The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

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SMR/1845-11

Conference on Structure and Dynamics in Soft Matter and Biomolecules: From Single Molecules to Ensembles

4 - 8 June 2007

Network glasses, terminal atoms intermediate phases

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Network glasses, terminal atoms intermediate phases.*

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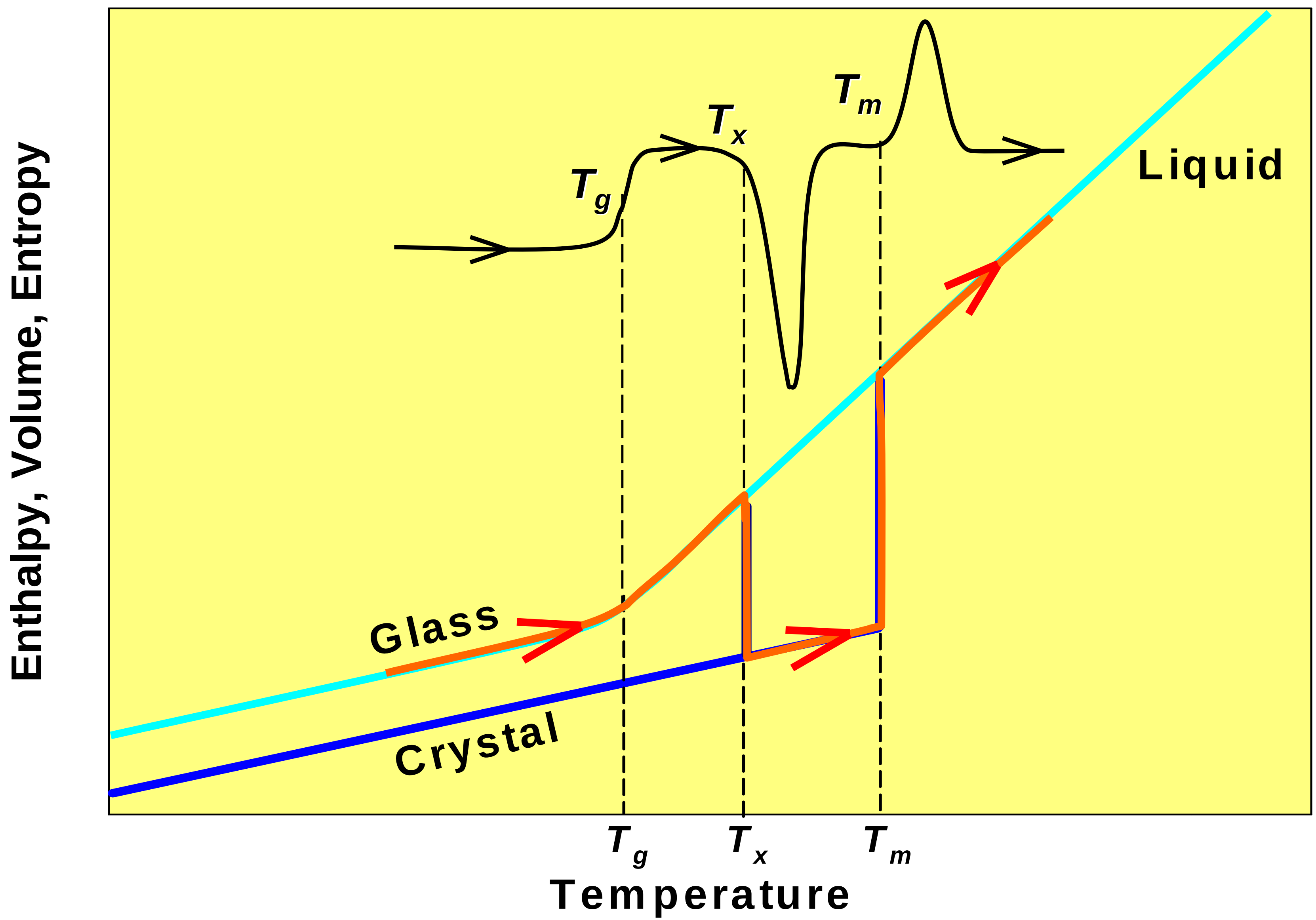
* Supported by NSF grant DMR-04-56472

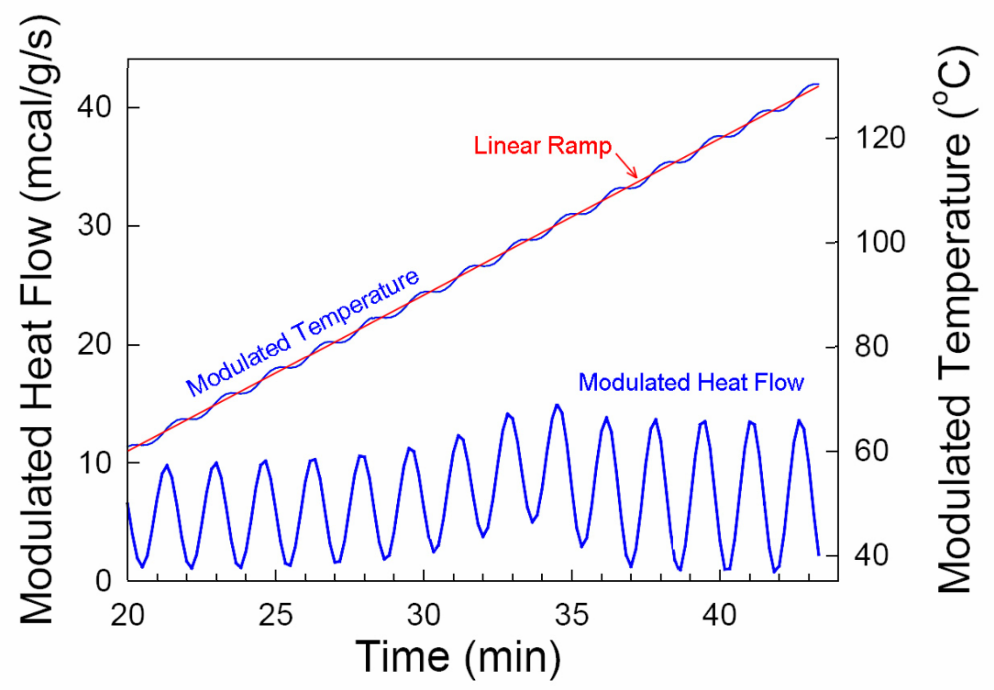


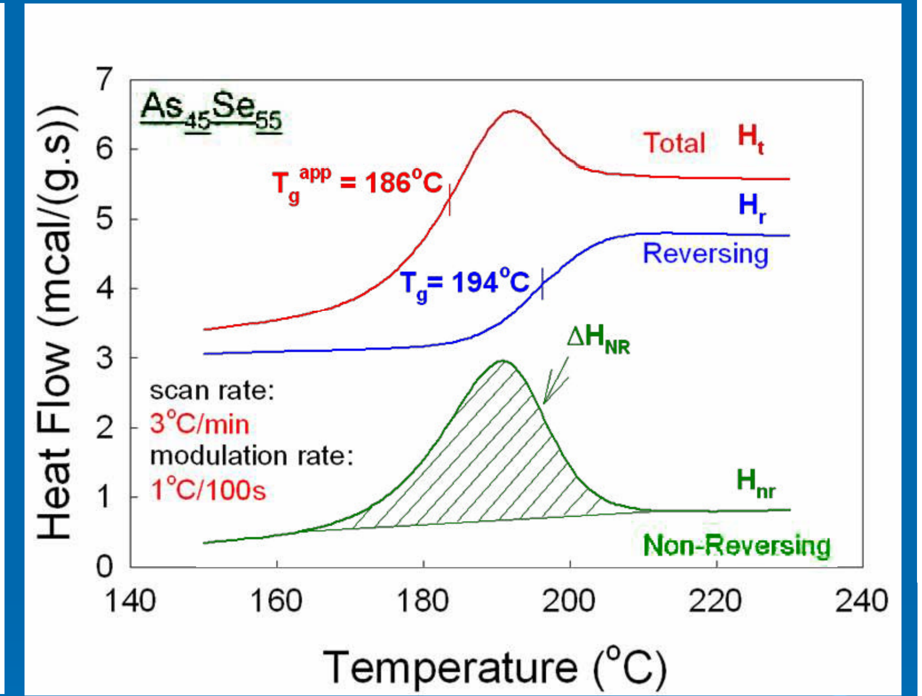
T_g
T_x
T_m
Liquid
Glass
Crystal
Enthalpy, Volume, Entropy
T_g
T_x
T_m
Temperature

Nature of glass transition

- Glass transitions are usually hysteretic.
- But in select compositional windows, T_gs become non-hysteretic.
- These windows occur when network connectivity or mean *r* resides in the $2.30 < r < 2.50$ range typically.

Modulated Differential Scanning Calorimetry- a probe of the nature of glass transitions





D.G. Georgiev, P.Boolchand, M.Micoulaut Phys. Rev B 62, R9228 (2000)

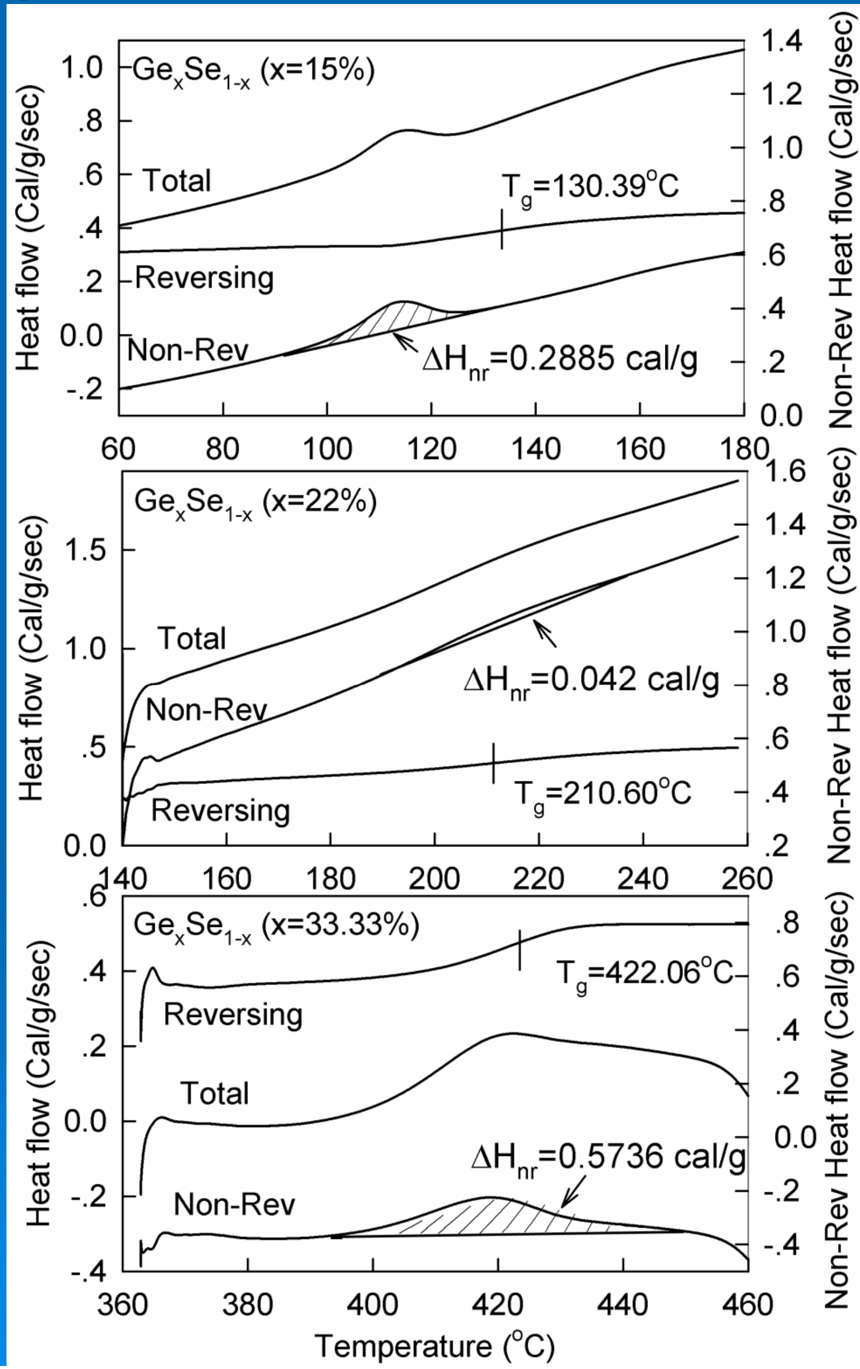
MDSC permits probing glass transitions more accurately than traditional DSC

