THE UNIVERSITY OF ARIZONA.

Structural Contributions to the Fragility of Network Glasses

THE UNIVERSITY OF ARIZONA. TUCSON ARIZONA

Pierre Lucas*, Zhiyong Yang, Ozgur Gulbiten, Ellyn KIng

UNIVERSITÉ DE RENNES 1

Wang Yang, Bruno Bureau, Catherine Boussard-Pledel

ASU

Prof. Jeff Yarger, Dr. Emmanuel Soignard

CUDOS

Rongping Wang, Barry Luther-Davies

Q: Is the Fragility of chalcogenide glass-formers controlled by the rigidity percolation (mean coordination)?

A: Probably not.

Talk Outline:

1- Rigidity percolation: review

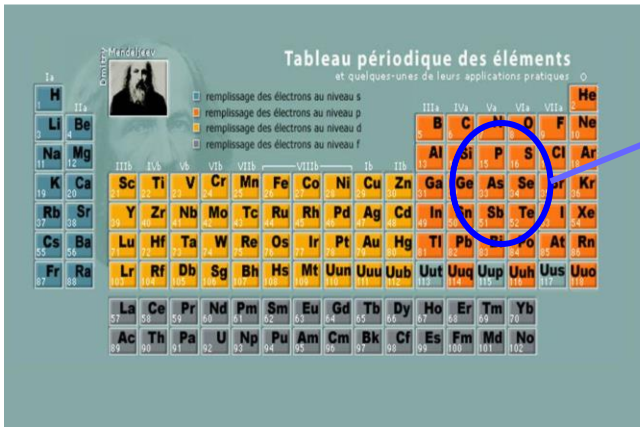
2- Structural origin of Fragility in the Ge-As-Se system

3- Structural origin of Fragility in the As-Se system

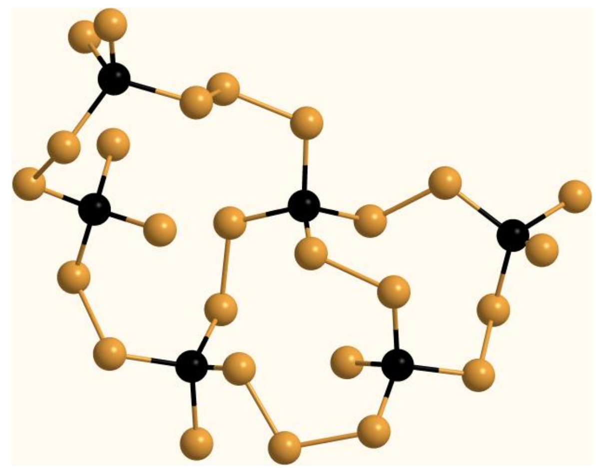
4- Structural origin of Fragility in the Ge-Se system

1- Rigidity percolation: review

CHALCOGENIDE GLASSES = COVALENT NETWORKS



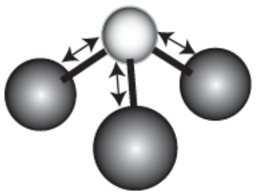
Ge, As, Sb, S, Se, Te,
Same electronegativity ≈ 2



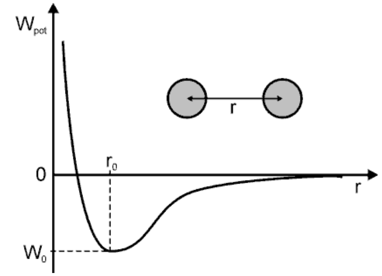
- Clear number of bonds
- Clear bond angles
- Good model glasses for counting structural constraints

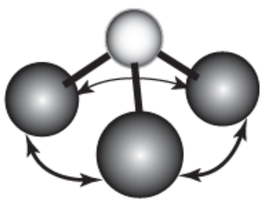
1- Rigidity percolation: review

Structural constraints for system with *r* bonds:

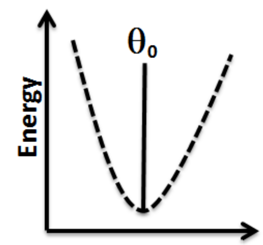


r bond constraints

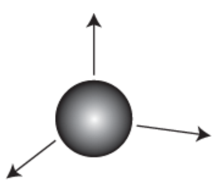




2r – 3 angle constraints



Atomic degrees of freedom= 3



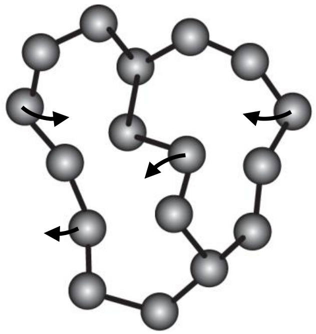
d=3 Three dimensional structure: x, y, z

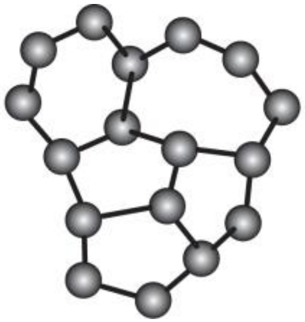
1- Rigidity percolation: review

If **<*r*>** is the **average coordination number** (average number of bonds per atoms)

$$< r >= \sum r_i a_i$$

a_i : molar fraction
r_i : covalent coordination





- If **<r> < 2.4** : floppy network
  underconstrained
  low coordination

- If **<r> > 2.4** : rigid network
  overconstrained
  high coordination

Talk Outline:

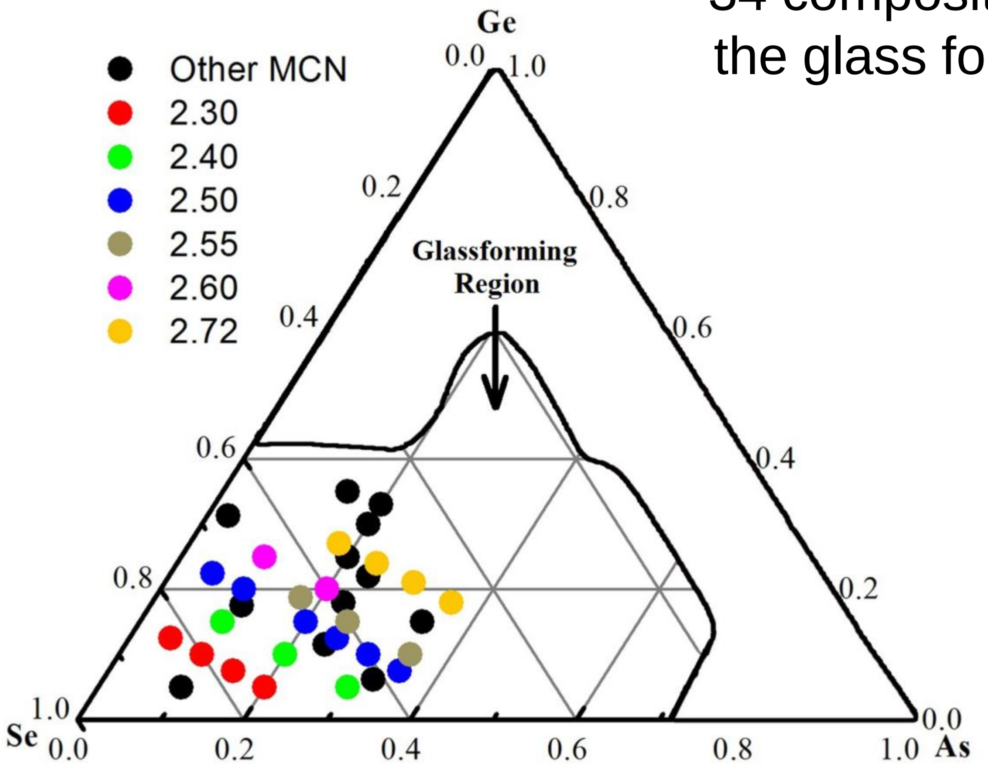
1- Rigidity percolation: review

2- Structural origin of Fragility in the Ge-As-Se system

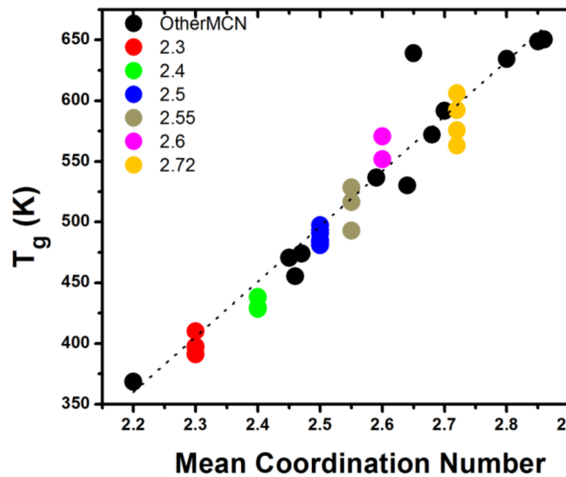
3- Structural origin of Fragility in the As-Se system

