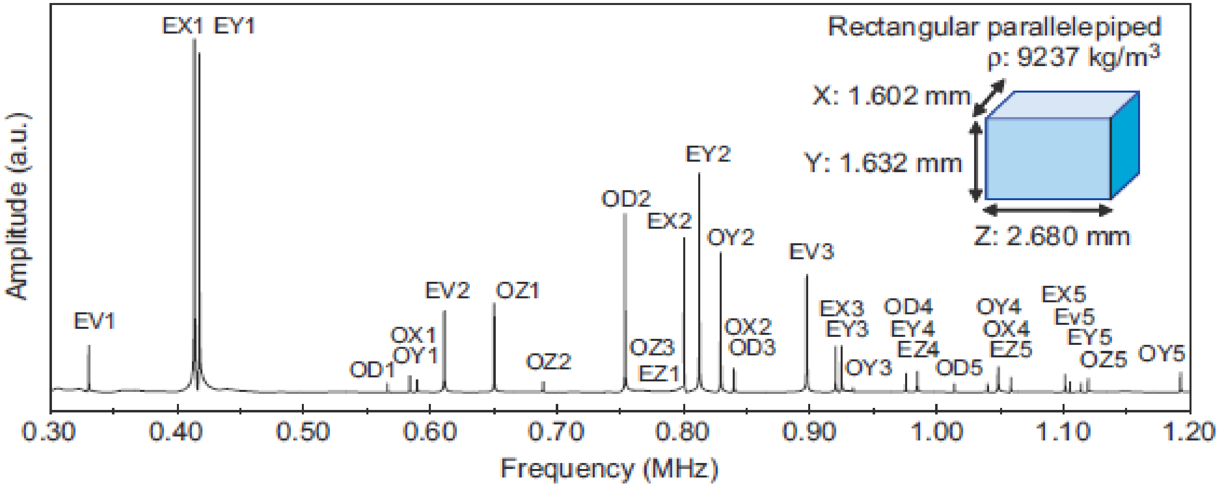


FIG. 2: RUS spectrum measured at room temperature for a $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ bulk metallic glass. The inset gives the sample information used in the present RUS measurement. The labeling of the vibrational modes (e.g., EV1, EX1, OD1, etc) follows Ohno's prescription.[22] About forty resonance peaks were used in the inverse analysis, and the root-mean-square error indicating the degree of convergence was about 0.2%. The inverse calculation yields $c_{11} = 209$ GPa and $c_{44} = 34.2$ GPa.

$C_L = 209\ \text{GPa} = \rho V_L^2 \Rightarrow V_L = 4.76\ \text{km/s}$

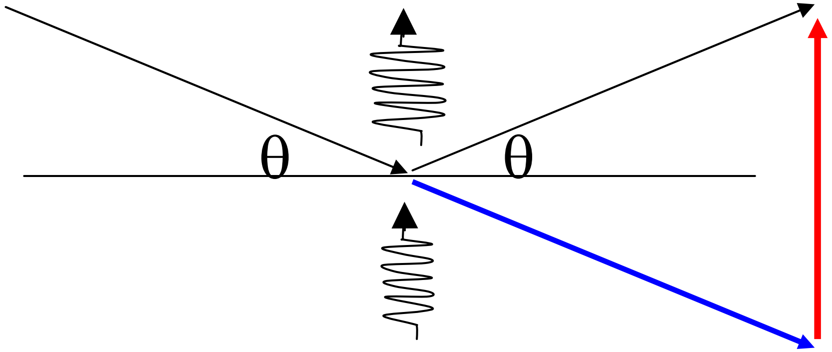
Phonon Velocity from Inelastic X-ray Scattering (IXS)