- far more sensitive (AC versus DC method)
- separates reversing (vibrational or thermodynamics) from non-reversing (Configurational or structural arrest, aging, and history related) events.
- Obtain scan-rate independent T_gs and ΔC_p from reversing heat flow.
- Feedback from MDSC has been crucial to optimize sample synthesis

Relevant Part of the Periodic Table for Chalcogen based glasses

	IV	V	VI	VII
	Si	P	S	Cl
	Ge	As	Se	Br
	Sn	Sb	Te	I
CN	4	3	2	1
	s^2p^2	s^2p^3	s^2p^4	s^2p^5

Three types of glass transitions observed in the Ge-Se binary

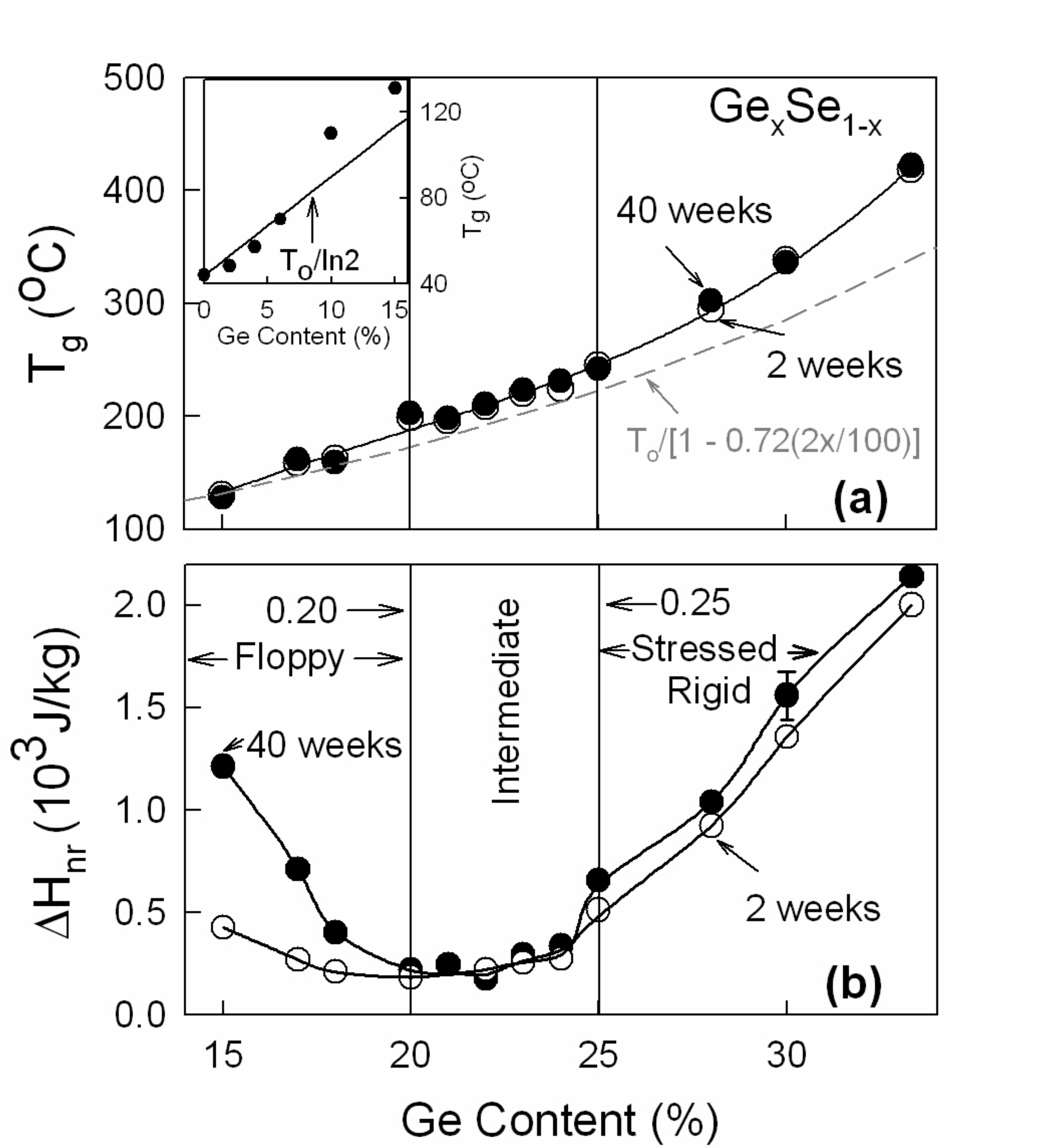


$\langle r \rangle = 2 (1 + x)$

Type 1: ΔH_{nr} finite, narrow, hysteretic and ages; $\langle r \rangle = 2.30$

Type 2: ΔH_{nr} minuscule ~ 0 , does not age; $\langle r \rangle = 2.44$

Type 3: ΔH_{nr} is broad, hysteretic and ages; $\langle r \rangle = 2.67$



Ge_xSe_{1-x}
T_g (°C)
40 weeks
2 weeks
$T_o/[1 - 0.72(2x/100)]$
(a)
T_o/ln2
Ge Content (%)
T_g (°C)
0.20
Floppy
Intermediate
0.25
Stressed Rigid
40 weeks
2 weeks
(b)
ΔH_{nr} (10^3 J/kg)
Ge Content (%)

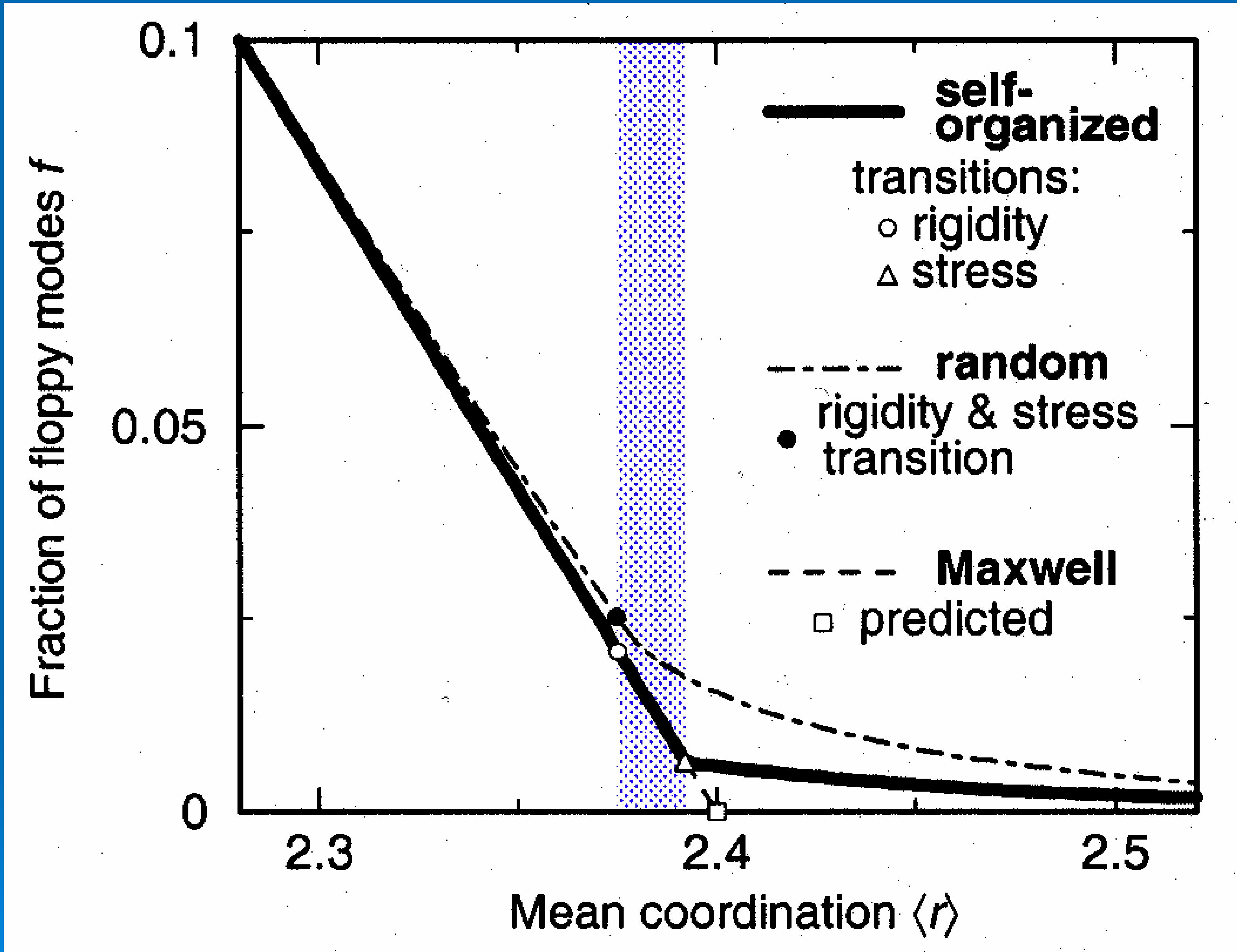
The 3 types of glass transitions are signatures of 3 distinct elastic phases.