4- Structural origin of Fragility in the Ge-Se system

2- Structural origin of Fragility in the Ge-As-Se system = Stoichiometry



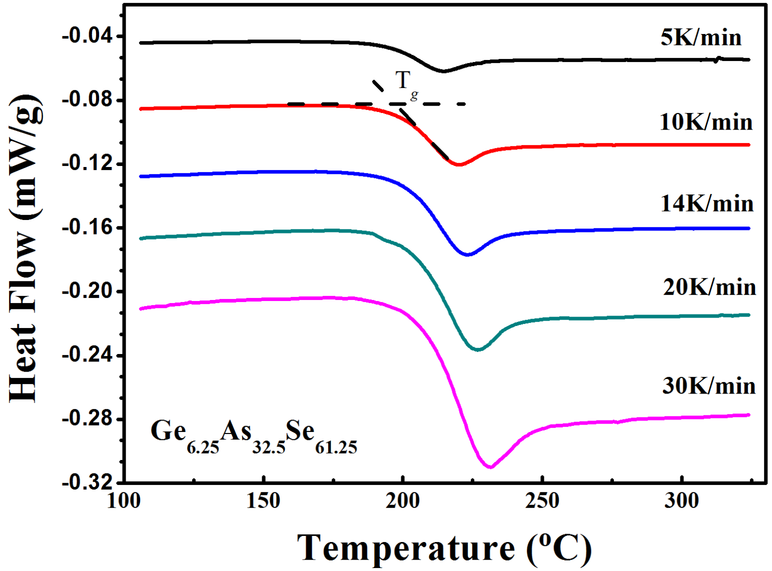
- 34 compositions throughout the glass forming domain.

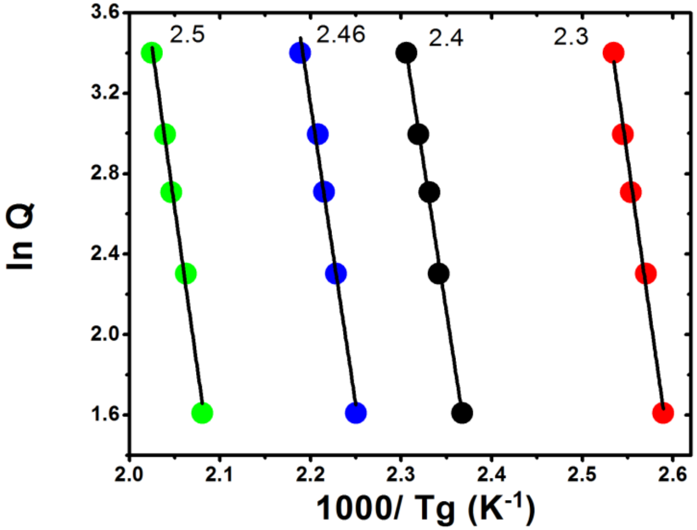


T_g increases linearly with <*r*>

2- Structural origin of Fragility in the Ge-As-Se system: Stoichiometry

Fragility index *m* is obtained calorimetrically:





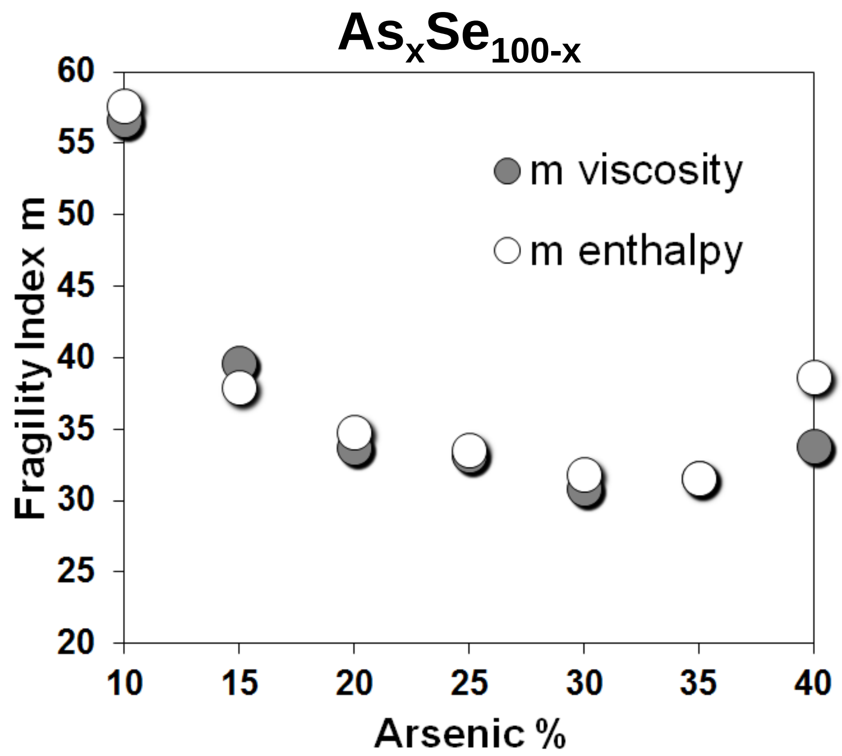
First, the activation energy for enthalpy relaxation $\boldsymbol{E_a}$ is calculated using Moynihan's cool-rate method:

$$\frac{d\ln Q}{d\left(\frac{1}{Tg}\right)} = -\frac{Ea}{R}$$

2- Structural origin of Fragility in the Ge-As-Se system: Stoichiometry

The Fragility Index ***m*** is then obtained from the activation energy for enthalpy relaxation $\boldsymbol{E_a}$ and the glass transition temperature T_g:

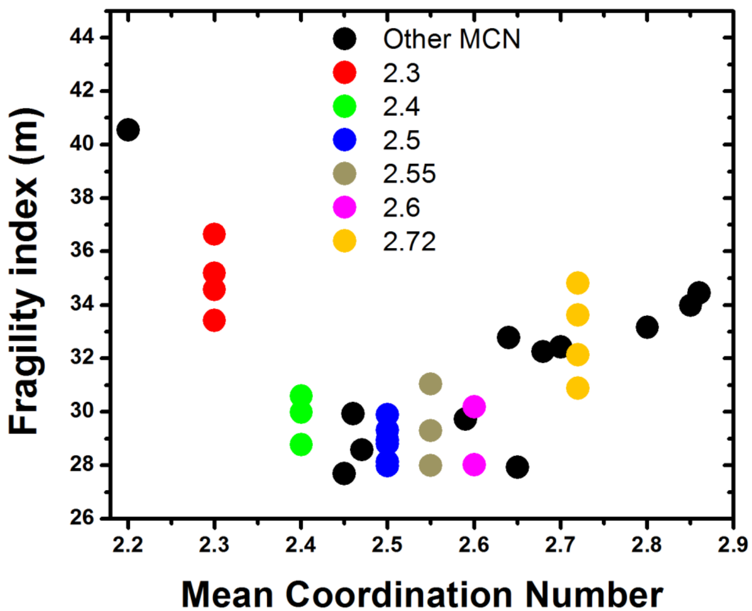
$$m = \frac{Ea}{RTg \ln 10}$$



The Fragility Index ***m*** values obtained from the activation energy for enthalpy relaxation $\boldsymbol{E_a}$ are in good agreement with that obtained from the viscosity activation energy $\boldsymbol{E_\eta}$.