BL35XU@SPring-8, Japan

Momentum transfer from photon to phonon

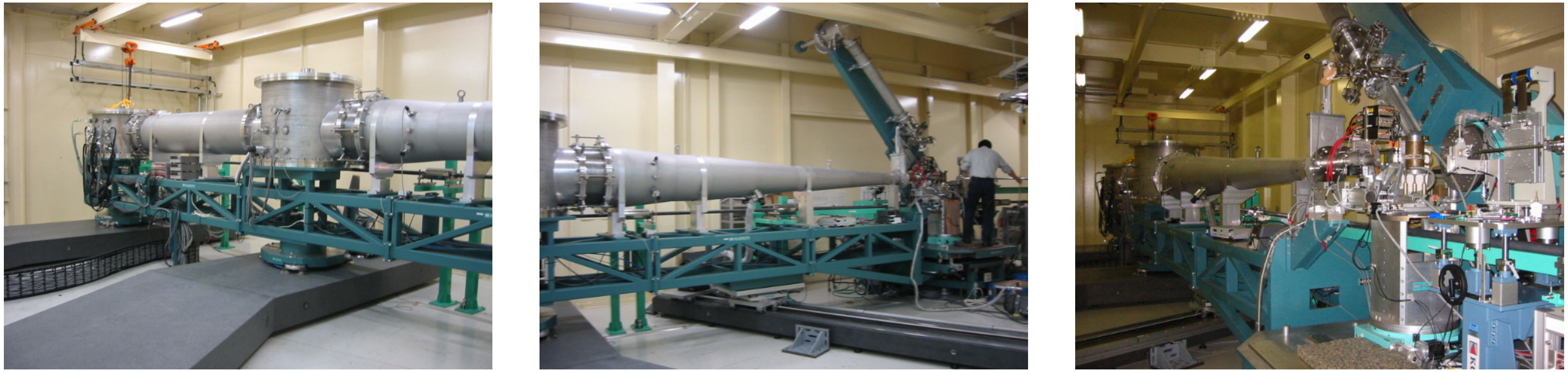
Incident X-ray
21.747 keV ± ΔE meV

Diffracted X-ray
21.747 keV

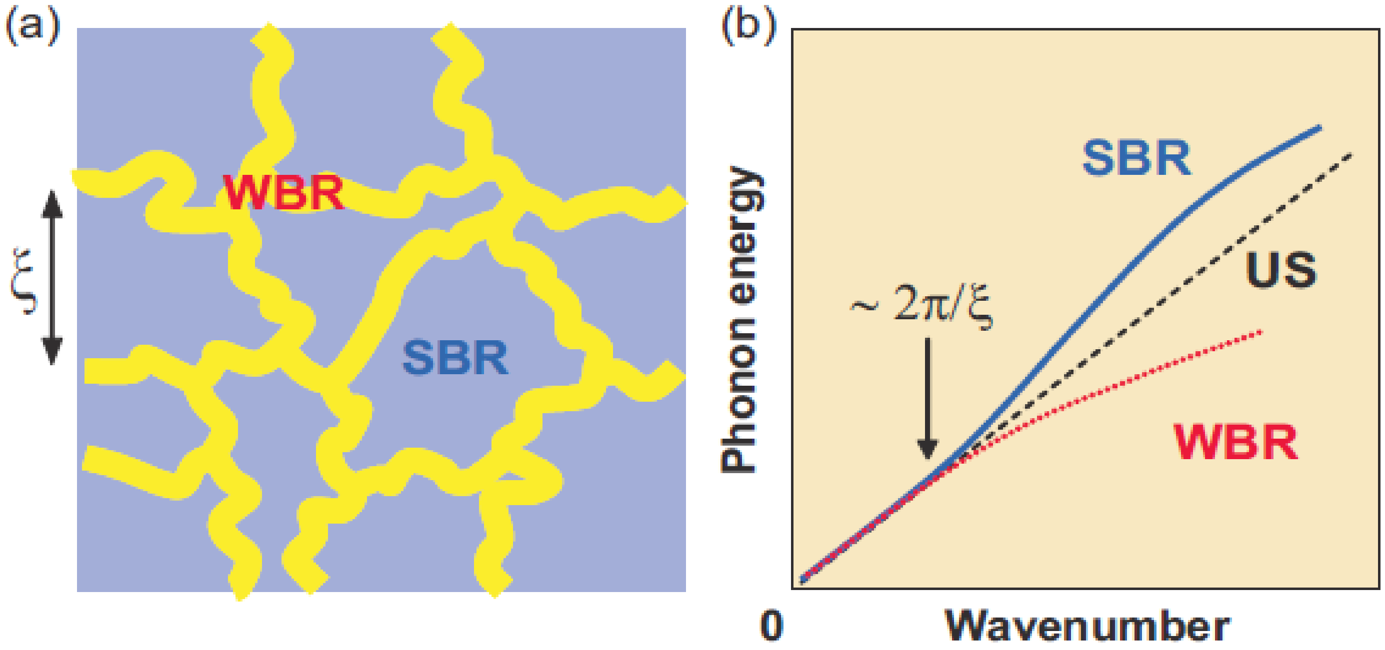


$$Q = \frac{4\pi \sin\theta}{\lambda}$$

wavenumber Q of phonon



Elastic inhomogeneity and phonon dispersion

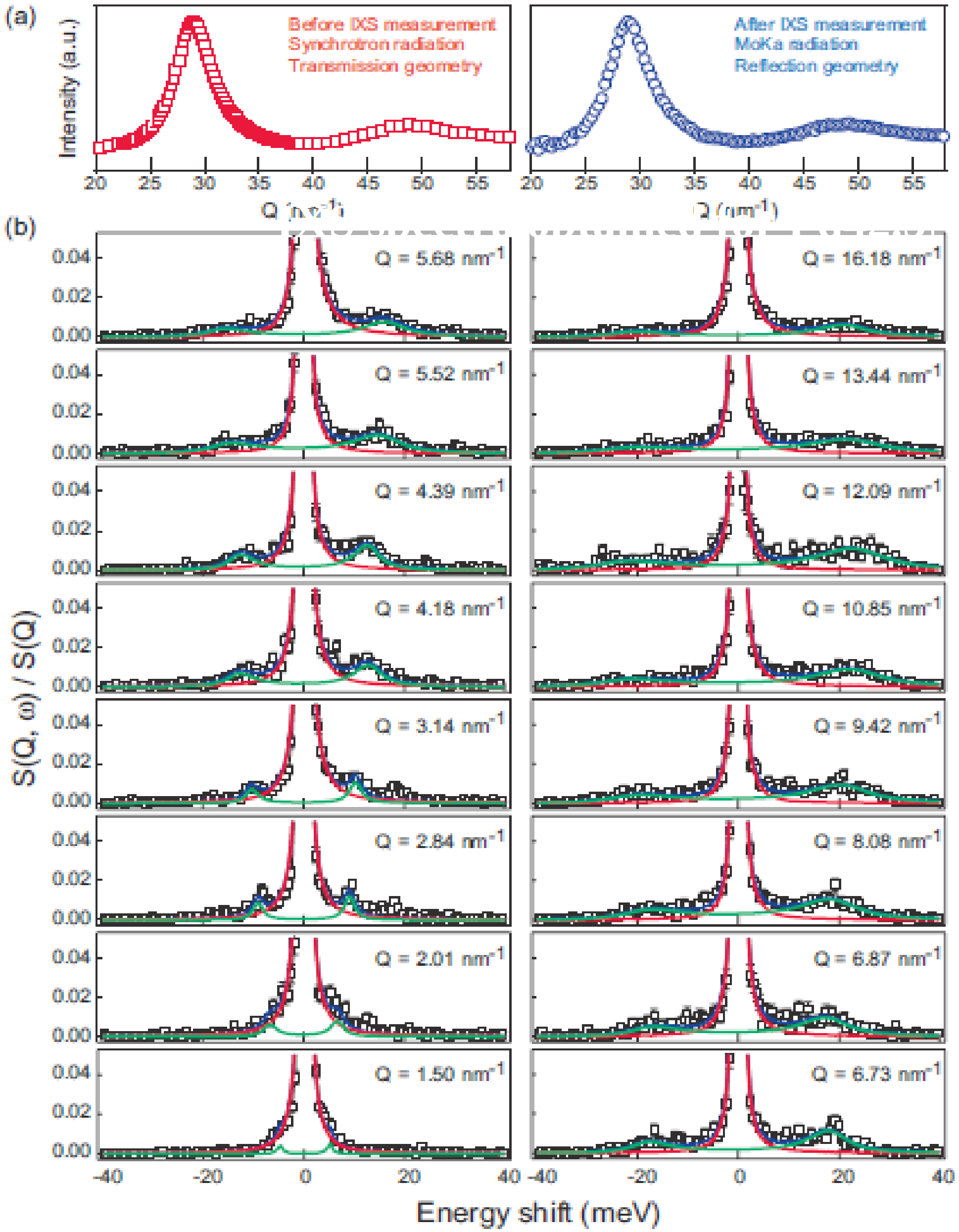


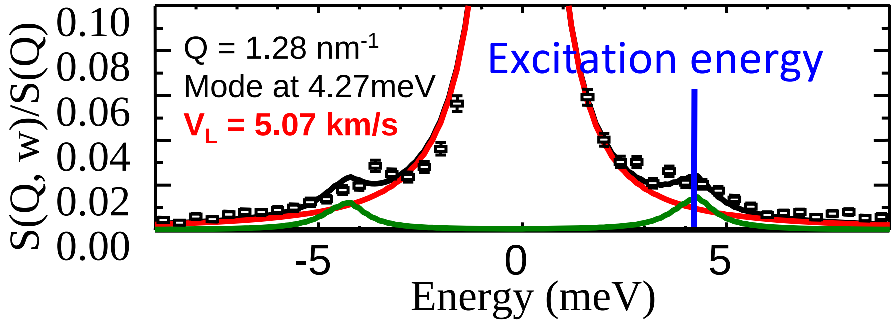
(a) Inhomogeneous microstructure model, (b) expected phonon-dispersion relation

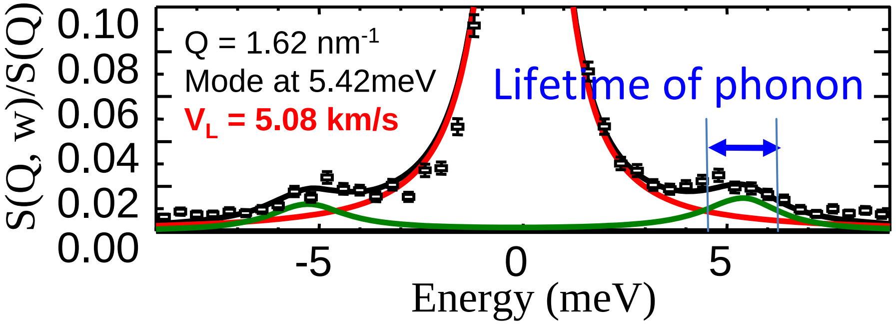
FIG. 1: Schematic illustration showing (a) inhomogeneous structural model of fragile metallic glasses[11] and (b) phonon dispersion relation in a very small Q region predicted from the model. "SBR" means strongly bonded region (i.e., elastically harder region) and "WBR" denotes weakly bonded region (i.e., elastically softer region).

In liquid, positive dispersion phenomenon is frequently observed.
e.g., G. Ruocco, T. Scopigno (Rome, Italy)…

IXS spectra obtained for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ at the fixed Q values







Damped harmonic oscillator (DHO) model: Single Excitation approximation

$$\frac{S(Q,\omega)}{S(Q)} = A_0 \frac{\Gamma_0}{\Gamma_0^2+\omega^2} + A_Q \frac{\Omega_Q^2 \Gamma_Q}{\left(\omega^2-\Omega_Q^2\right)^2+\omega^2\Gamma_Q^2}$$

Phonon-dispersion curve obtained from the IXS data (bottom) and sound velocities of the longitudinal sound (top) in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$