- Narrow T_gs with symmetric ΔH_{nr} profiles that age: Flexible
- Reversing T_g profiles ($\Delta H_{nr} \sim 0$) that do not age : Intermediate
- Wide Tgs with asymmetric ΔH_{nr} profiles that age : Stressed-Rigid

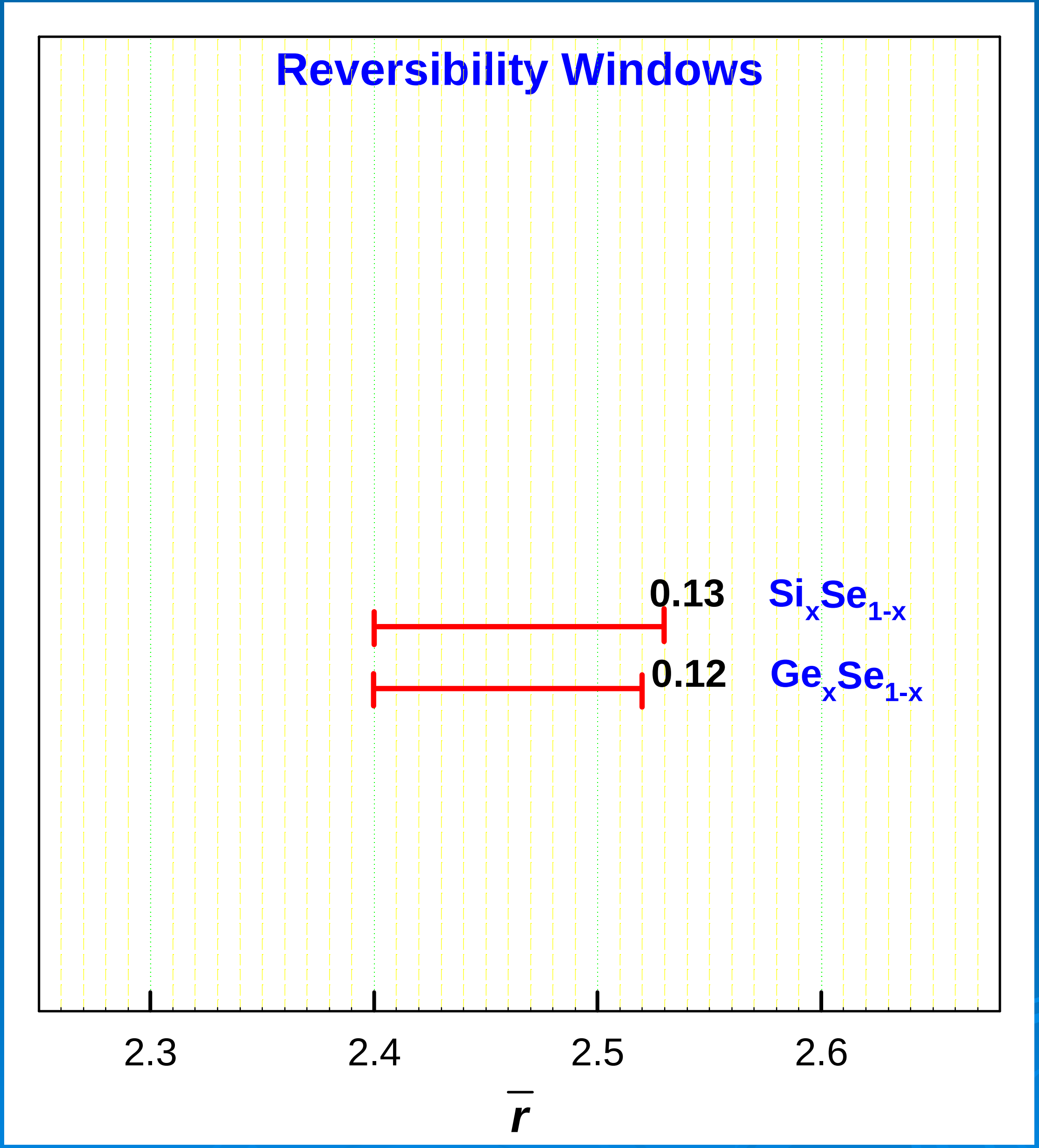
Reversibility windows are centered around r = 2.4

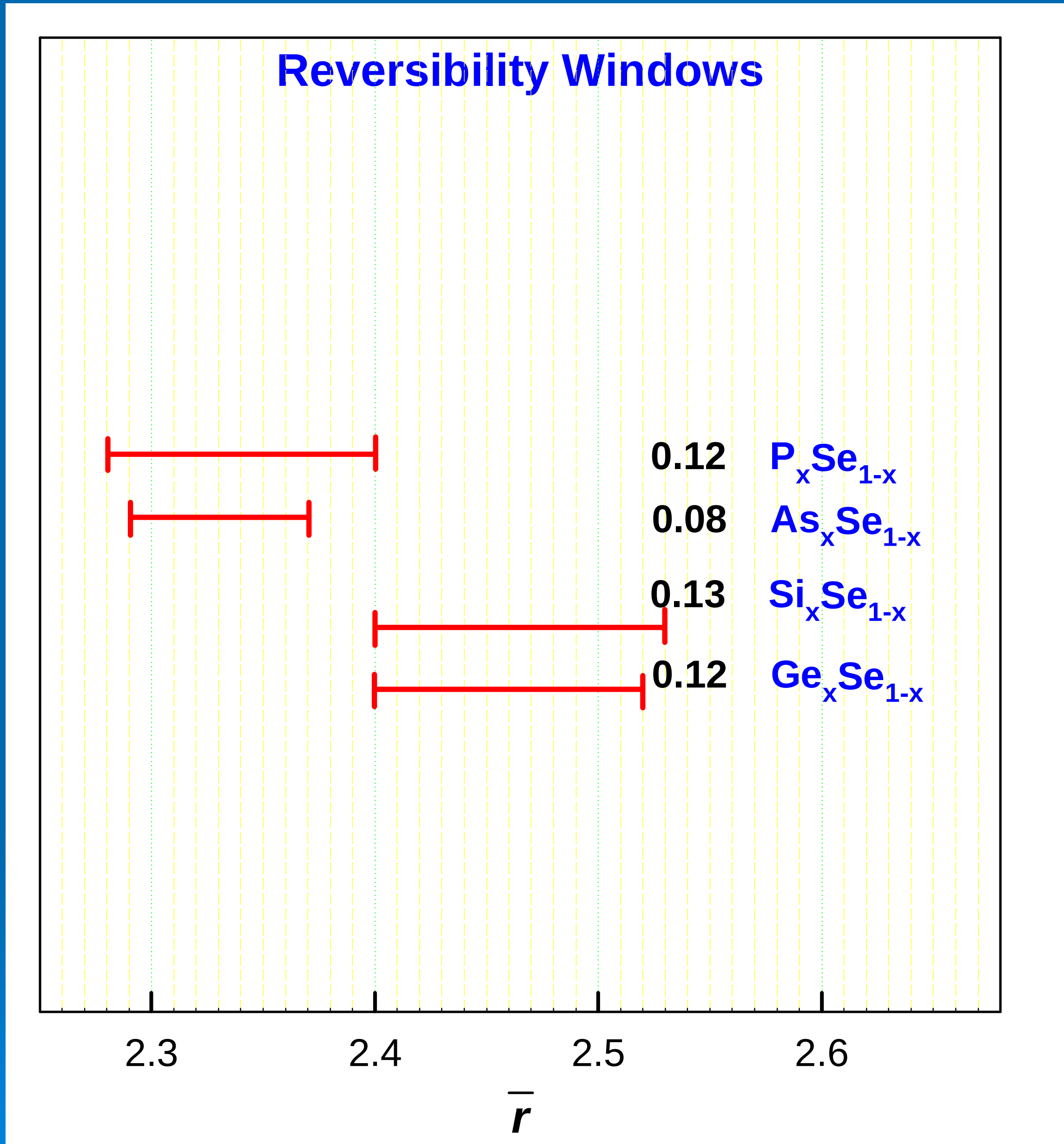
- This is not a coincidence. Early studies* showed this magic number to be signature of the onset of stressed-rigidity in *random* networks.
- More recent work shows that networks usually self-organize, i.e., display two transitions, a rigidity- and a stress-transition that define an intermediate phase.

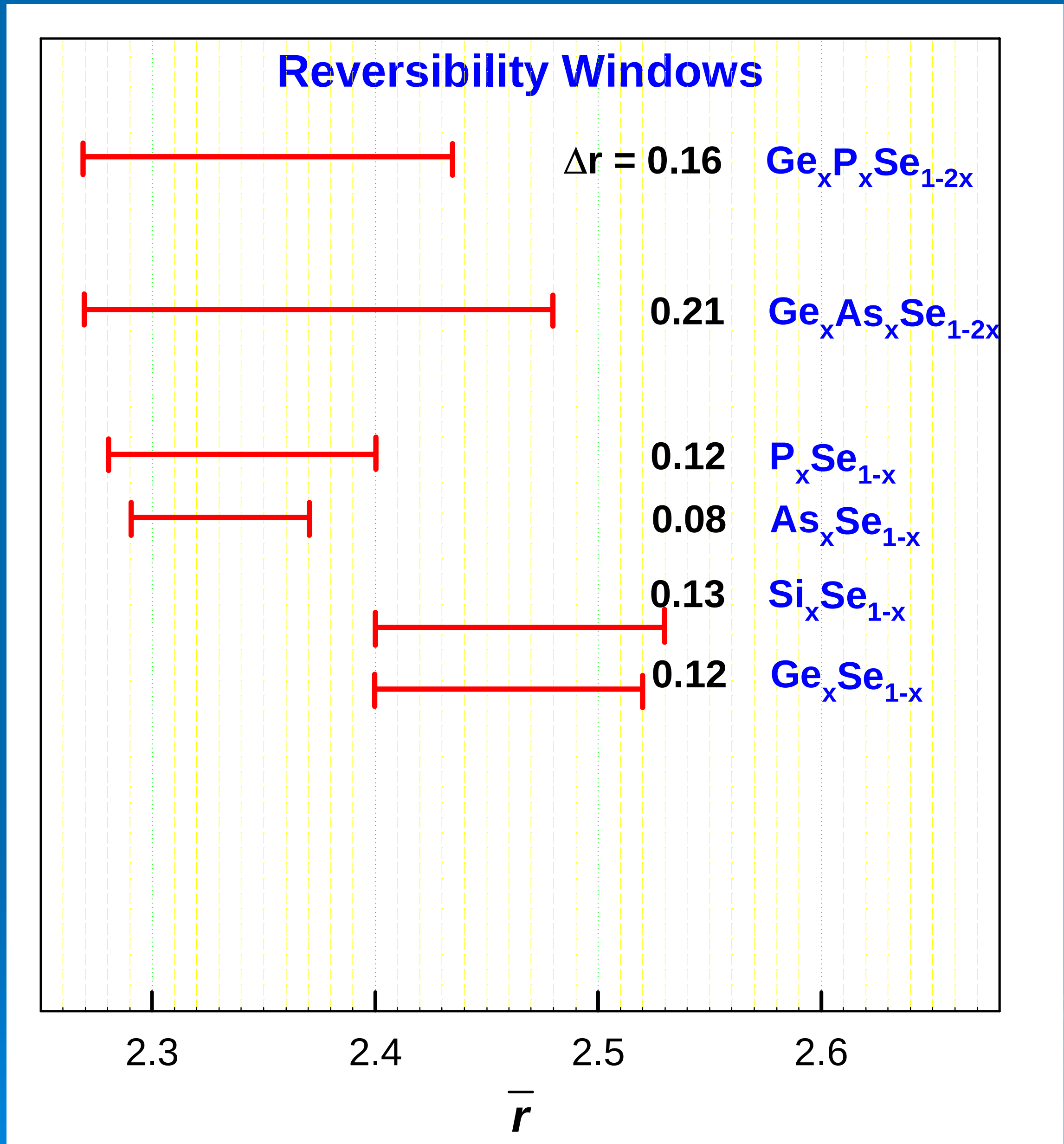
*J.C.Phillips JNCS 34,153 (1979); M.F.Thorpe JNCS 57,355 (1983)