2- Structural origin of Fragility in the Ge-As-Se system: Stoichiometry

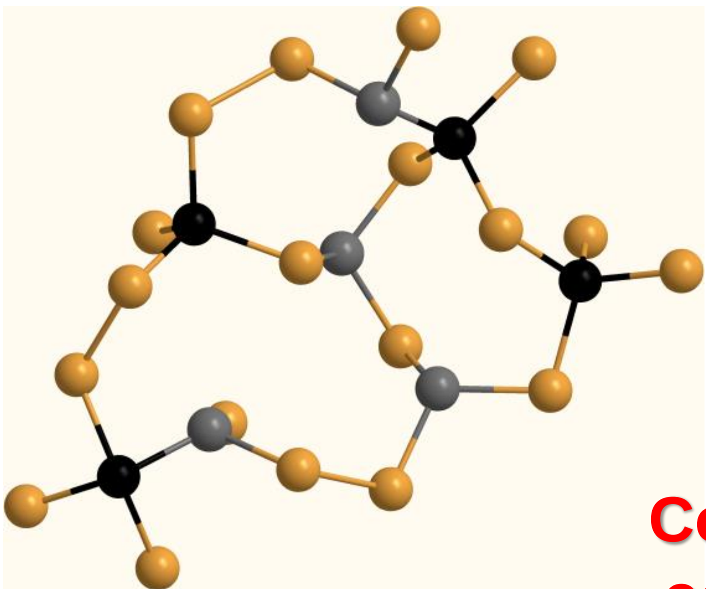
Poor correlation between Fragility index *m* and average coordination number:



No clear minimum in *m*.
Not centered at <*r*>=2.4

2- Structural origin of Fragility in the Ge-As-Se system: Stoichiometry

Ge-As-Se glasses are known to satisfy chemical order:



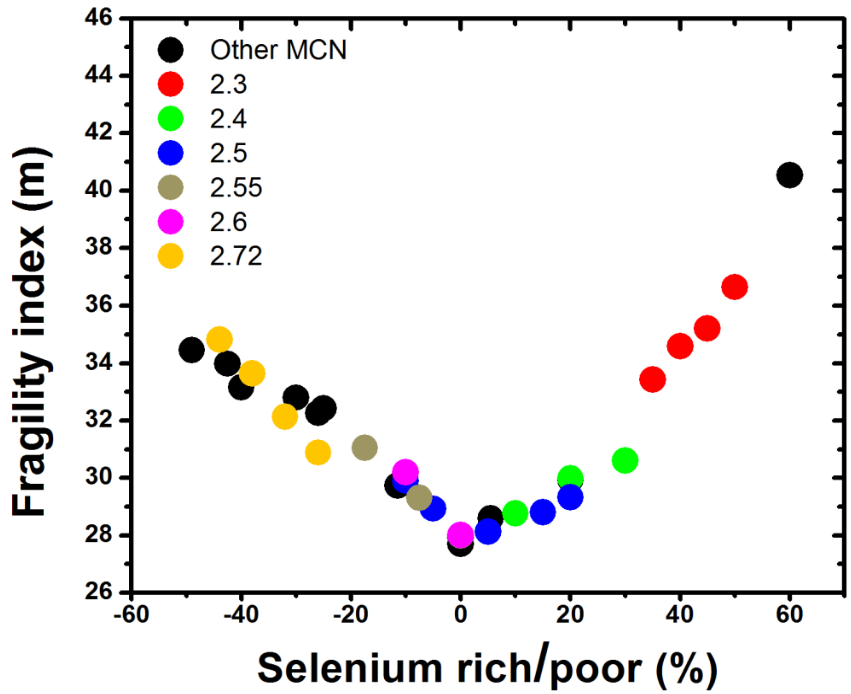
Not a random network of Ge, As and Se.

Each Ge and As is surrounded preferentially by Se atoms (if the stoichiometry permits).

Could these chemical effects correlate with the Fragility ?

2- Structural origin of Fragility in the Ge-As-Se system: Stoichiometry

Excellent correlation between Fragility index *m* and deviation from stoichiometry:



Clear minimum in *m* for stoichiometric compositions where all Ge and As atoms are linked by exactly one Se. (5 data points at “0”)

Only heteropolar bonds in the stoichiometric compositions.

Fragility is controlled by stoichiometry in Ge-As-Se glasses

Talk Outline:

1- Rigidity percolation: review

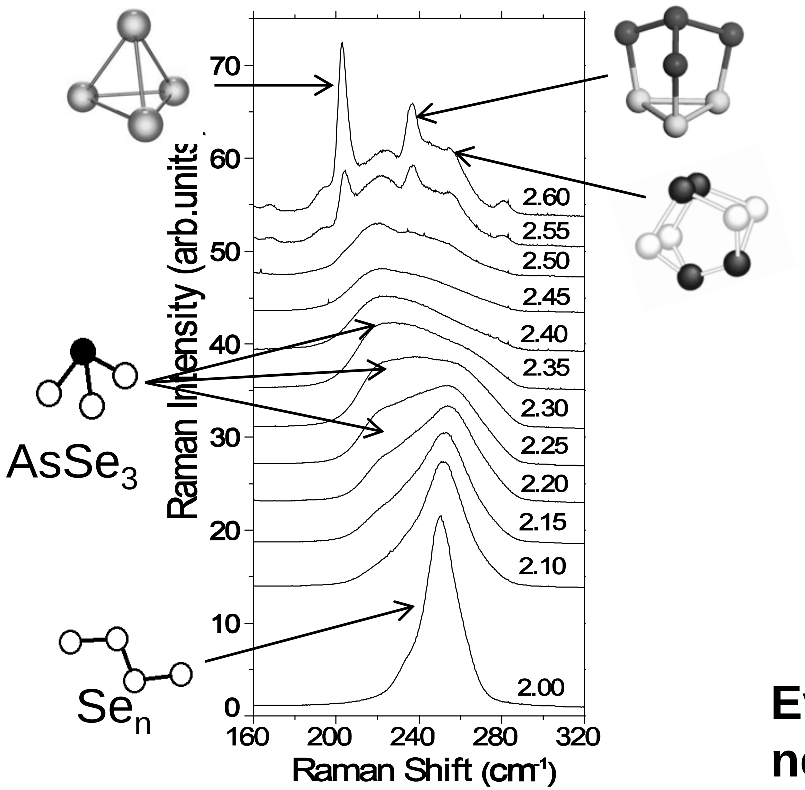
2- Structural origin of Fragility in the Ge-As-Se system

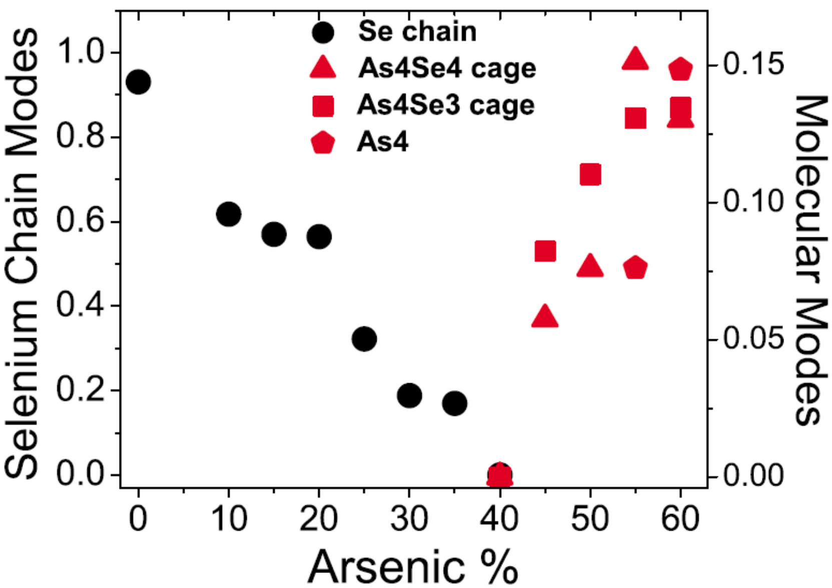
3- Structural origin of Fragility in the As-Se system

4- Structural origin of Fragility in the Ge-Se system

3- Structural origin of Fragility in the As-Se system: Dimensionality

Structural evolution of As-Se network with <r>: RAMAN

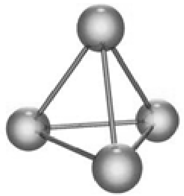


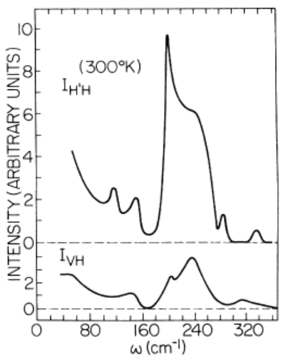


Evolution from Se-chains to pyramidal network, to phase separated molecular glass.