4.76 km/s for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$

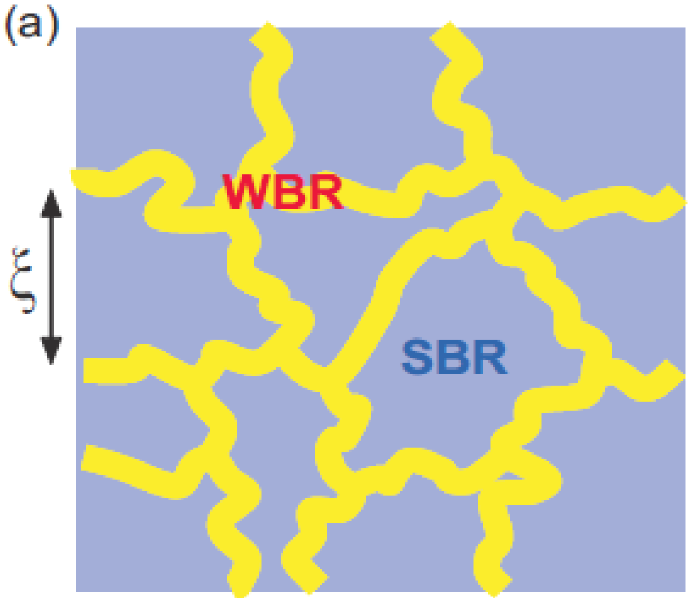
Ref. 4.82 km/s K. Tanaka

4.51 km/s N. Nishiyama

~5.07 km/s at Q =1.28 nm^{-1}

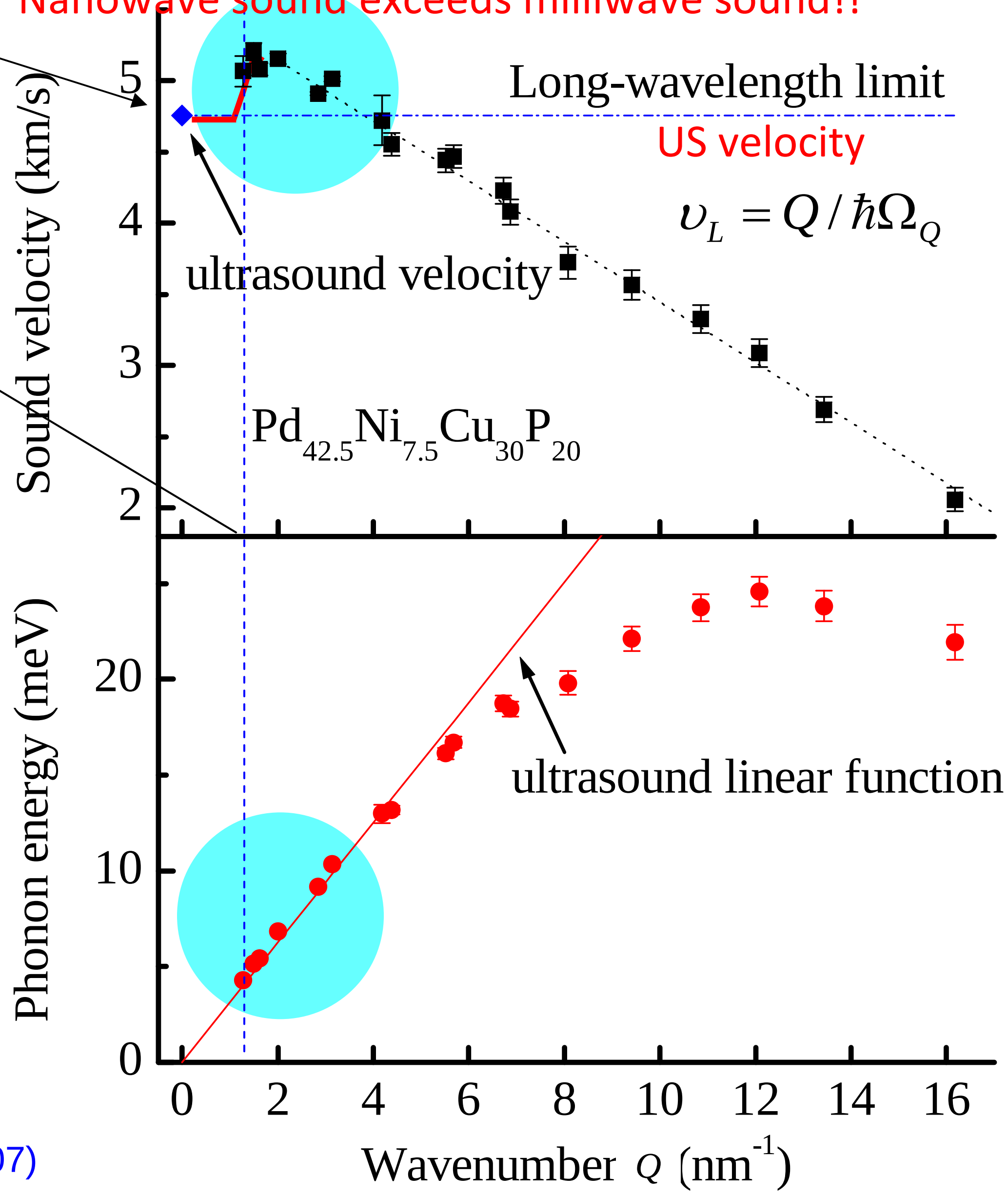
c_{11} =240 GPa

The size ξ of SBR > 4-5 nm.

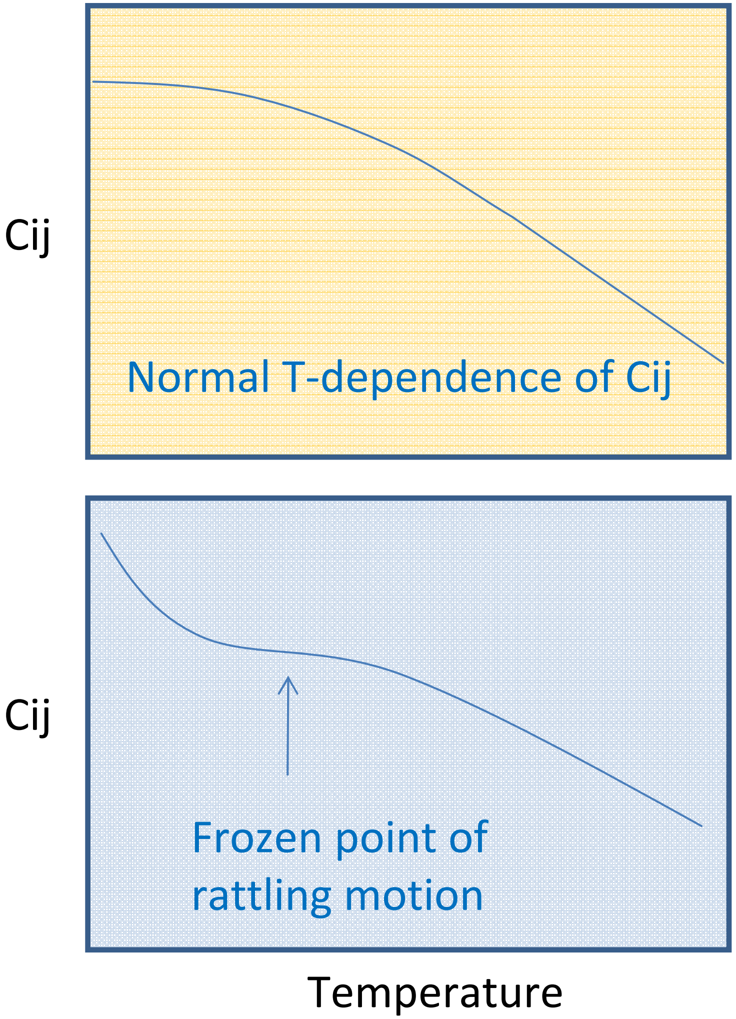


Ichitsubo et al., Phys. Rev. B 76, 140201(R) (2007)

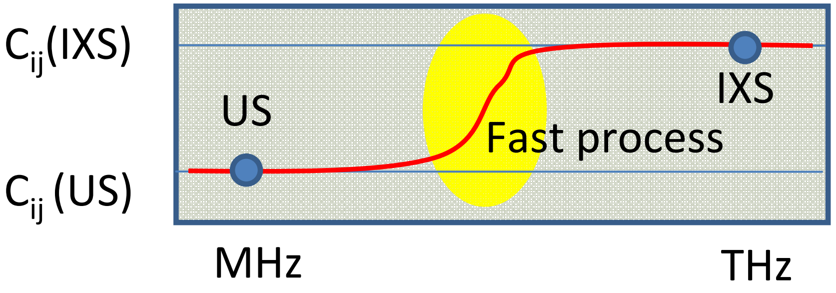
Nanowave sound exceeds milliwave sound!!

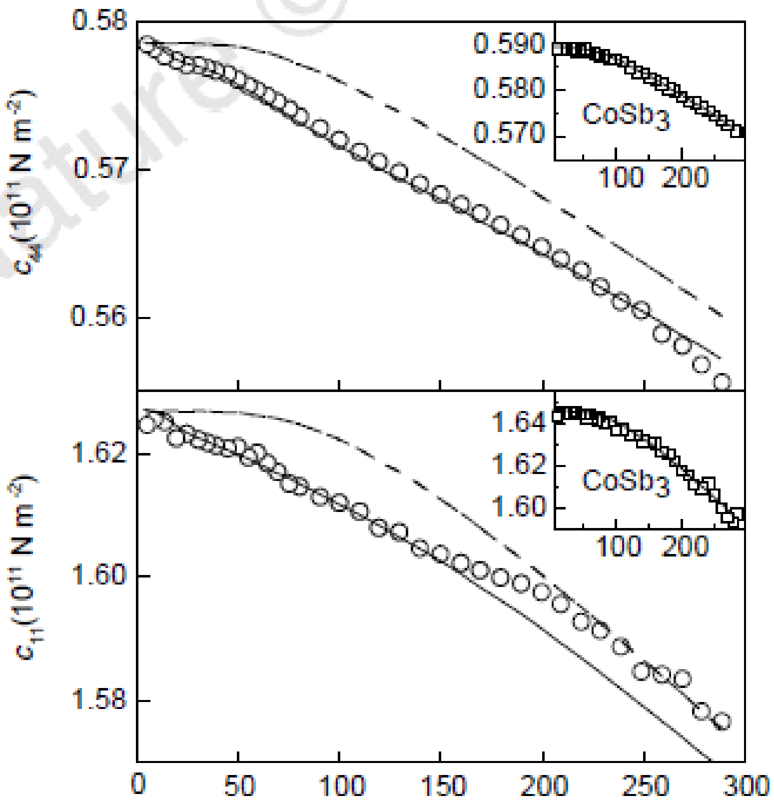


Existence or absence of fast process (rattling motion)???