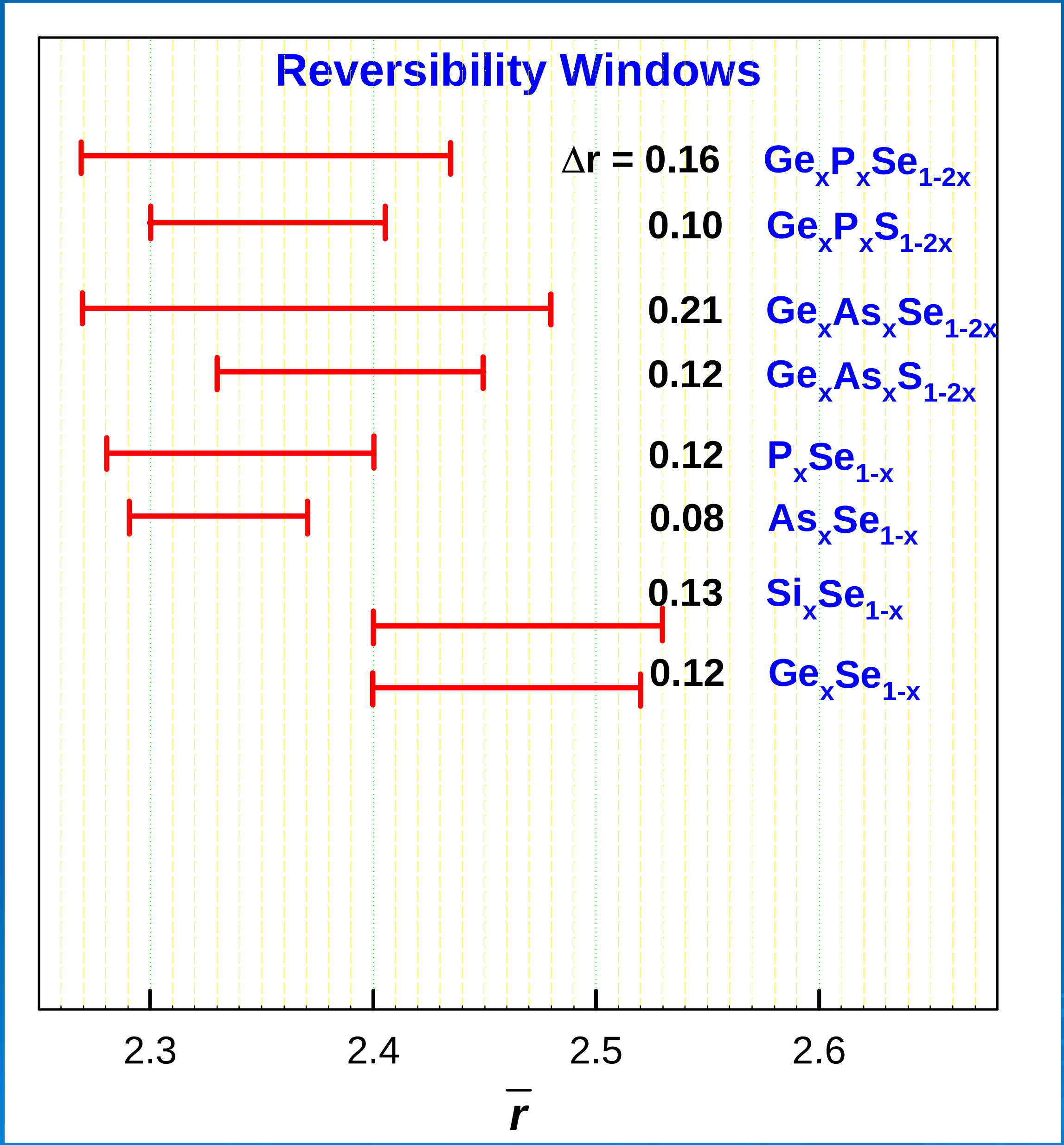
M.F. Thorpe et al. J.Non Cryst. Solids 266-269,859 (2000).


Reversibility Windows
0.13
Si_xSe_{1-x}
0.12
Ge_xSe_{1-x}
2.3
2.4
2.5
2.6
$\bar{r}$

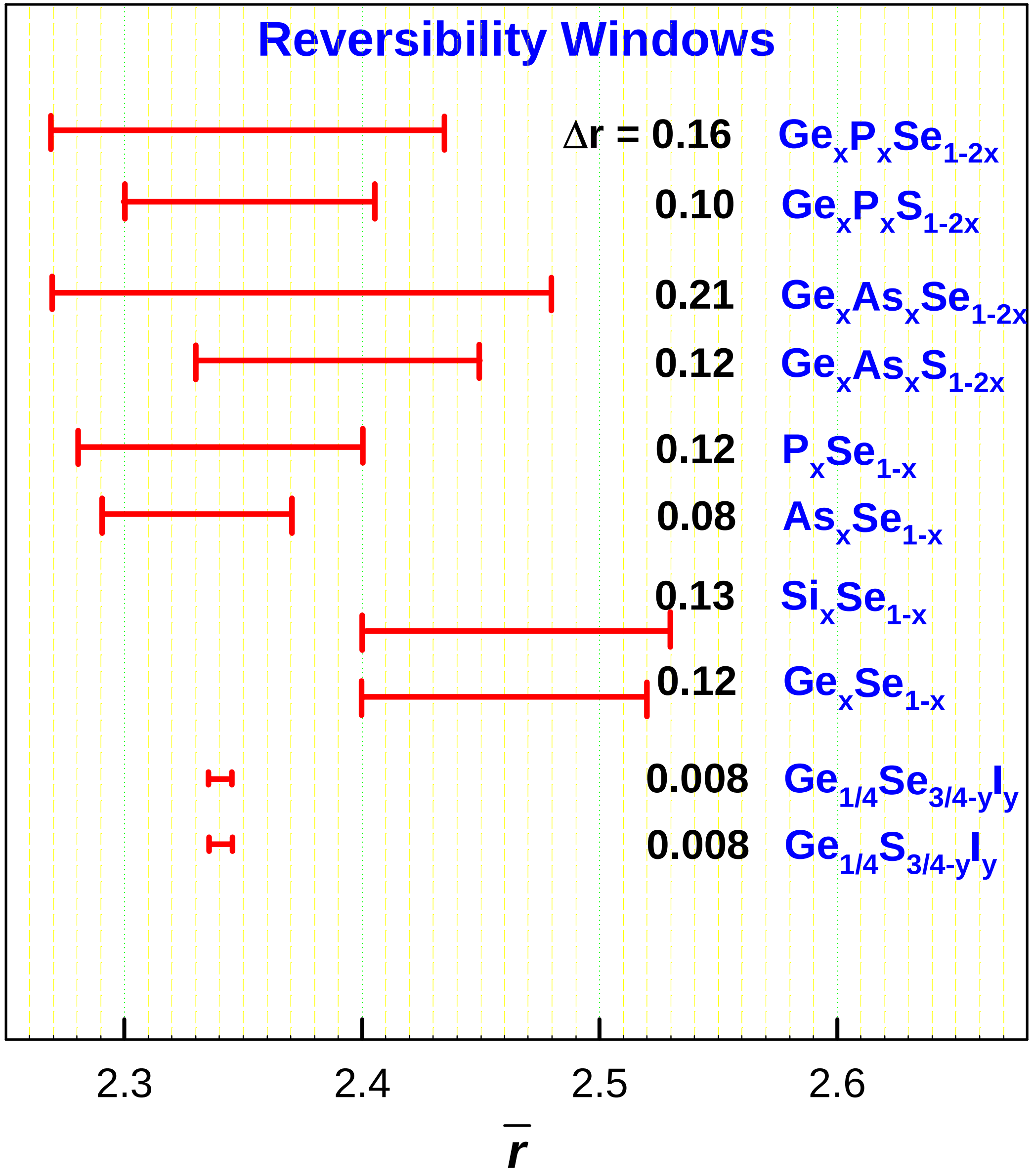

Reversibility Windows
0.12 P_xSe_{1-x}
0.08 As_xSe_{1-x}
0.13 Si_xSe_{1-x}
0.12 Ge_xSe_{1-x}
2.3
2.4
2.5
2.6
$\bar{r}$



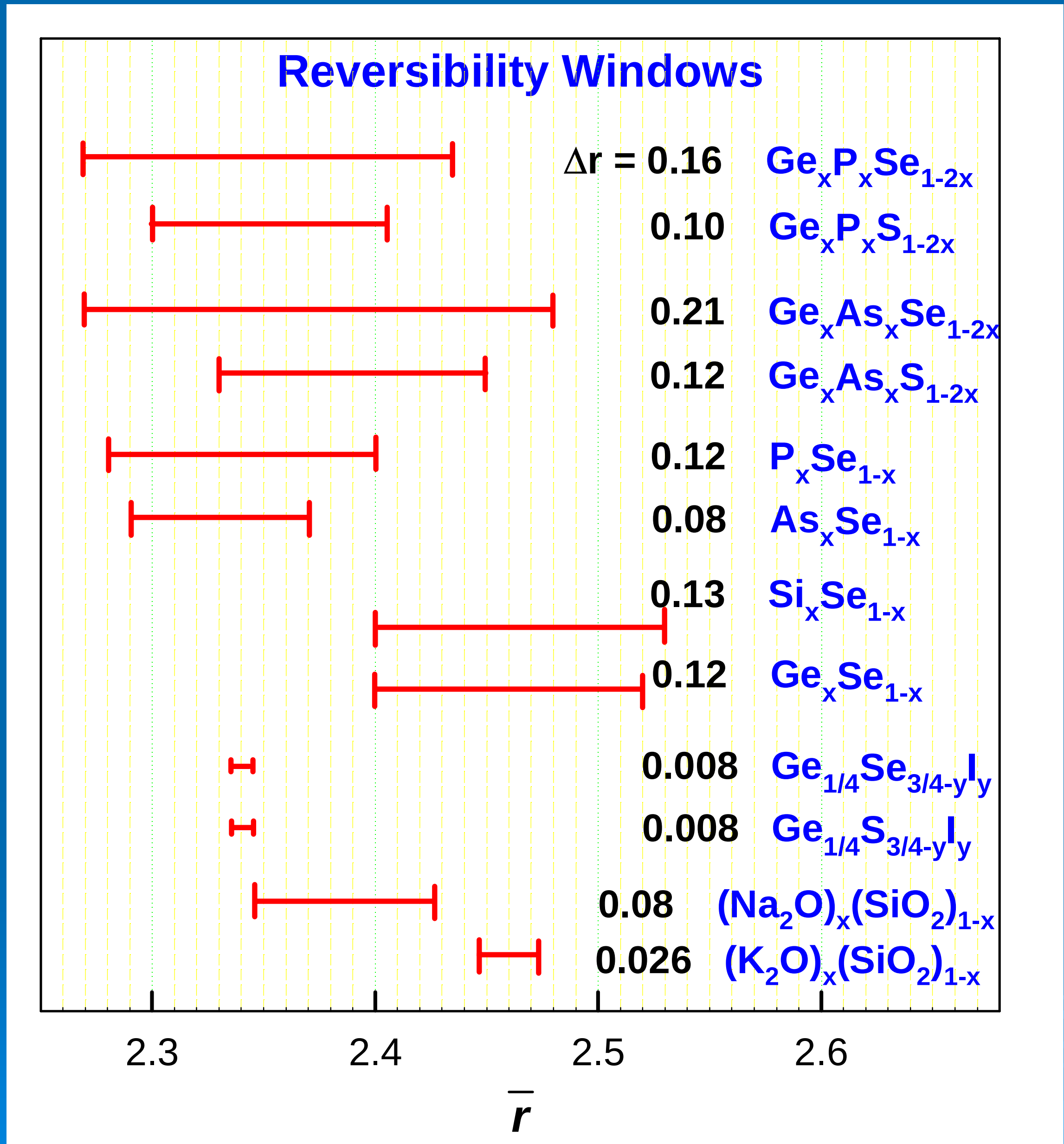
Reversibility Windows
Δr = 0.16
$Ge_xP_xSe_{1-2x}$
0.21
$Ge_xAs_xSe_{1-2x}$
0.12
P_xSe_{1-x}
0.08
As_xSe_{1-x}
0.13
Si_xSe_{1-x}
0.12
Ge_xSe_{1-x}
2.3
2.4
2.5
2.6
$\bar{r}$