PRB **82, 195206 (2010)**

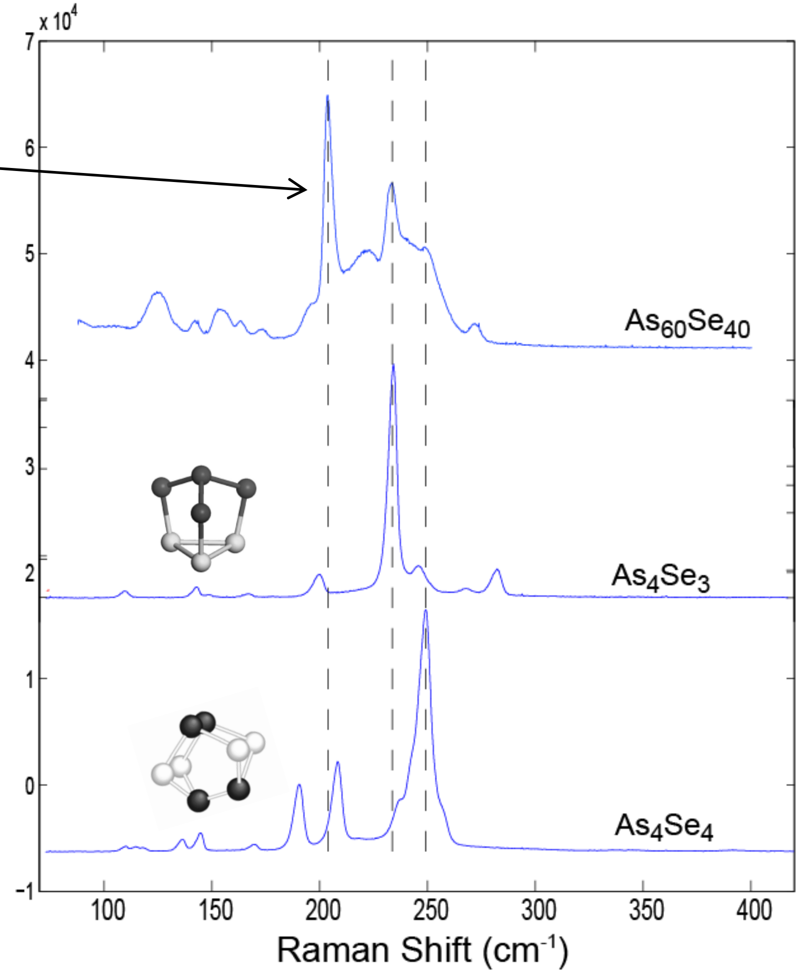
As_4

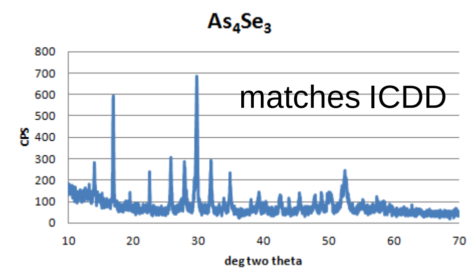


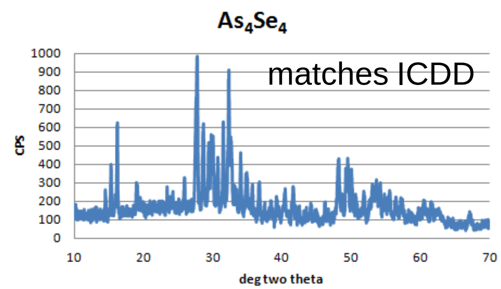


Amorphous As

Phys Rev B **15** 3863 (1977)



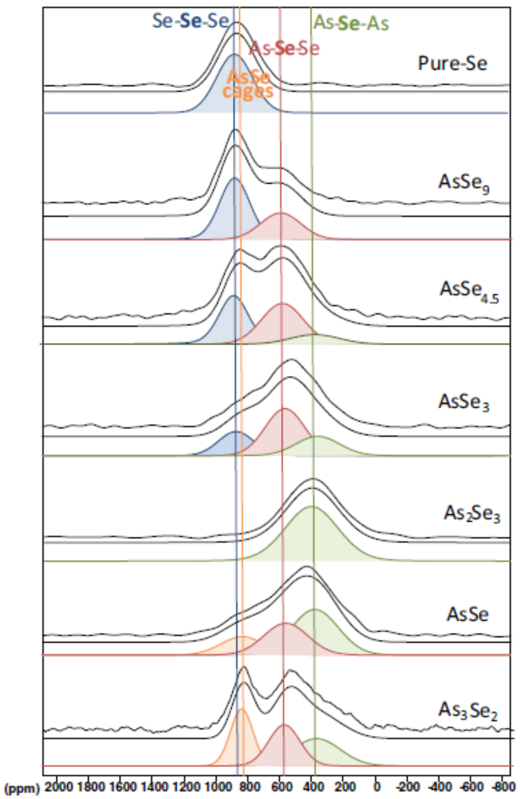


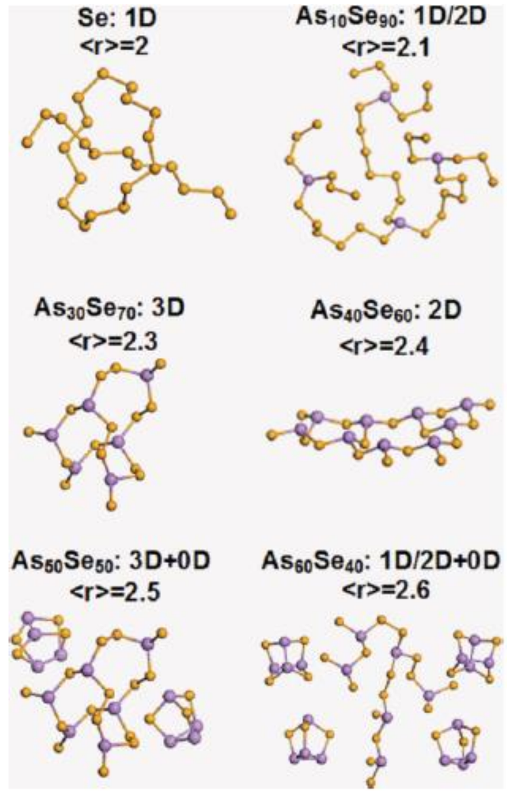


THE UNIVERSITY OF ARIZONA.