If the fast process (rattling motion) is frozen at a certain temperature, the elastic modulus steeply increases below the temperature…



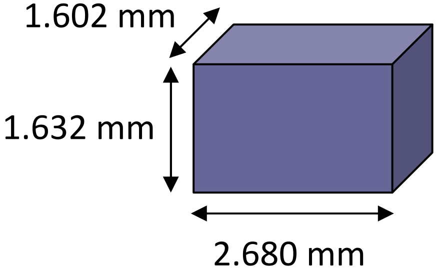


LaFeCoSb

V. Kappens et al., Nature 395,

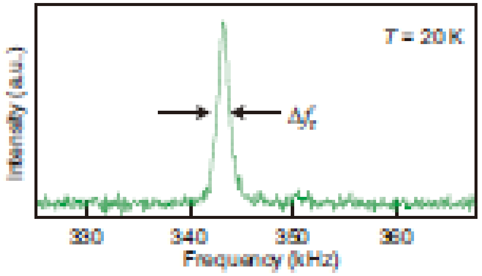
Low-temperature C_{ij} and Q^{-1} from 10 K to 300K to check the absence of a fast process

$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$

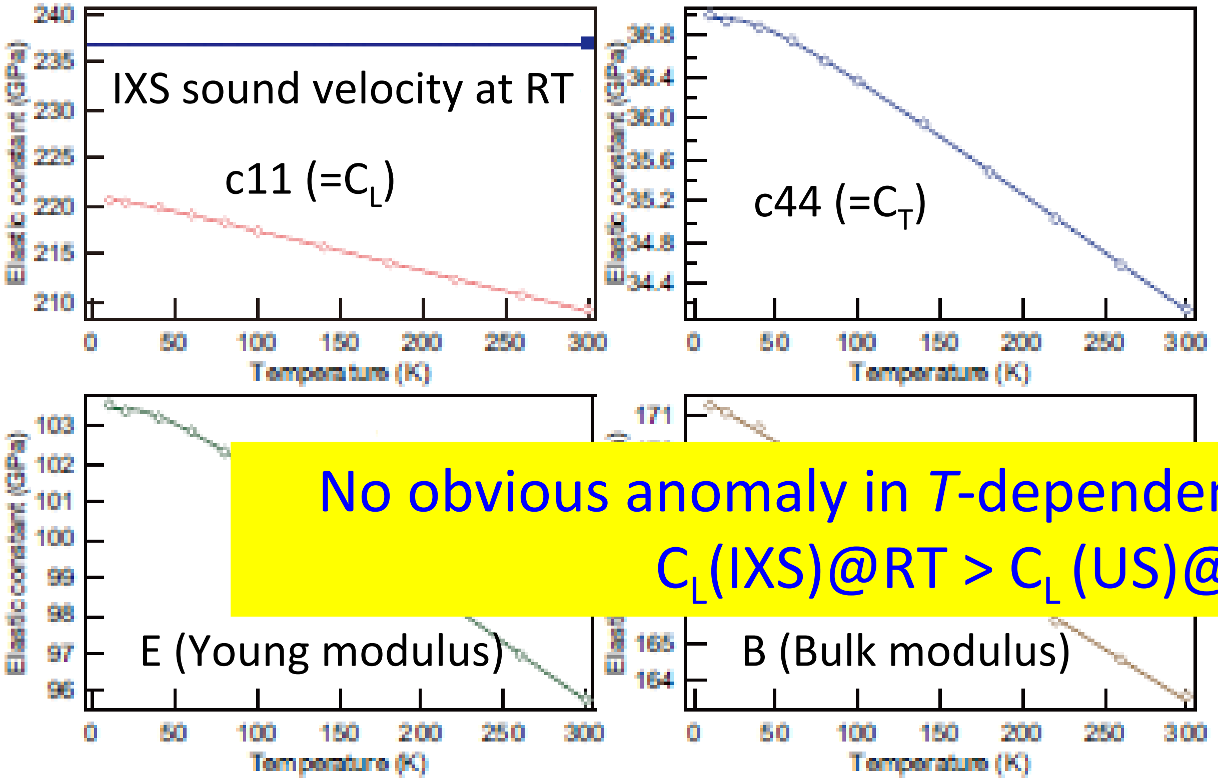


Density : 9236.80 kg/m^3

Internal friction



Elastic moduli



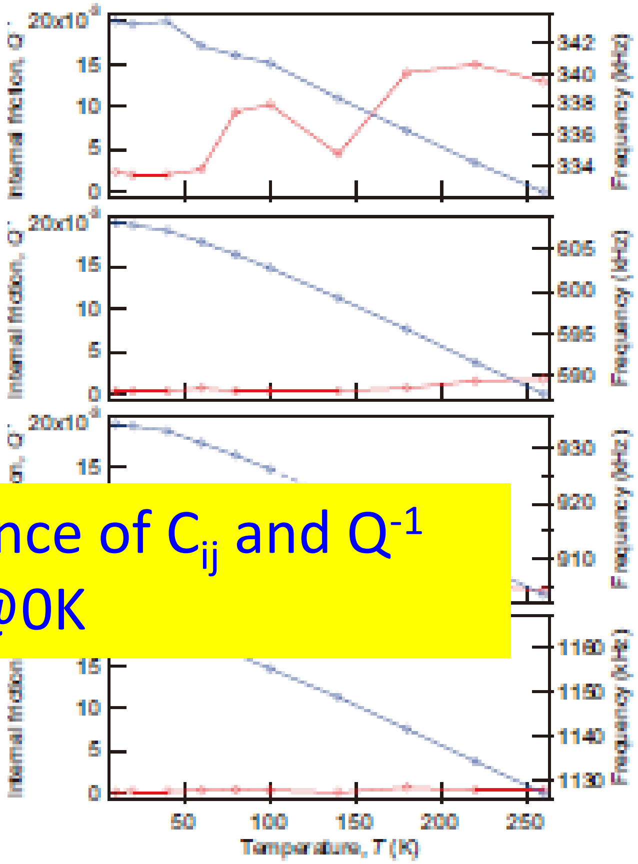
IXS sound velocity at RT

c11 (=C_L)

c44 (=C_T)

E (Young modulus)

B (Bulk modulus)

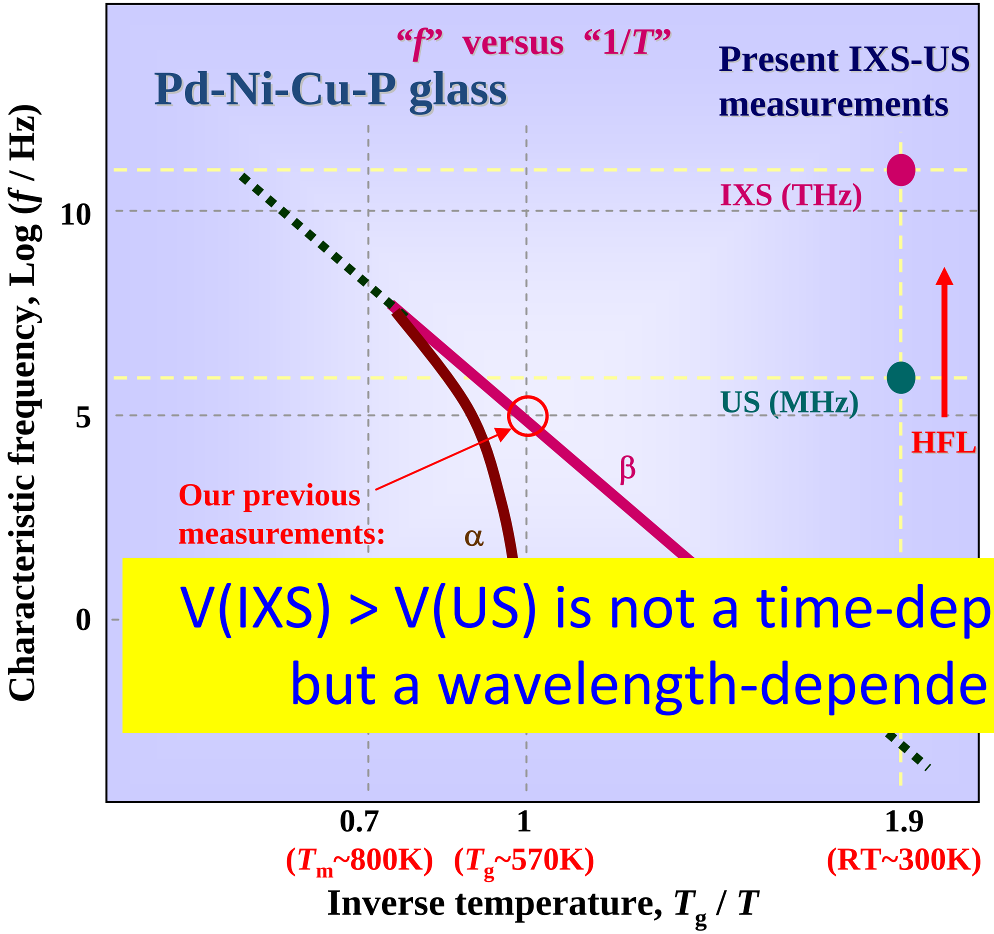


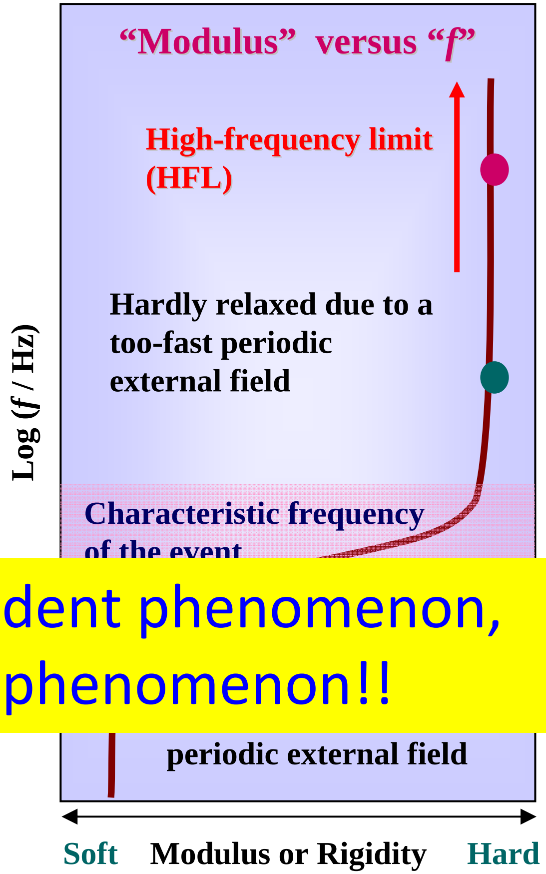
No obvious anomaly in *T*-dependence of C_{ij} and Q^{-1}