Reversibility Windows
Δr = 0.16 Ge$_x$P$_x$Se$_{1-2x}$
0.10 Ge$_x$P$_x$S$_{1-2x}$
0.21 Ge$_x$As$_x$Se$_{1-2x}$
0.12 Ge$_x$As$_x$S$_{1-2x}$
0.12 P$_x$Se$_{1-x}$
0.08 As$_x$Se$_{1-x}$
0.13 Si$_x$Se$_{1-x}$
0.12 Ge$_x$Se$_{1-x}$
2.3
2.4
2.5
2.6
$\bar{r}$



Reversibility Windows
Δr = 0.16 $Ge_xP_xSe_{1-2x}$
0.10 $Ge_xP_xS_{1-2x}$
0.21 $Ge_xAs_xSe_{1-2x}$
0.12 $Ge_xAs_xS_{1-2x}$
0.12 P_xSe_{1-x}
0.08 As_xSe_{1-x}
0.13 Si_xSe_{1-x}
0.12 Ge_xSe_{1-x}
0.008 $Ge_{1/4}Se_{3/4-y}I_y$
0.008 $Ge_{1/4}S_{3/4-y}I_y$
2.3
2.4
2.5
2.6
$\bar{r}$



Reversibility Windows
Δr = 0.16 Ge$_x$P$_x$Se$_{1-2x}$
0.10 Ge$_x$P$_x$S$_{1-2x}$
0.21 Ge$_x$As$_x$Se$_{1-2x}$
0.12 Ge$_x$As$_x$S$_{1-2x}$
0.12 P$_x$Se$_{1-x}$
0.08 As$_x$Se$_{1-x}$
0.13 Si$_x$Se$_{1-x}$
0.12 Ge$_x$Se$_{1-x}$
0.008 Ge$_{1/4}$Se$_{3/4-y}$I$_y$
0.008 Ge$_{1/4}$S$_{3/4-y}$I$_y$
0.08 (Na$_2$O)$_x$(SiO$_2$)$_{1-x}$
0.026 (K$_2$O)$_x$(SiO$_2$)$_{1-x}$
2.3
2.4
2.5
2.6
$\bar{r}$

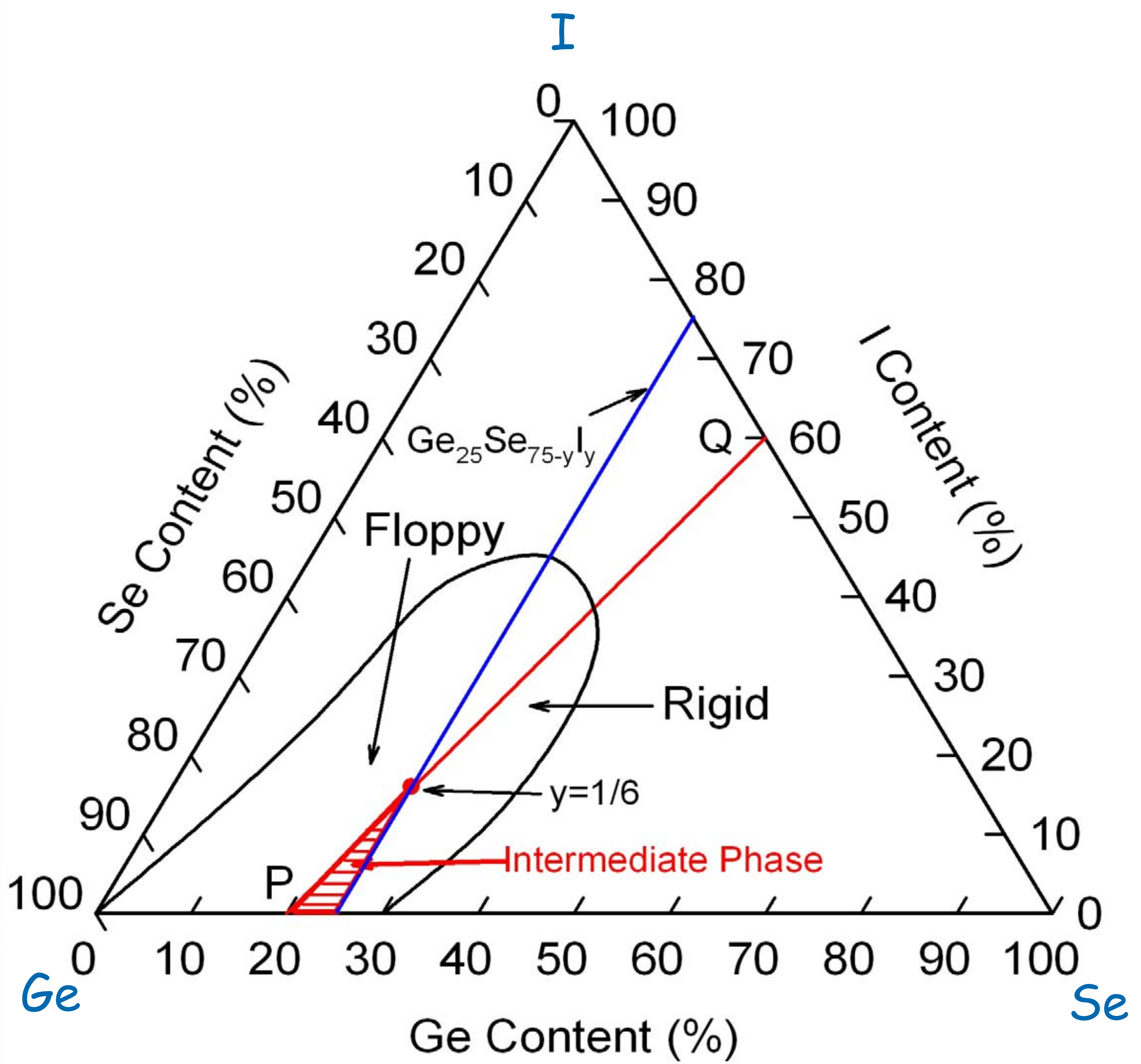
Collapse of Reversibility windows in networks with terminal atoms*.

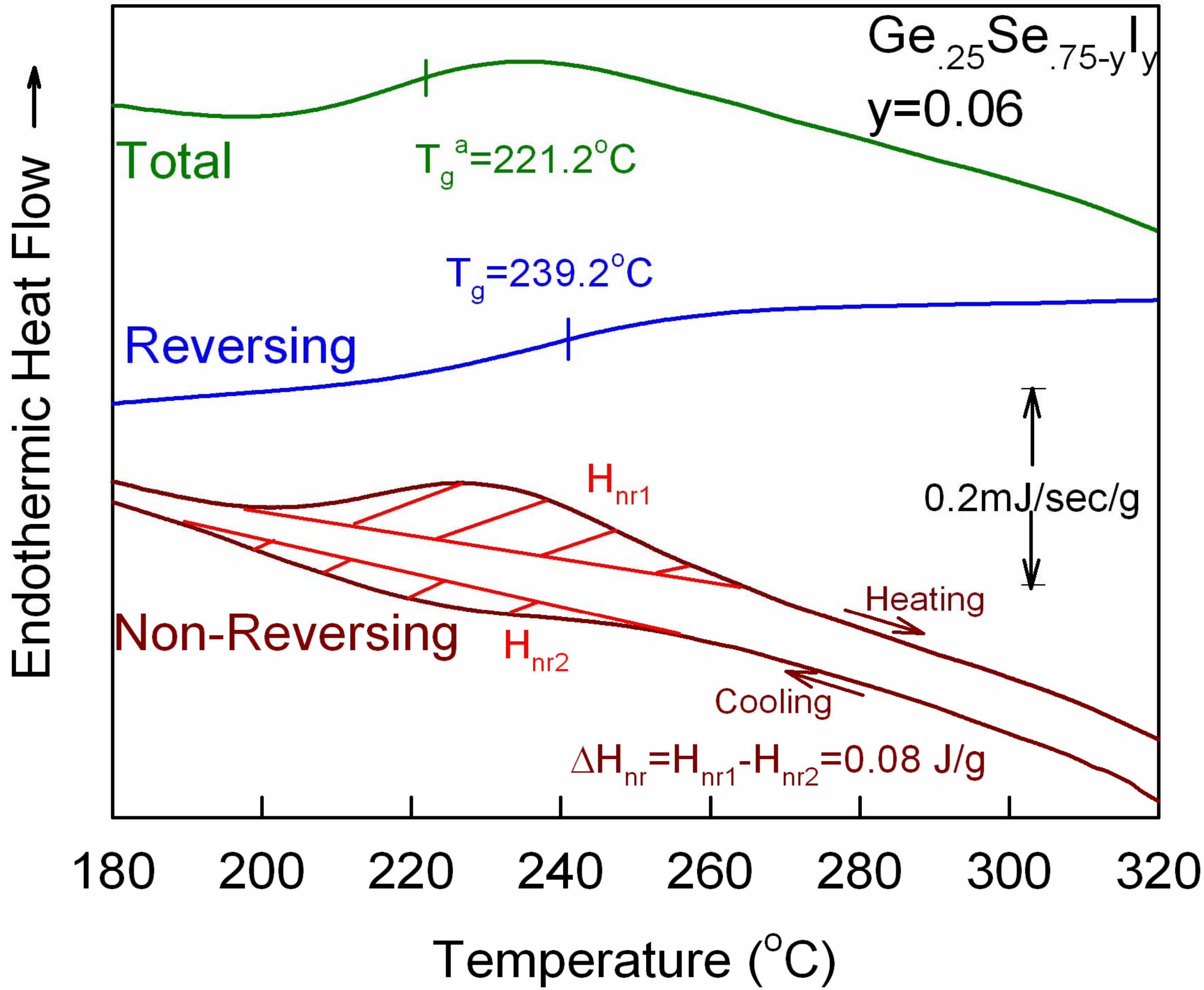
- What is the experimental evidence?