3- Structural origin of Fragility in the As-Se system: Dimensionality

Structural evolution of As-Se network with <r>: Se^{77}NMR



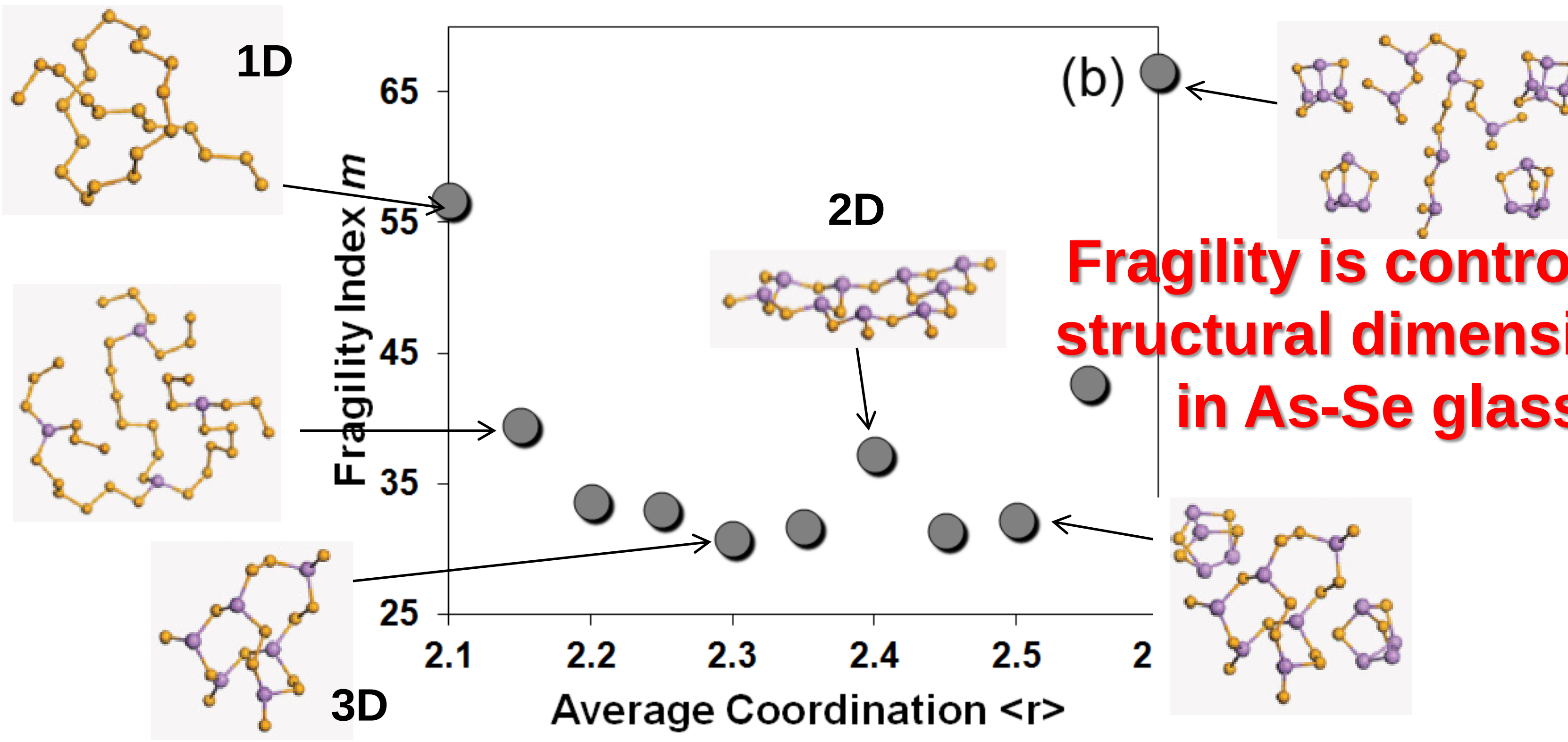


NMR confirms that the structure evolves from 1D Se-chains to 3D chain crossing model to 2D pyramidal network, to 0D phase separated molecular glass.

PRB **85, 144107 (2012)**

3- Structural origin of Fragility in the As-Se system: Dimensionality

Fragility index *m* is obtained from viscosity: $m = \frac{E_\eta}{RT_g \ln(10)}$



Fragility is controlled by structural dimensionality in As-Se glasses

Talk Outline:

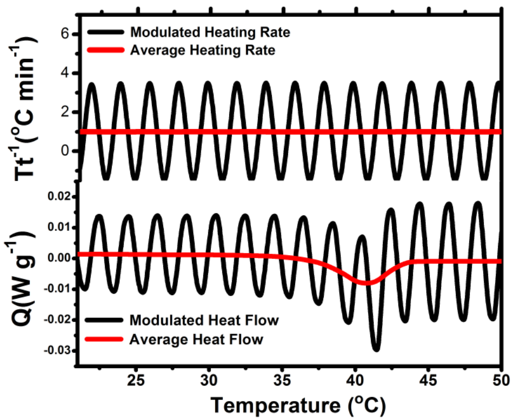
1- Rigidity percolation: review

2- Structural origin of Fragility in the Ge-As-Se system

3- Structural origin of Fragility in the As-Se system

4- Structural origin of Fragility in the Ge-Se system

Heat Capacity Spectroscopy: Modulated DSC



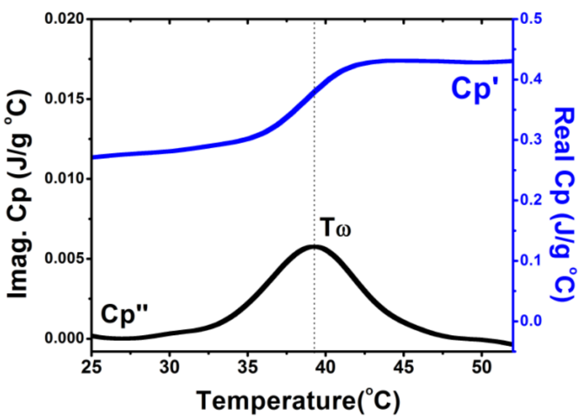
Raw MDSC data: $\dot{T}$: temperature rate
$\dot{Q}$: heat flow

From which is extracted two important parameters:

$$C_p = \frac{\dot{Q}}{\dot{T}}$$ Modulated heat capacity

ω = 60 sec

φ_0 Phase lag between $\dot{T}$ and $\dot{Q}$



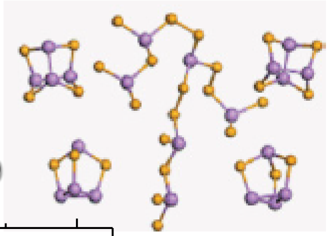
Which leads to the complex heat capacity:

$$C_p^*(\omega) = C' + iC'' = |C_p^*(\omega)| \exp(i\varphi_0)$$

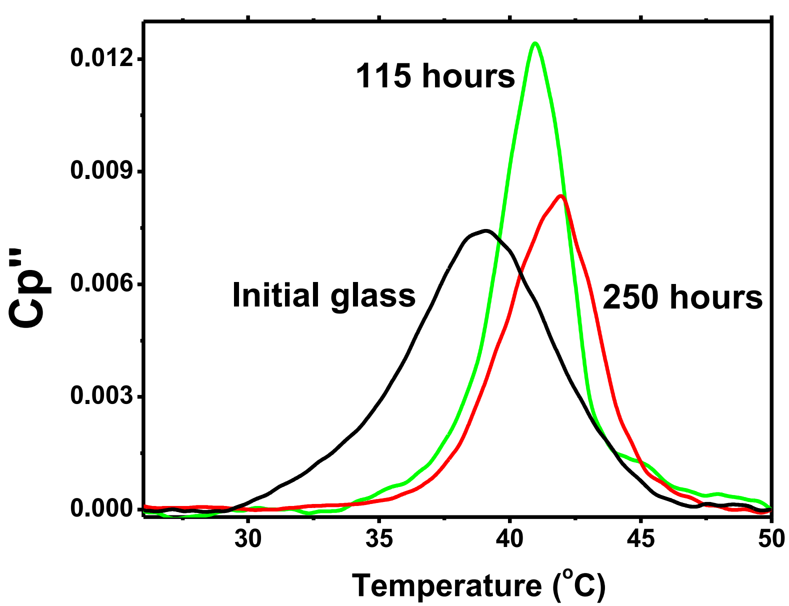
Phase lag φ_0 = 0 below and above T_g
Within transition: slow structural processes are probed