C_L(IXS)@RT > C_L (US)@0K

Meaning of IXS and US measurements without the fast process

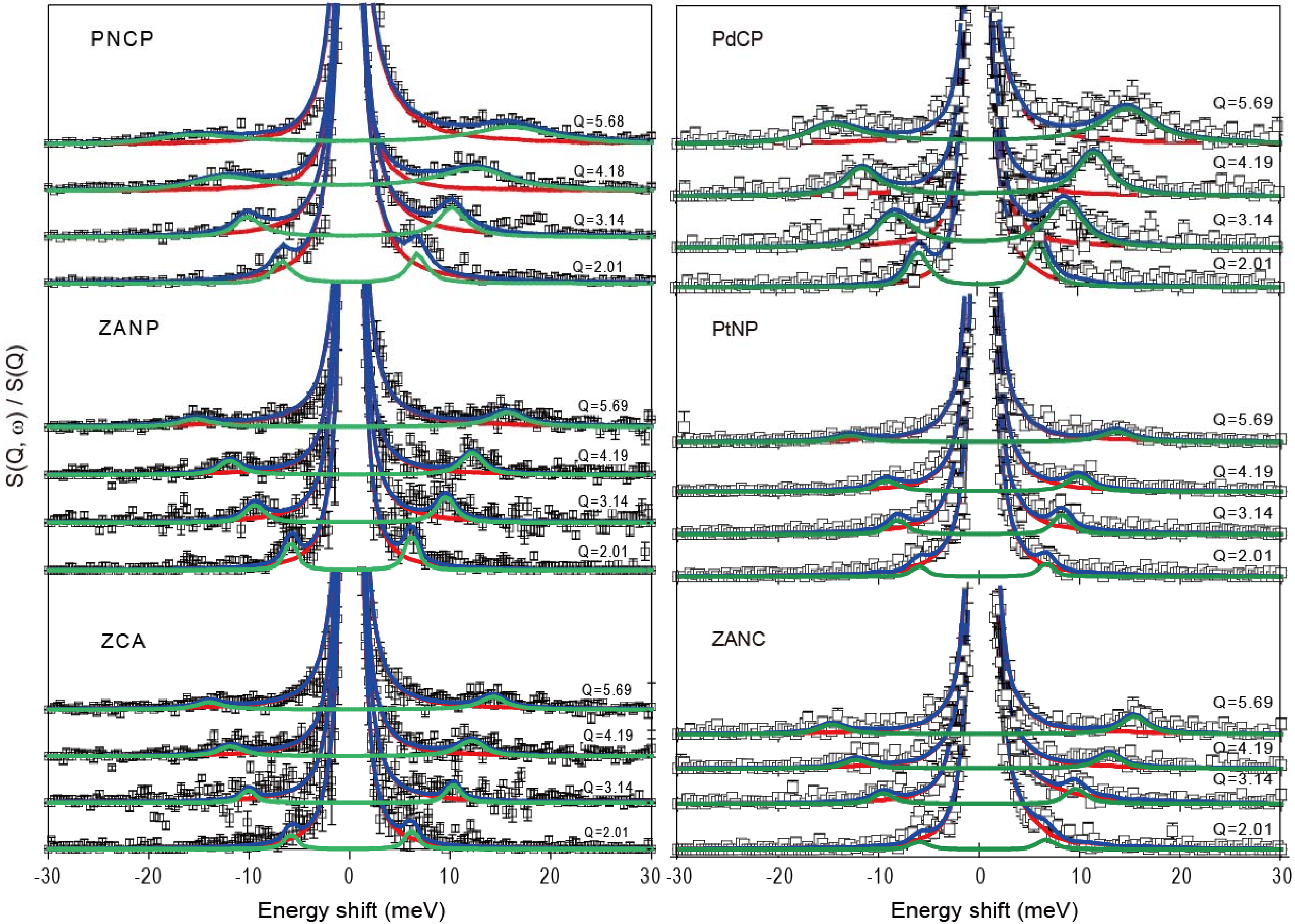
The present IXS and US measurements are at room temperature (300 K), far below the glass transition temperature T_g (570 K), being about $0.5T_g$. So, the both frequency regions (MHz and THz) are much higher than the characteristic frequencies of the possible relaxation processes at 300 K, i.e., both are high-frequency, so that the measured sound velocities at such a low temperature by the two measurements do not include any relaxation effects. The difference between the two velocities is only attributed to what is caused by the difference between their wavelengths.





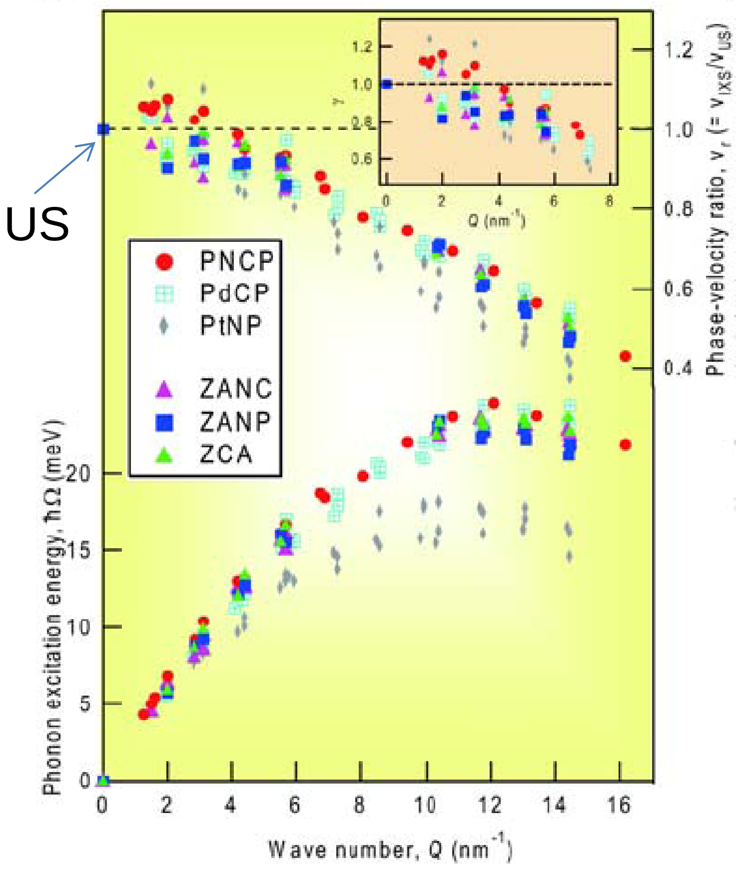
V(IXS) > V(US) is not a time-dependent phenomenon, but a wavelength-dependent phenomenon!!

IXS spectra for six metallic glasses at low Q

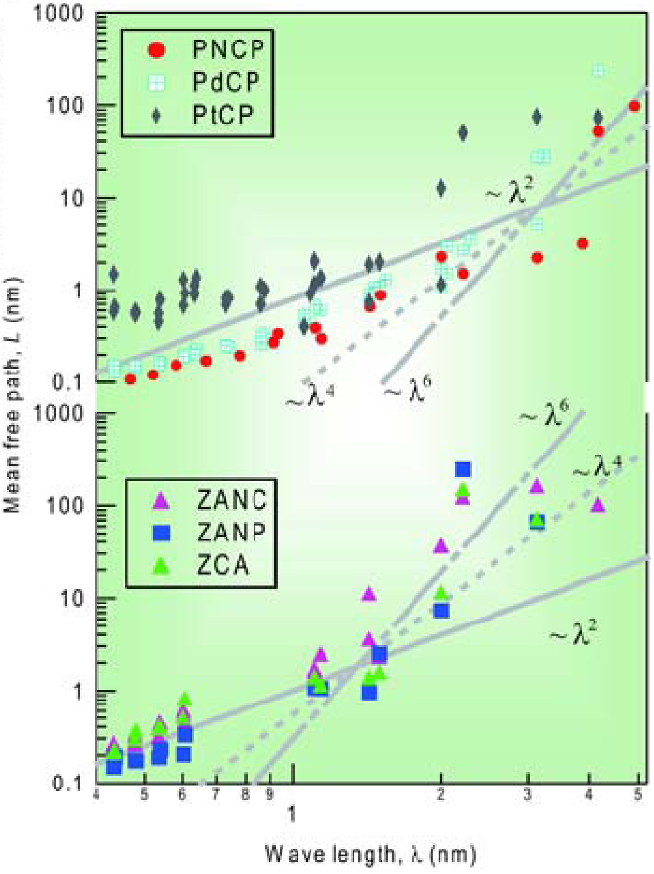


IXS and RUS of six metallic glasses

PdNiCuP, PdCuP, PtNiP, ZrAlNiCu, ZrAlNiPd, ZrCuAl



Phase velocity vs Q (2π/wavelength)