- Why do windows collapse ?

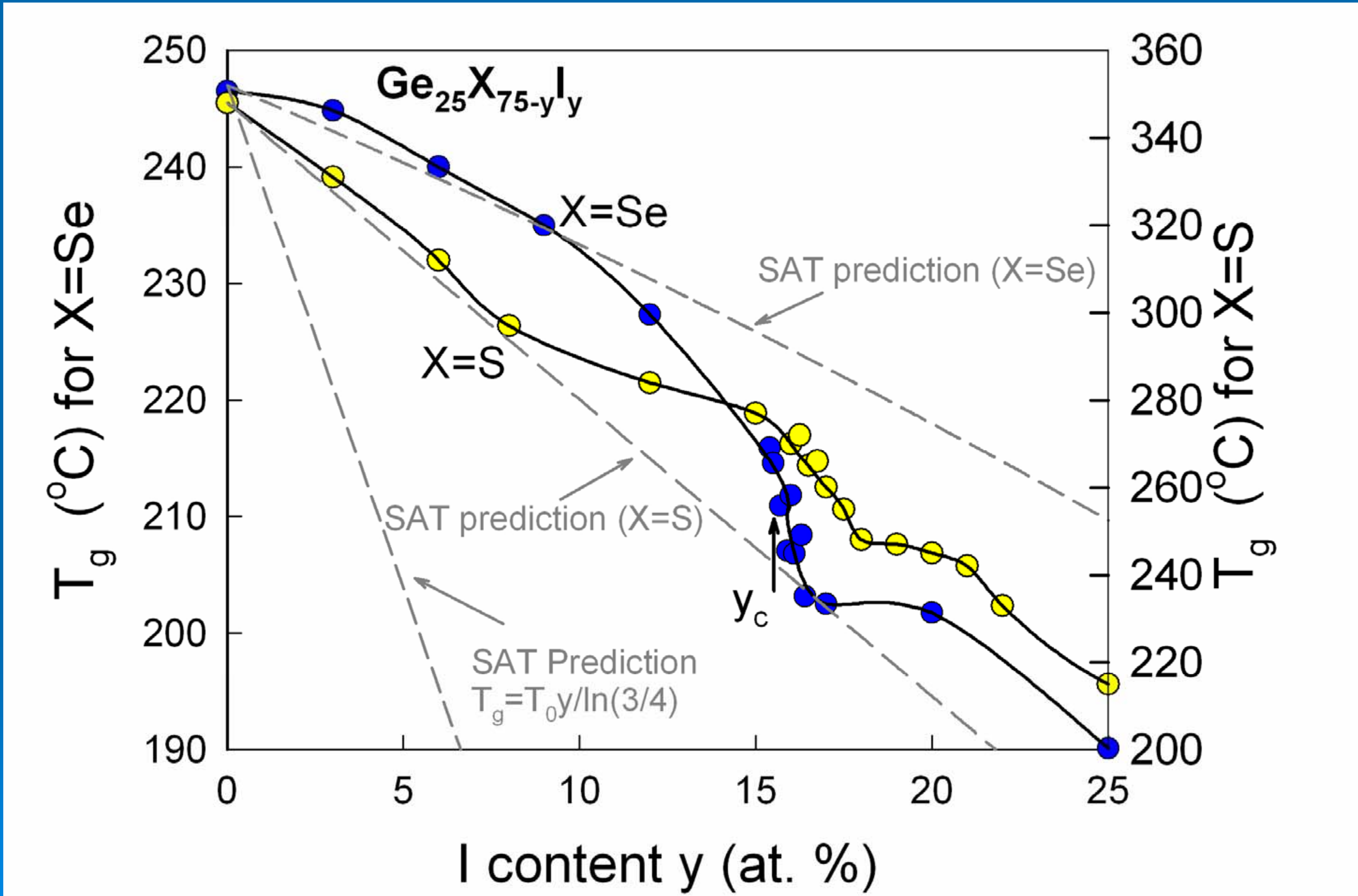
- We shall see that even in these narrow windows, atom size mismatch plays an important role as networks self-organize to minimize stress.

*Fei Wang ,PB, K.A.Jackson, M.Micoulaut, J.Phys.:Condens. Matter 19, 226201(2007).

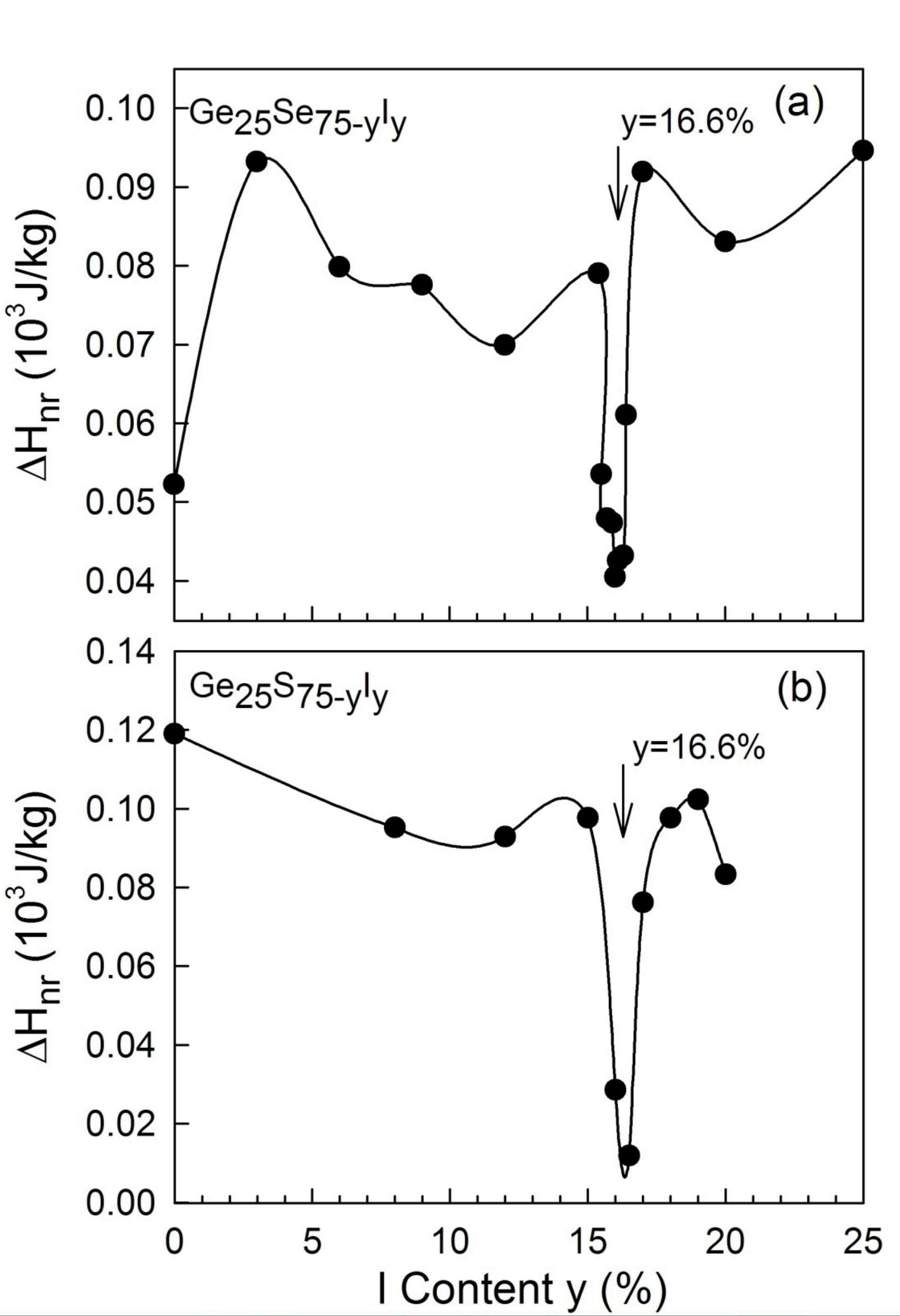

I
Ge
Se
Se Content (%)
I Content (%)
Ge Content (%)
$Ge_{25}Se_{75-y}I_y$
Floppy
Rigid
Q
P
y=1/6
Intermediate Phase
0
10
20
30
40
50
60
70
80
90
100



Ge.25Se.75-yIy
y=0.06
Total
Tga=221.2°C
Tg=239.2°C
Reversing
Hnr1
0.2mJ/sec/g
Heating
Non-Reversing
Hnr2
Cooling
ΔHnr=Hnr1-Hnr2=0.08 J/g
180
200
220
240
260
280
300
320
Temperature (°C)
Endothermic Heat Flow



$Ge_{25}X_{75-y}I_y$
X=Se
X=S
SAT prediction (X=Se)
SAT prediction (X=S)
SAT Prediction
$T_g=T_0y/\ln(3/4)$
y_c
T_g (°C) for X=Se
T_g (°C) for X=S
I content y (at. %)
250
240
230
220
210
200
190
360
340
320
300
280
260
240
220
200
0
5
10
15
20
25



Ge25Se75-yIy
(a)
y=16.6%
0.10
0.09
0.08
0.07
0.06
0.05
0.04
ΔHnr (10^3 J/kg)
Ge25S75-yIy
(b)
y=16.6%
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
ΔHnr (10^3 J/kg)
0
5
10
15
20
25
I Content y (%)

Networks with terminal atoms

Mean- field rigidity transition occurs when,

$$\boldsymbol{r} = 2.40 - 0.4(n_1/N)\ *$$

$Ge_{0.25}S_{0.75-y}I_y$ taking CN of Ge,S and I as 4,2 and 1,

$$r = 4x1/4 + 2(3/4-y) + 1(y) = 2.4- 0.4y$$

or $\quad y = 1/6$

* PB and MFT , Phys. Rev B 50, 10366 (1994).

- Mean-Field Rigidity Transition predictions do not distinguish between S or Se.

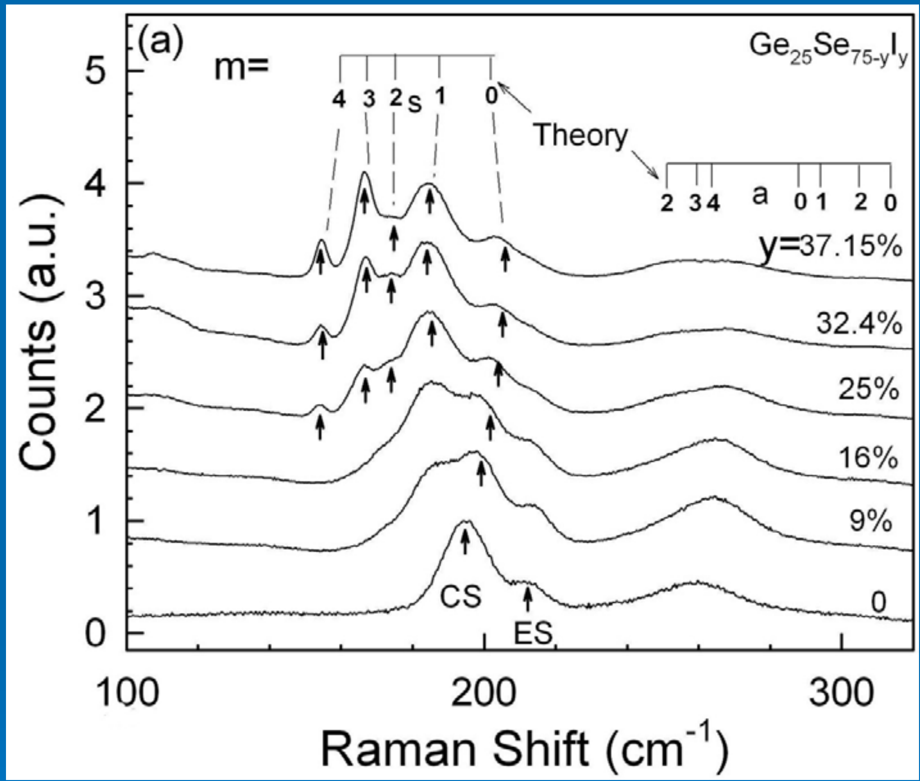
- Thermal results would appear to be consistent with mean-field results. But there is more!