THE UNIVERSITY OF ARIZONA

Heat capacity spectroscopy

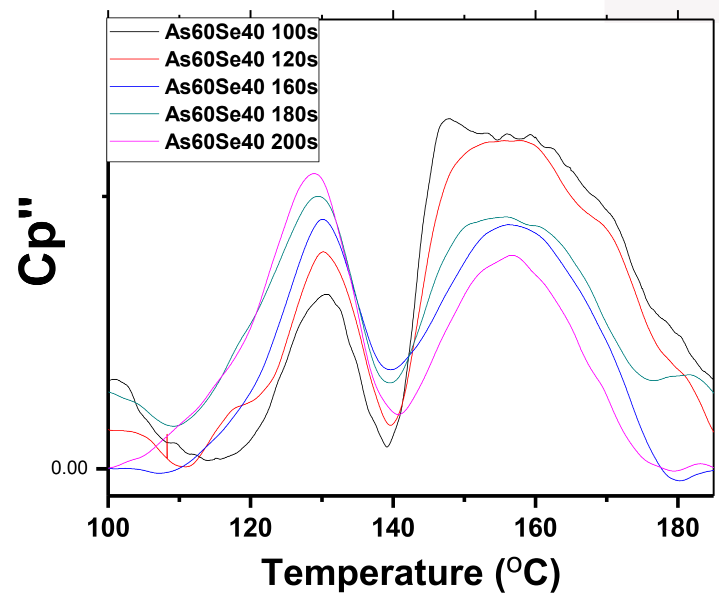


Aging of Se glass at 25° C



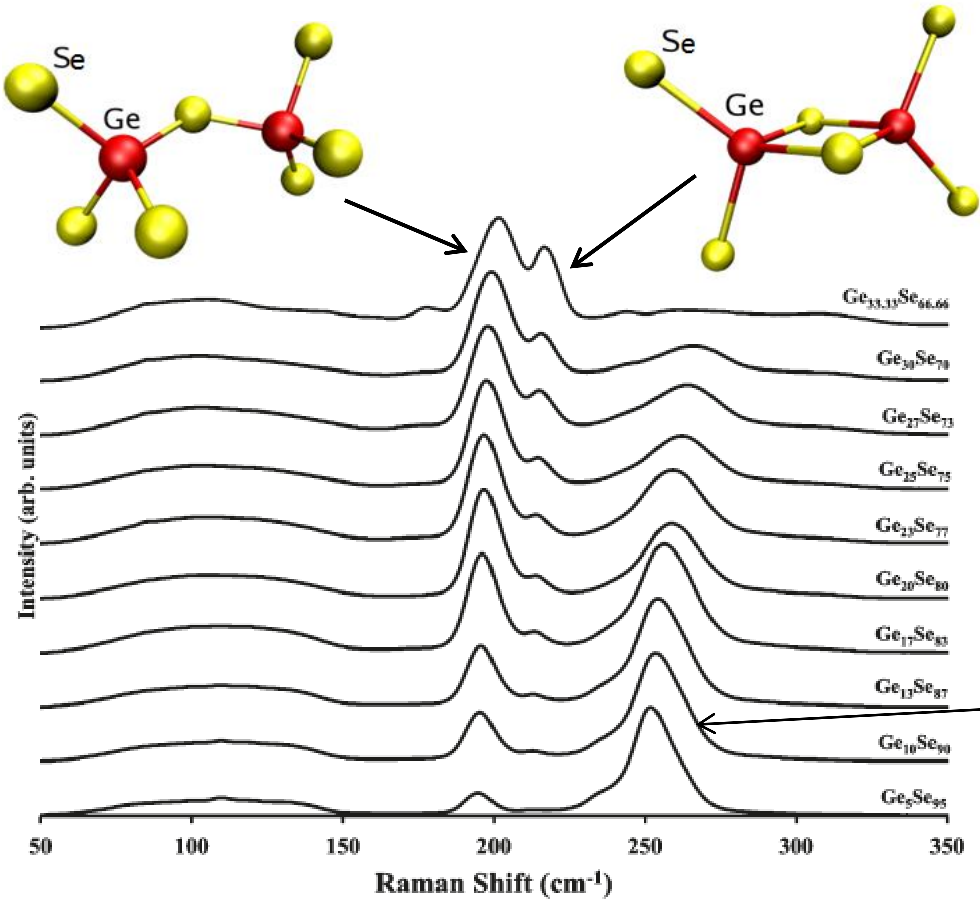
Fast relaxing domains vanish after long aging

$As_{60}Se_{40}$



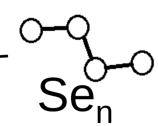
Cp" show two very distinct relaxation processes.

4- Structural origin of Fragility in the Ge-Se system: Heterogeneity



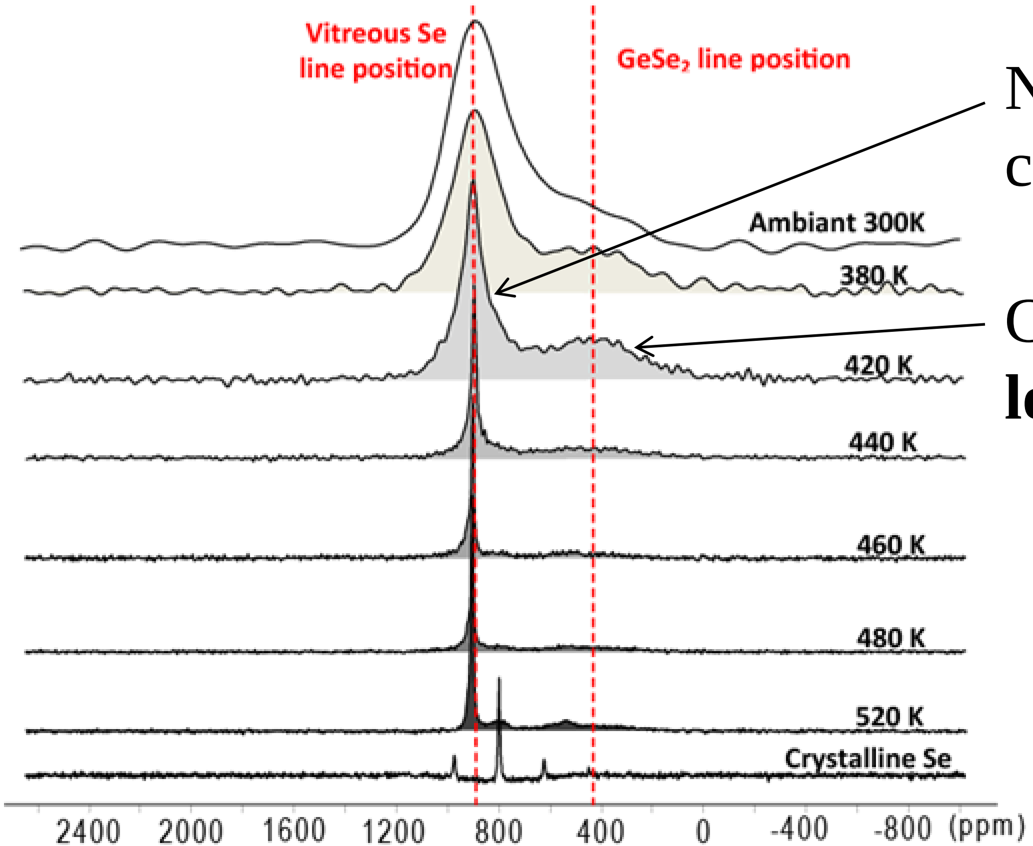
Significant amount of edge sharing $GeSe_4$ tetrahedra even in Se-rich glass

$GeSe_4$ tetrahedra tend to cluster in the glass.