Propagation length vs wavelength

The mean free path (propagation length) of phonon is defined as

$$L \sim v \cdot \tau = \frac{\Omega}{\hbar Q} \cdot \frac{\hbar}{\Gamma} = \frac{\Omega}{\Gamma Q}$$

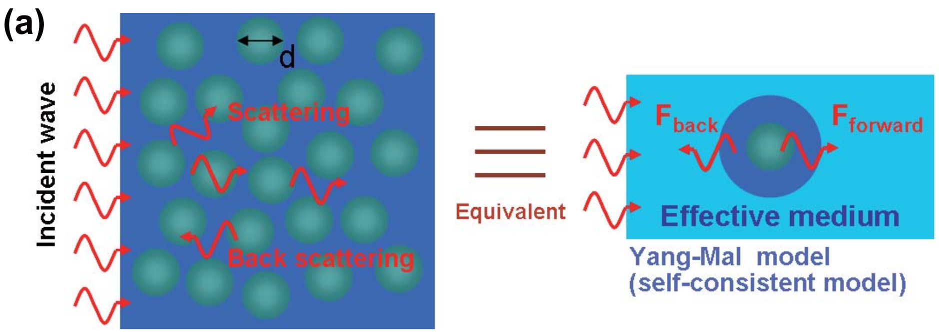
(1) The phase velocity of phonon of Pd-, Pt-based glasses tends to exceed the US velocity in the low Q range….In contrast, in the case of Zr-based metallic glasses, the phonon velocity tends to be close to the US velocity.

(2) The propagation length of phonon tends to increase at a certain wavelength….

Calculation with Yang-Mal's elastic wave scattering theory

Shear horizontal wave is only considered in a two-dimensional model for the sake of simplicity.

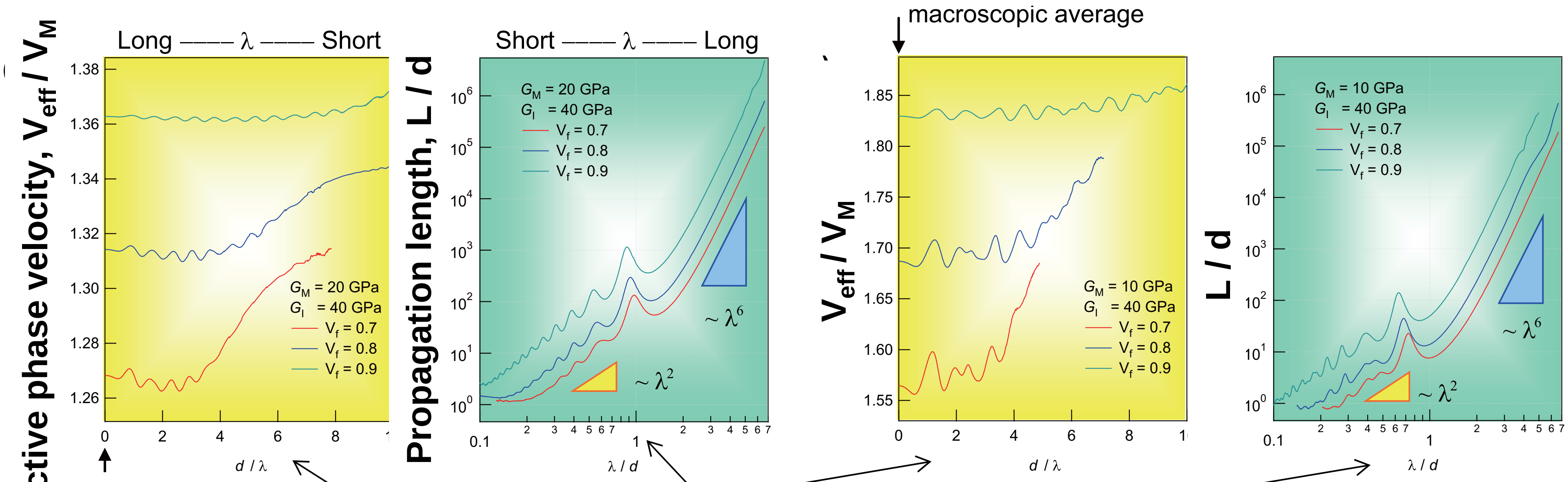
$$1 = \left(1 - \frac{2in_s f_0}{{k_{\mathrm{eff}}}^2}\right)^2 - \left(\frac{2in_s f_\pi}{{k_{\mathrm{eff}}}^2}\right)^2$$



Tendency:

(1) The sound velocity tends to exceed the US velocity with increase in volume of soft region

(2) Propagation length of phonon steeply increases around the wavelength exceeding the inclusion diameter, without regard to the degree of elastic inhomogeneity….



US velocity

Q value

Wavelength normalized by diameter

G_M = 20, G_I = 40 GPa

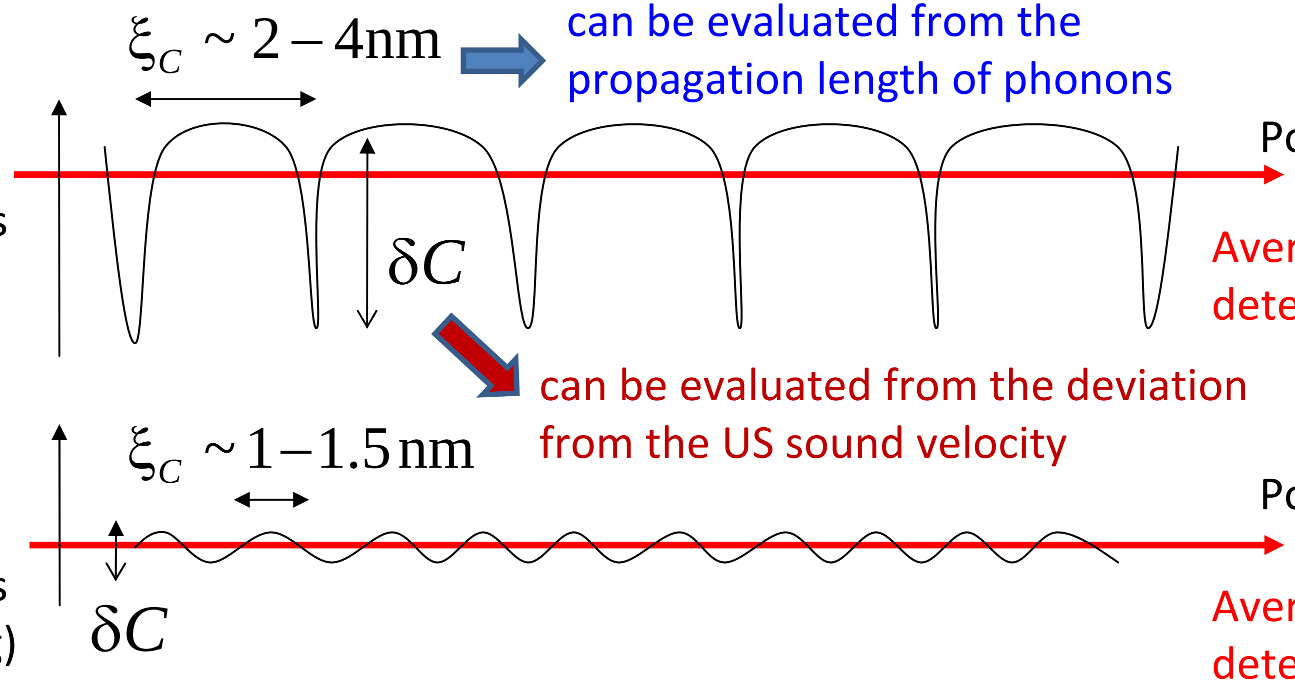
G_M = 10, G_I = 40 GPa

Elastic-constants fluctuation of glasses

Elastic constant fluctuation : $C(x) \sim \langle C \rangle + \delta C(x)$

Correlation : $\langle \delta C(x) \delta C(x+x') \rangle = \frac{1}{V} \int_V \delta C(x) \delta C(x+x') dx' \sim \exp(-\frac{x}{\xi})$

Correlation length : ξ



Elasticity, *C*

PNCP, PdCP, PtNP

Pd-based metallic glass (fragile)

$\xi_C \sim 2-4\text{nm}$

can be evaluated from the propagation length of phonons

Average moduli detected by US

can be evaluated from the deviation from the US sound velocity

ZANC, ZANP, ZCA

Zr-based metallic glass (more strong)