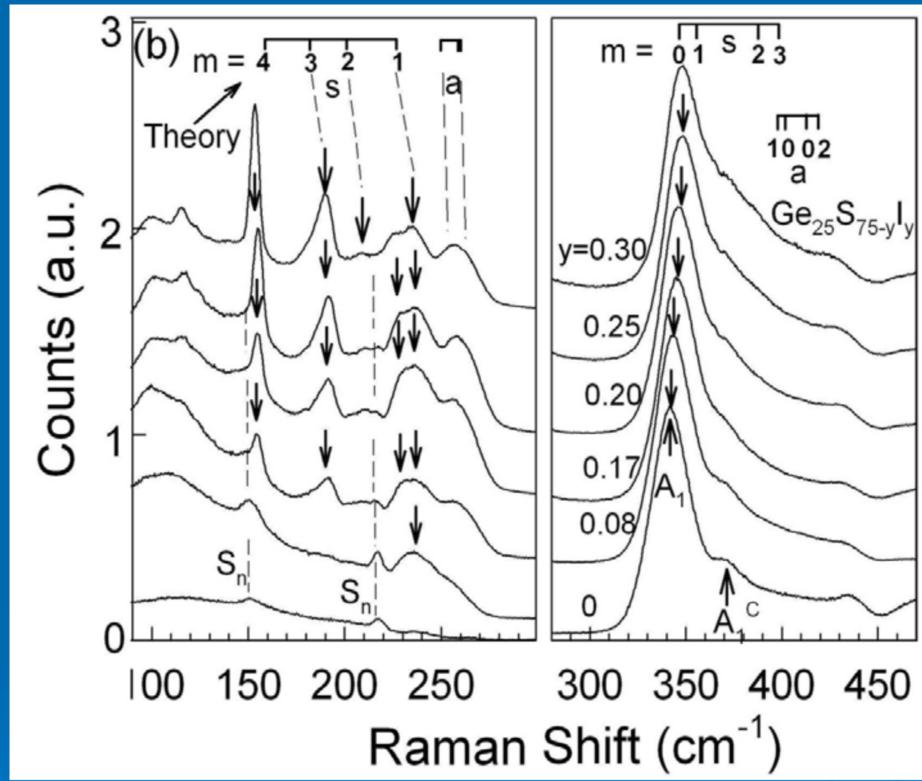
- Raman scattering provides more clues. Atom sizes play a role in relieving network stress as networks self-organize.