Sen et al. JPC b **115, 4307 (2011)**

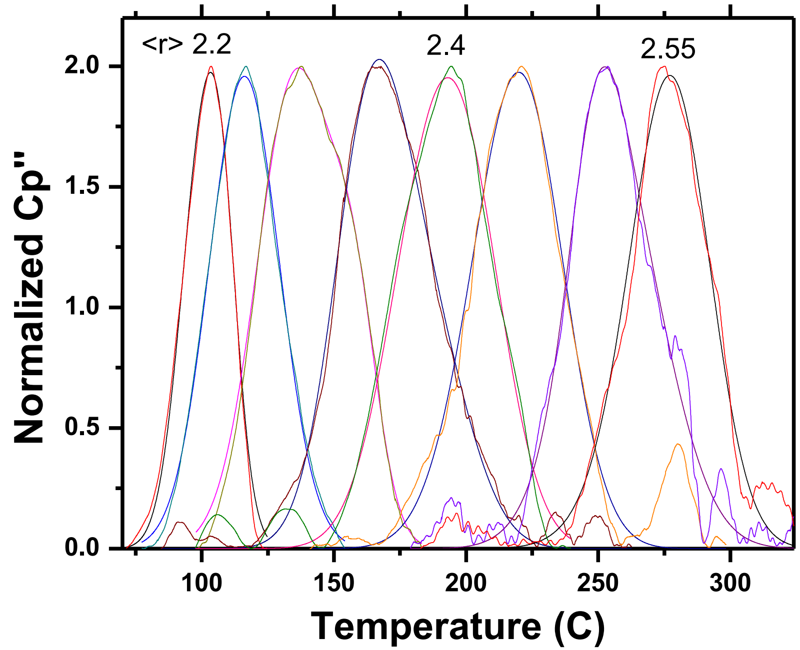
High T NMR of $GeSe_9$

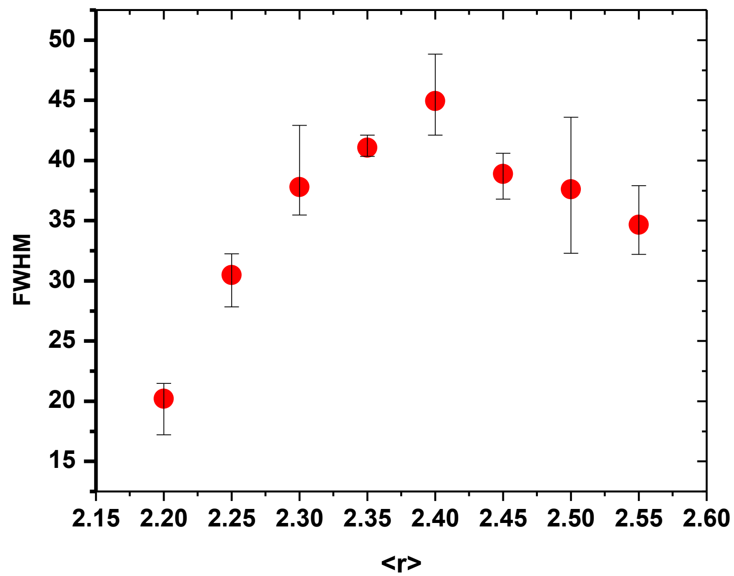


Net sharpening of the Se chain line: **mobile phase**.

$GeSe_{4/2}$ line stays broad: **low mobility**.

4- Structural origin of Fragility in the Ge-Se system: Heterogeneity

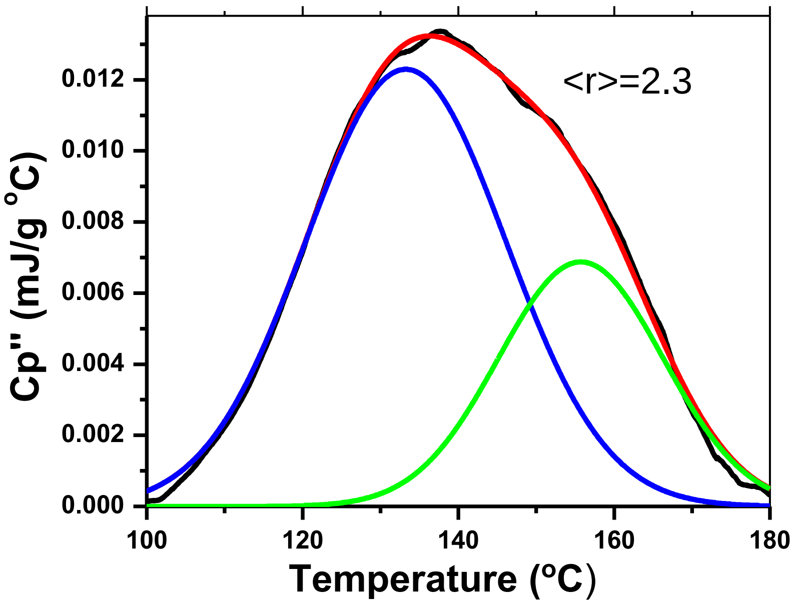


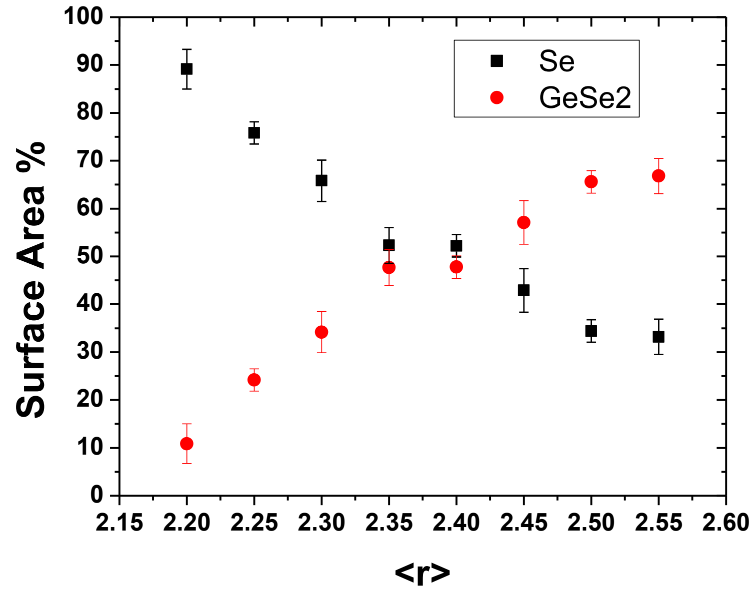


FWHM of the Cp” peak as a function of composition (averaged over all measured modulation frequencies ω)

- The dynamics of structural domains in Ge-Se glasses can be probed by heat capacity spectroscopy.
- The Cp” peak FWHM then shows a clear maximum at <r> = 2.4.

4- Structural origin of Fragility in the Ge-Se system: Heterogeneity

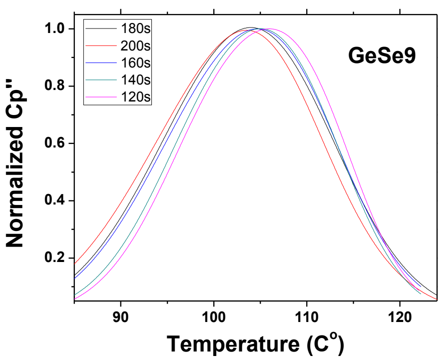


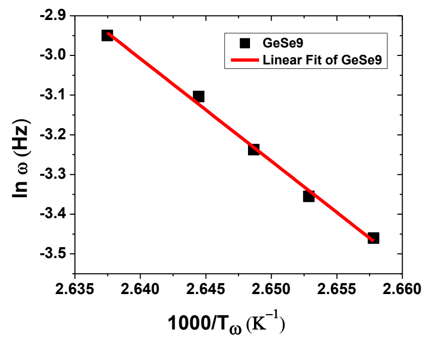


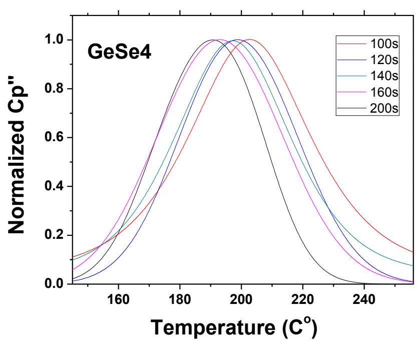
•Ge-Se glass near <r>=2.4 can not be fitted with a single Gaussian.
• Two structural units gain mobility at different temperatures

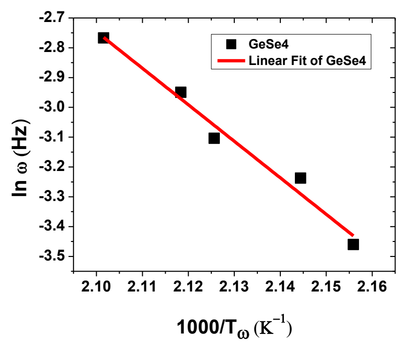
• Surface area of fast relaxing domain (Se chain) and slow relaxing domain ($GeSe_{4/2}$ tetrahedra) crosses over at <r> = 2.4.