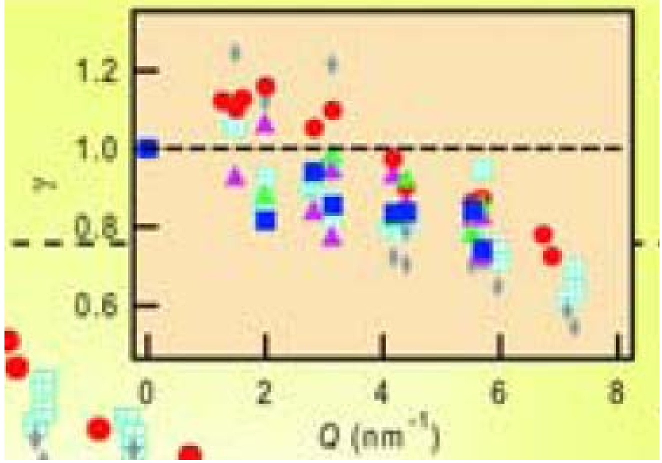
$\xi_C \sim 1-1.5\,\text{nm}$

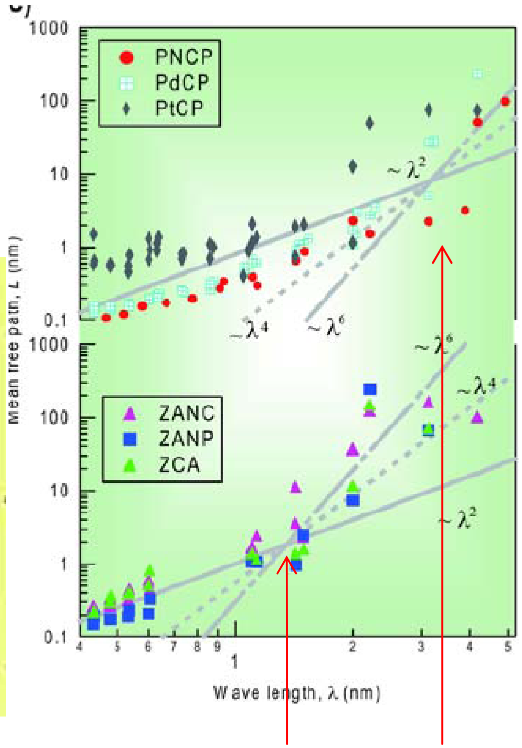
Average moduli detected by US

Physical properties of several metallic glasses

Glass sample	$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$	$Pd_{46}Cu_{35.5}P_{18.5}$	$Pt_{60}Ni_{15}P_{25}$	$Zr_{50}Cu_{40}Al_{10}$	$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	$Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$
Abbreviation	PNCP	PdCP	PtNP	ZCA	ZANC	ZANP
Density, ρ (kg/m^3)	9237	9485	15270	6837	6430	7145
Fragility, m	58.5 (51.4)	52.3	67.2	47.8	45.8 (43.2)	(39.8)
by Inelastic X-ray Scattering (IXS)						
λ_c (nm)	~ 4	~ 3	~ 2	~ 1.5	~ 1	~ 1.5
$v_{r,\max} \equiv v_{\max}^{IXS}/v_L^{US}$	1.083	1.034	1.116	0.999	1.031	0.970
$\gamma_{\max}$ $(\equiv v_{r,\max}^2)$	1.172	1.069	1.246	0.998	1.063	0.941

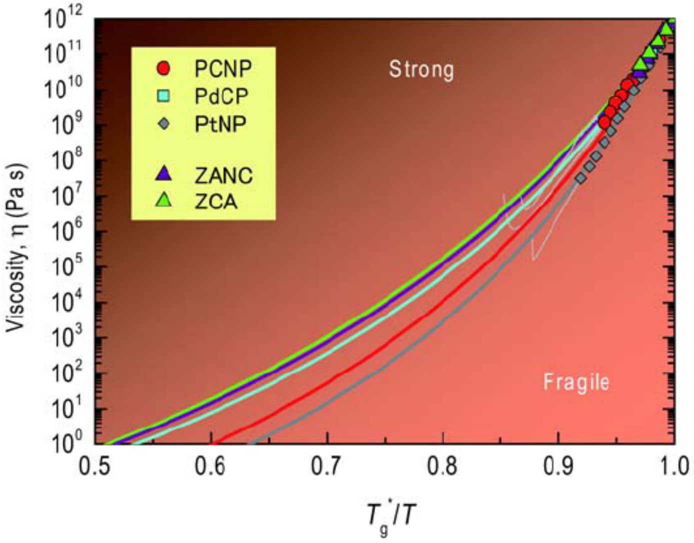
Max value in square of relative sound velocity = Degree of elastic inhomogeneity