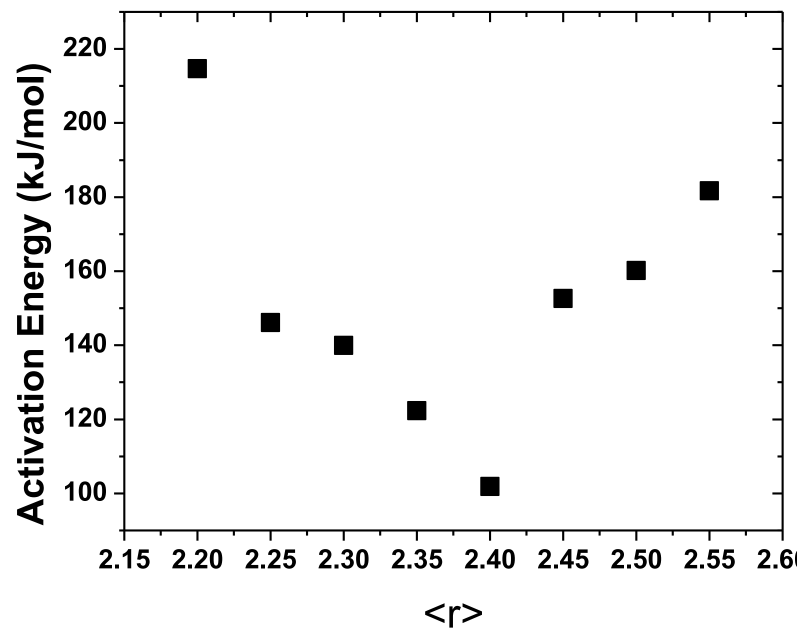
4- Structural origin of Fragility in the Ge-Se system: Heterogeneity







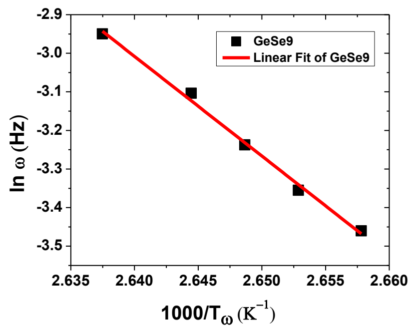


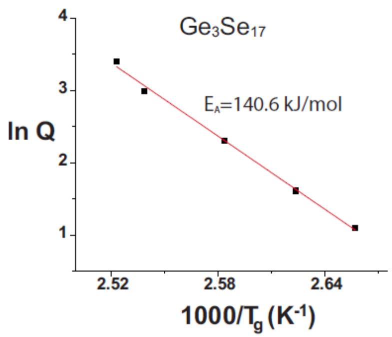


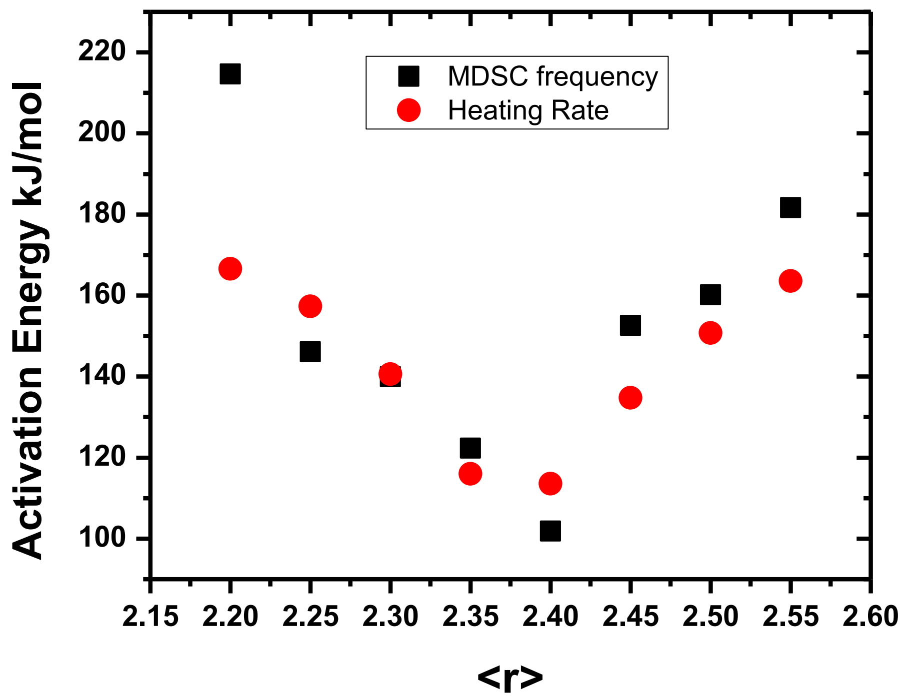
Cp” peaks shift to high T with higher frequencies ω : Derive activation energy E_a

Activation energy E_a shows sharp minimum at <r>=2.4 : Strong glasses gain structural degrees of freedom over wider temperature range.

4- Structural origin of Fragility in the Ge-Se system: Heterogeneity

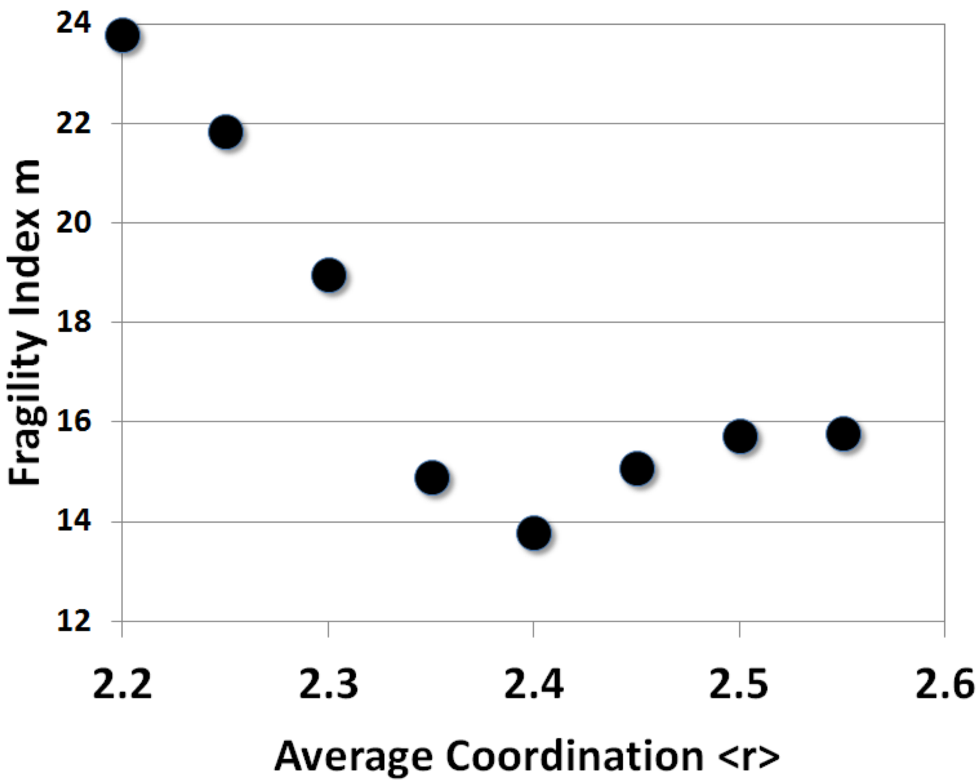






- Activation energy obtain by MDSC or conventional cool rate method shows the same sharp minimum in fragility at <r>=2.4
- There is again no evidence for an Intermediate Phase

4- Structural origin of Fragility in the Ge-Se system: Heterogeneity



$$m = \frac{Ea}{RTg \ln 10}$$

The minimum in fragility at <*r*>=2.4 is consistent with rigidity percolation threshold value but originate from maximum in structural heterogeneity due to highest ratio of Se-chains and $GeSe_4$ tetrahedra

Fragility is controlled by structural heterogeneity in Ge-Se glasses

CONCLUSIONS

Fragility shows no trend with <*r*> in Ge-As-Se but instead is controlled by deviation from stoichiometry.

Fragility does not follow predictions from rigidity percolation in As-Se but instead correlates with structural dimensionality.

Fragility shows a minimum at <*r*>=2.4 which correlates to maximum in structural heterogeneity aassociated with highest ratio of Se-chains and $GeSe_{4/2}$ tetrahedra.

Structural rather than topological factors appear to control the Fragility of chalcogenide glasses.

This work was performed through the **International Associated Lab for Materials and Optics** (LIA-MATEO) as part of a bi-national collaboration between France (University of Rennes) and the USA (University of Arizona).

We acknowledge financial support from CNRS and PUF.

CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

puf PARTNER UNIVERSITY FUND a program of FACE