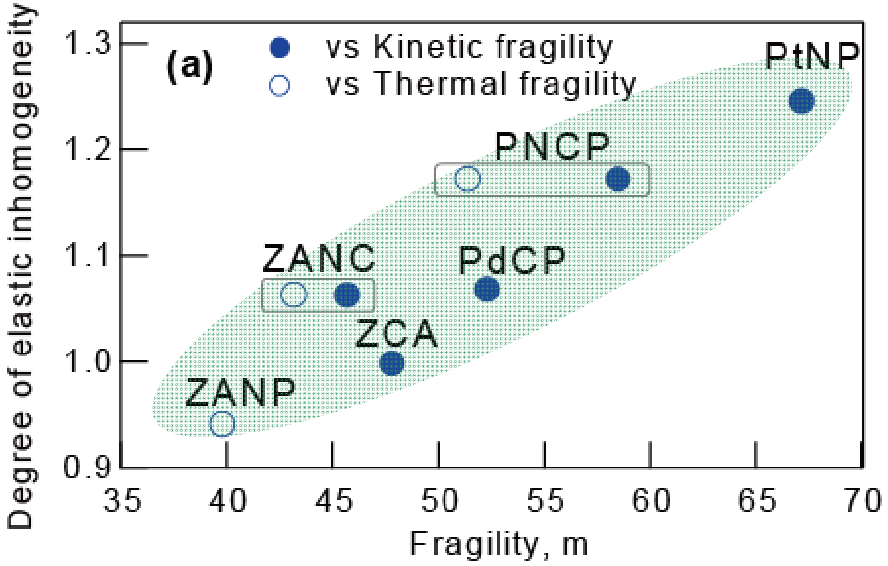
Correlation length λc

Fragility from T-dependence of viscosity

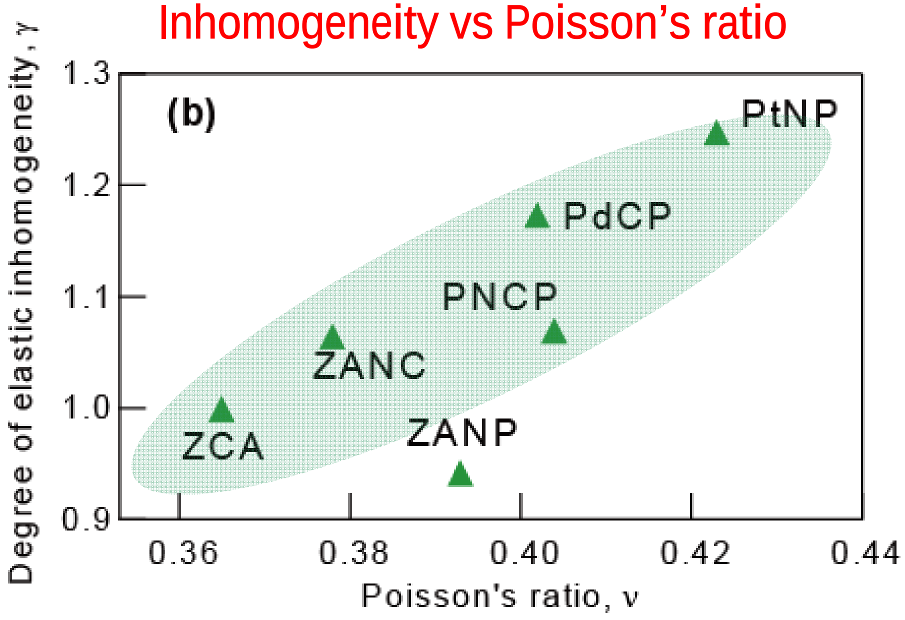


Correlation between the elastic inhomogeneity and fragility and Poisson’s ratio

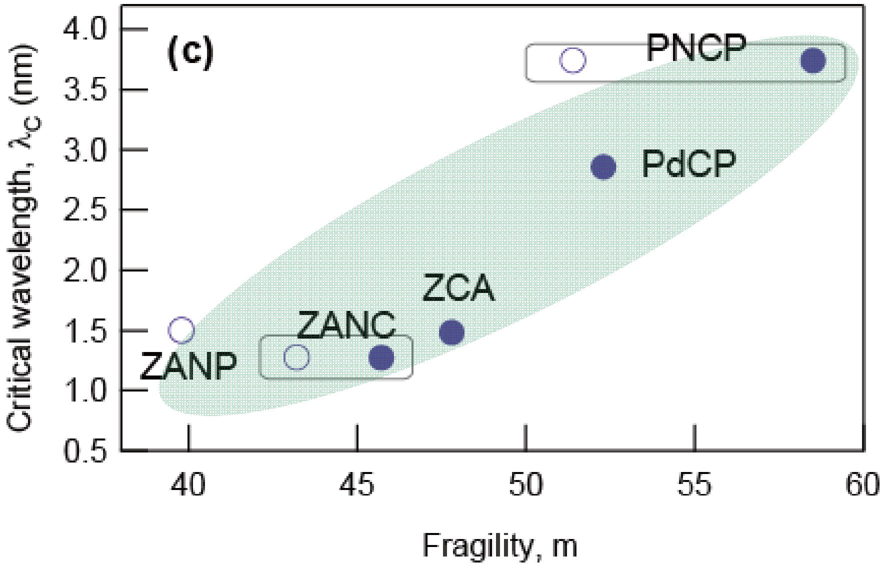
Inhomogeneity vs Fragility



Inhomogeneity vs Poisson’s ratio



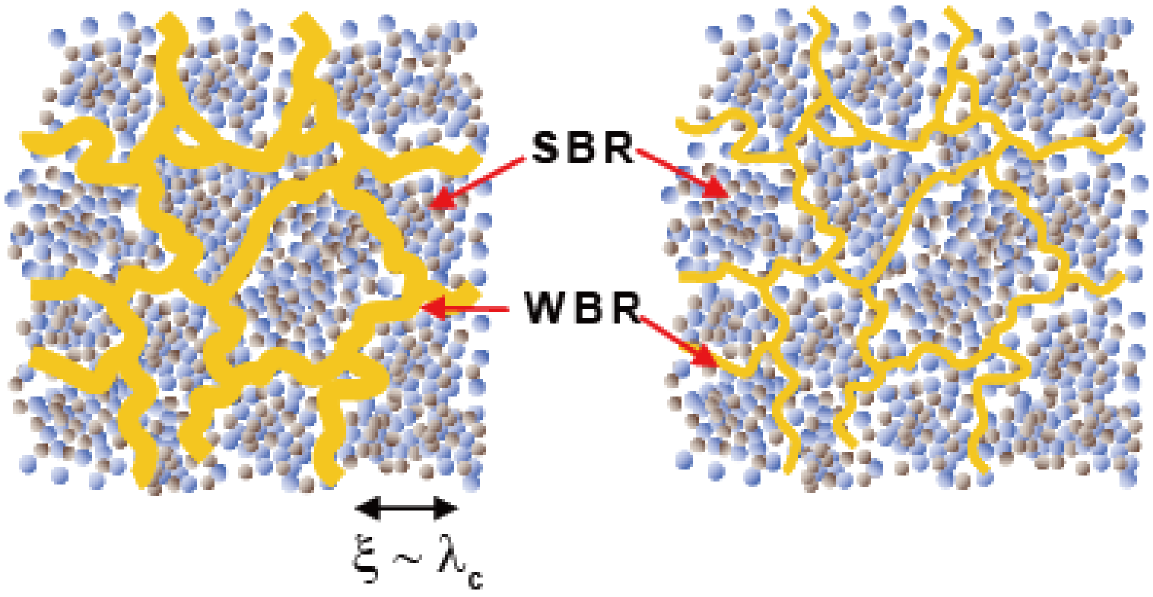
Critical wavelength (correlation size) vs Fragility



Structure model of strong and fragile metallic glasses

Fragile glass
Pd, Pt-based glasses
Relatively inhomogeneous

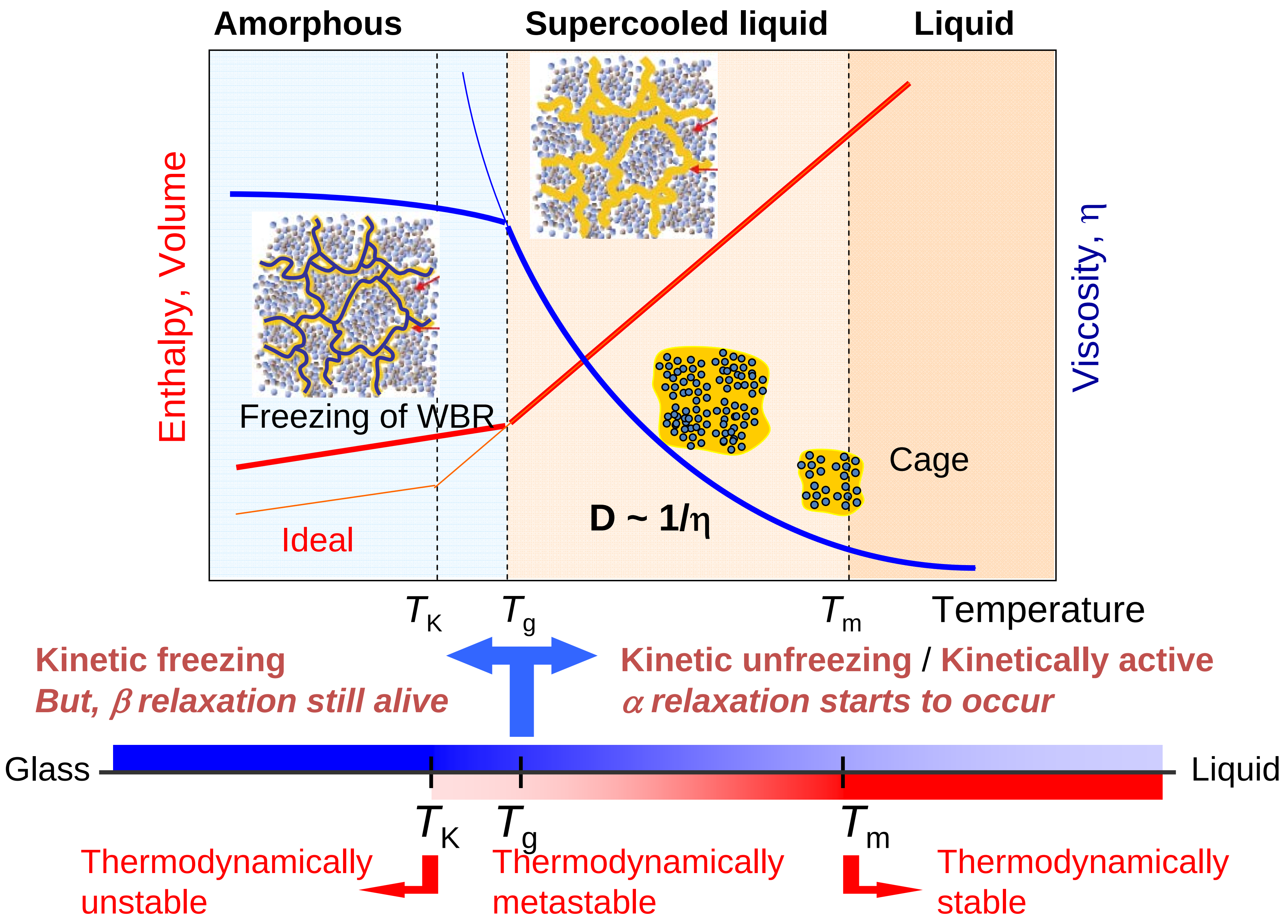
Strong glass
Zr-based glasses
Relatively homogeneous



Components
- Strongly bonded region (SBR)
  - low Poisson's ratio (high shear modulus)
- Weakly bonded region (WBR)
  - high Poisson's ratio (low shear modulus)

Distinction
- Strong glass: low fraction of WBR ← **Low degree of inhomogeneity**
- Fragile glass: high fraction of WBR ← **High degree of inhomogeneity**

Structural interpretation of glass transition



Kinetic freezing

But, β relaxation still alive

Kinetic unfreezing / Kinetically active

α relaxation starts to occur

Thermodynamically unstable

Thermodynamically metastable

Thermodynamically stable

Summary of static heterogeneity in metallic glass

From US experiments (US-induced instability);

- The beta-relaxation locally occurs (not homogeneously).
- The beta-relaxation eventually deteriorates the glass structure.

From partially-crystallized structure of PNCP glass;

- Glass is considered to consist of SBRs surrounded by WBRs.

From low-temperature dependence of elasticity C_{ij};

- Fast process, i.e., rattling motion, does not occur!!!

From IXS and US measurements at RT (far below Tg) in which there are not any relaxation effects;

- Nanometer-wave sound velocity exceeds millimeter-wave sound velocity strongly indicates nanometer-scale elastic inhomogeneity....
- Nanoscale elastic-constants fluctuation is evaluated from phonon propagation length and deviation ΔC_{ij} from macro-C_{ij}.

Remaining issues:

1. **What is the glass transition? More physically…**

2. **How are the complicated relaxation processes related with the inhomogeneous domain structure? With MCT.**

3. **Why is such a inhomogeneous structure formed? This should be understood from a statistical thermodynamic viewpoint…**

4. **Some efforts to the consistency with other similar models, e.g., Prof. Egami, Prof. Wang…**