Raman Scattering

$Ge_{25}Se_{75-y}I_y$

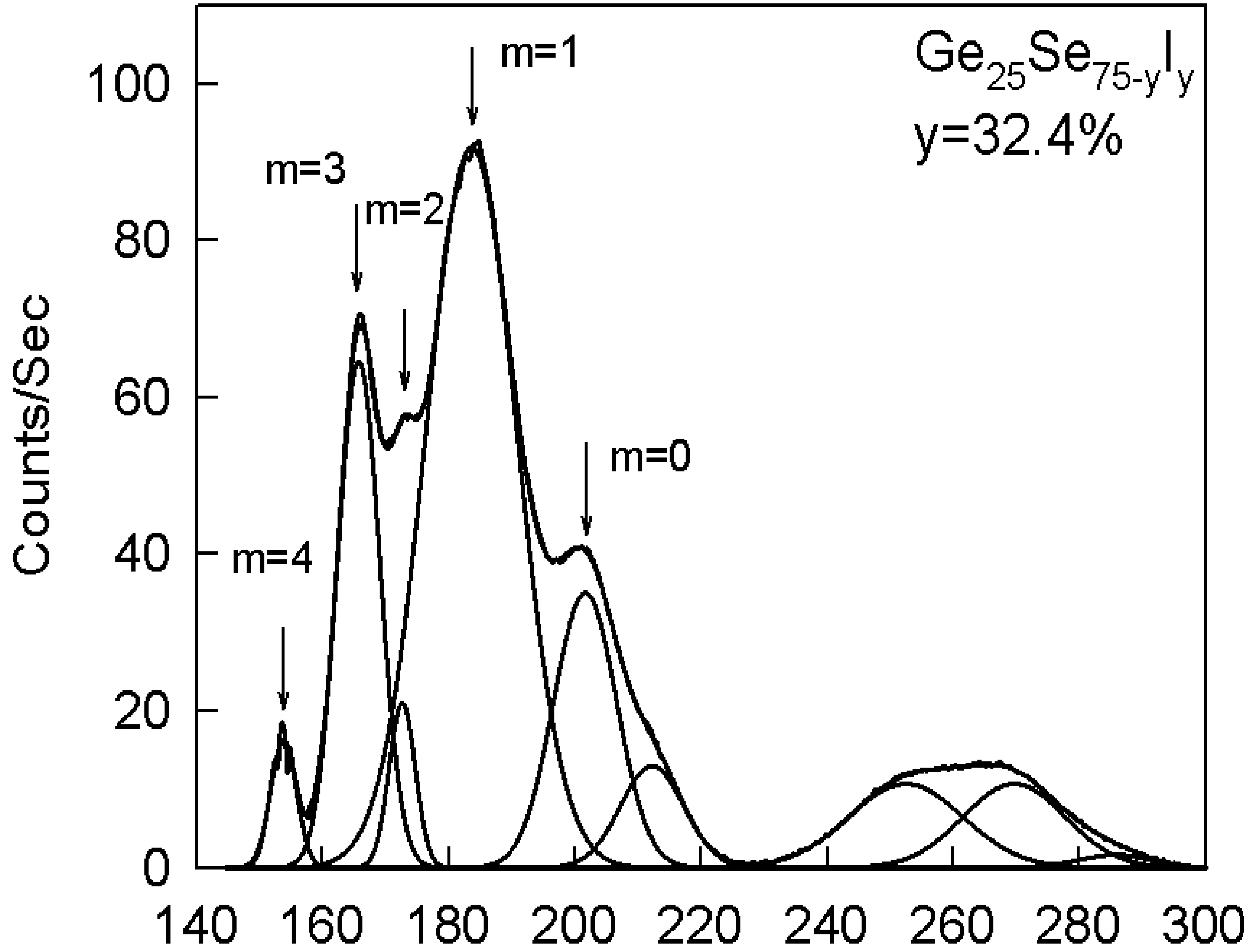
$Ge_{25}S_{75-y}I_y$



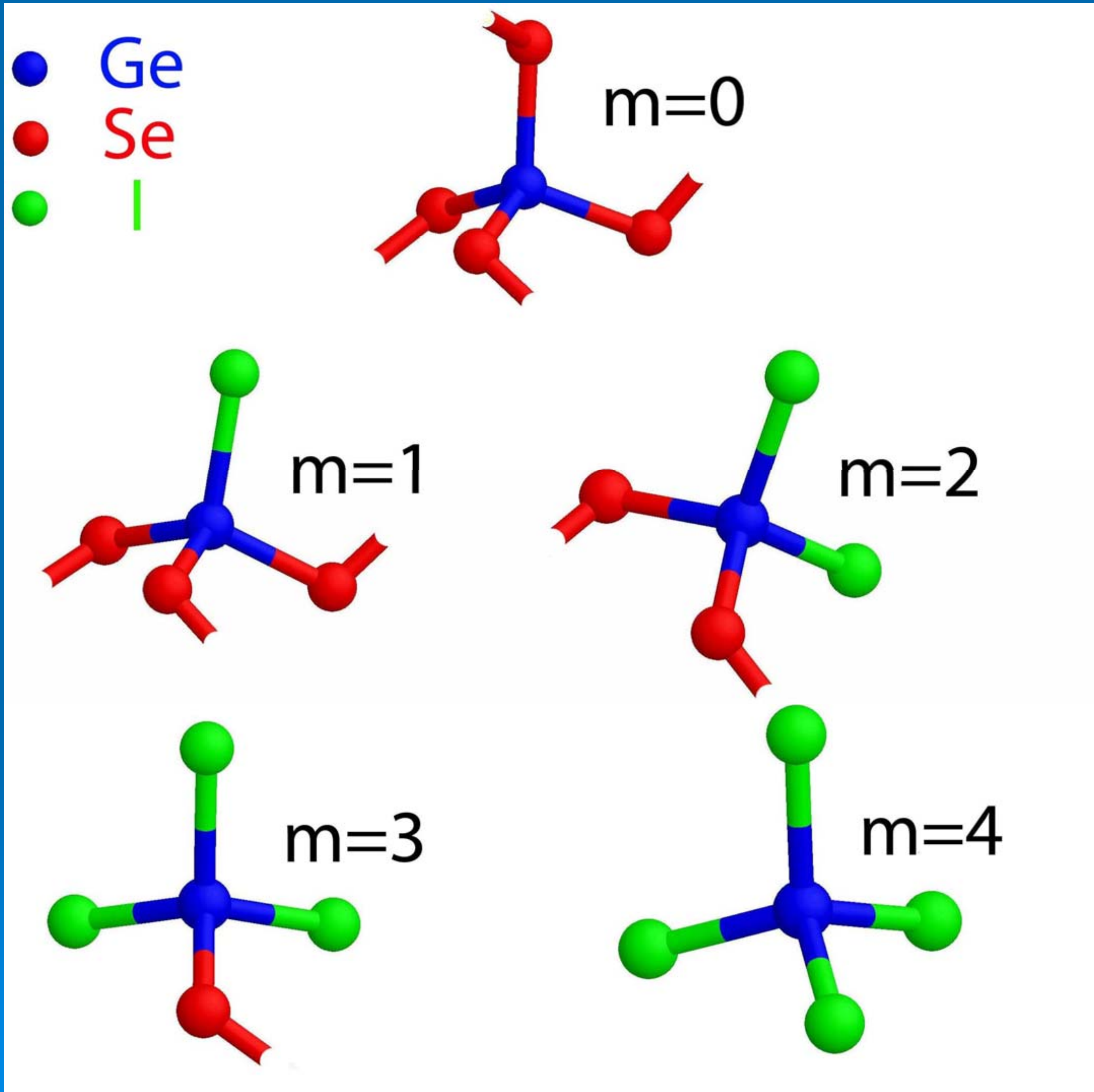


Y. Wang et al. PRL 87, 18, 5503 (2001).

F. Wang et al. J Phys. Condens. Matter 19, 226201 (2007).

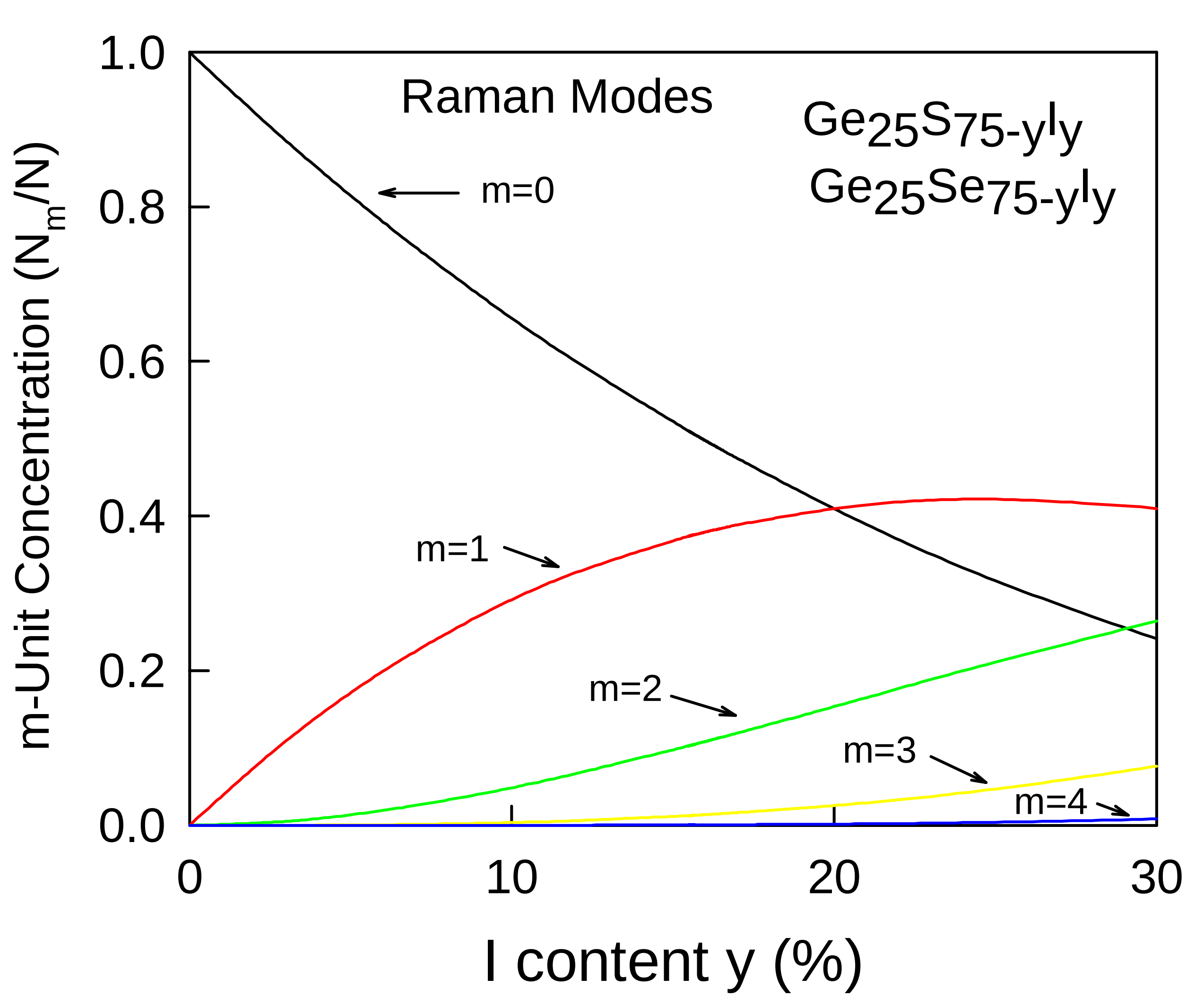


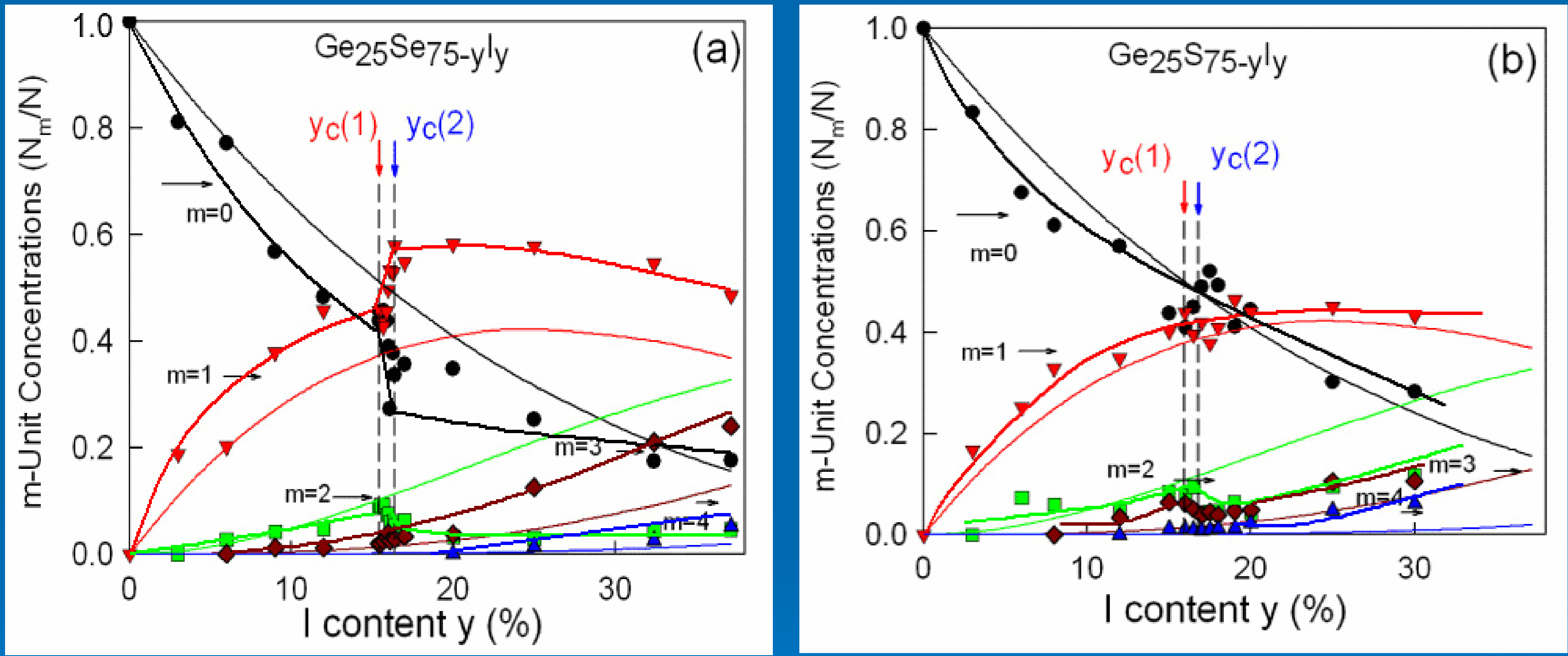
$Ge_{25}Se_{75-y}I_y$
y=32.4%
m=1
m=3
m=2
m=0
m=4
Counts/Sec
100
80
60
40
20
0
140
160
180
200
220
240
260
280
300


Ge
Se
I
m=0
m=1
m=2
m=3
m=4

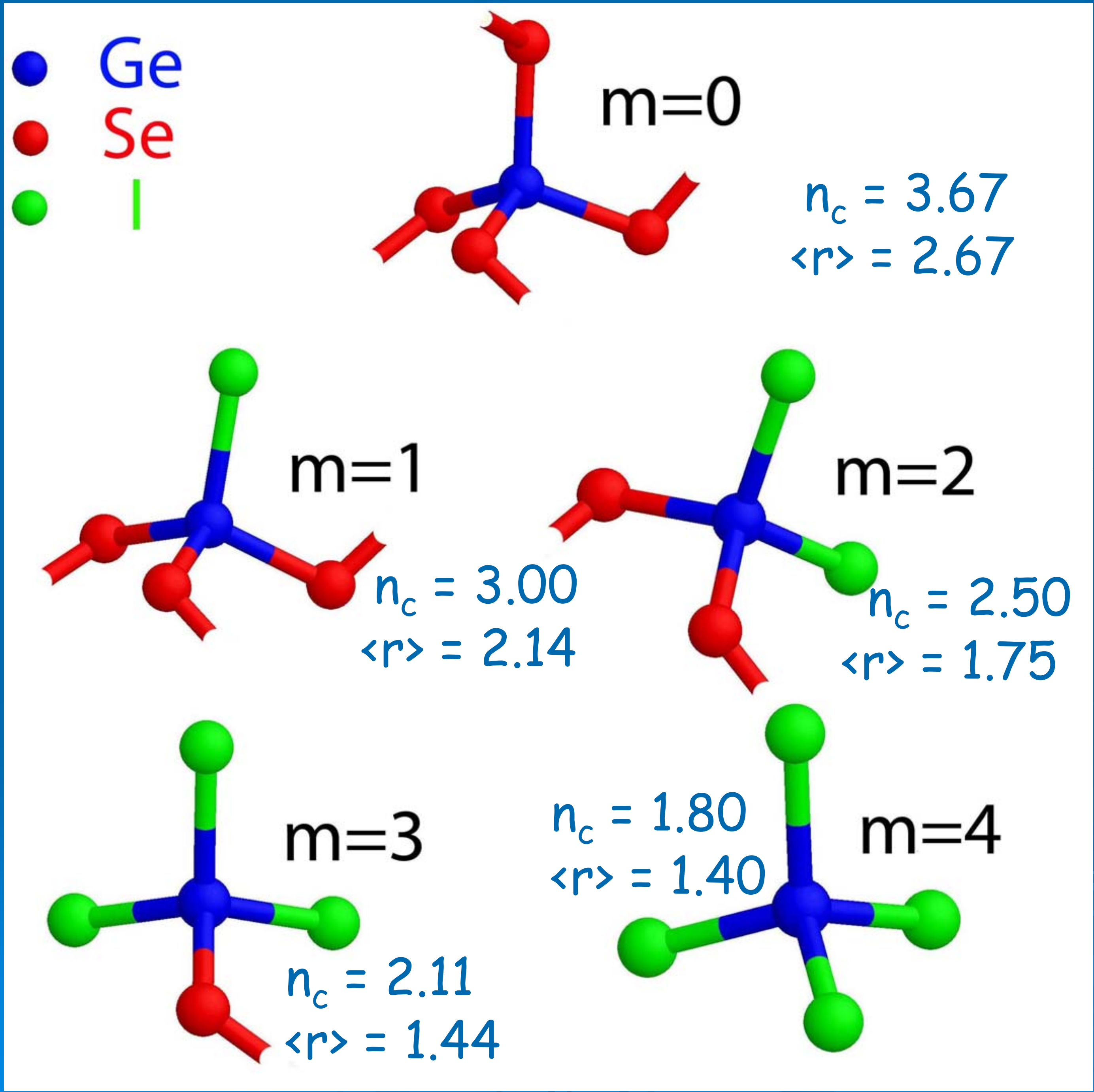
Stochastic networks and m-unit concentrations from combinatorics

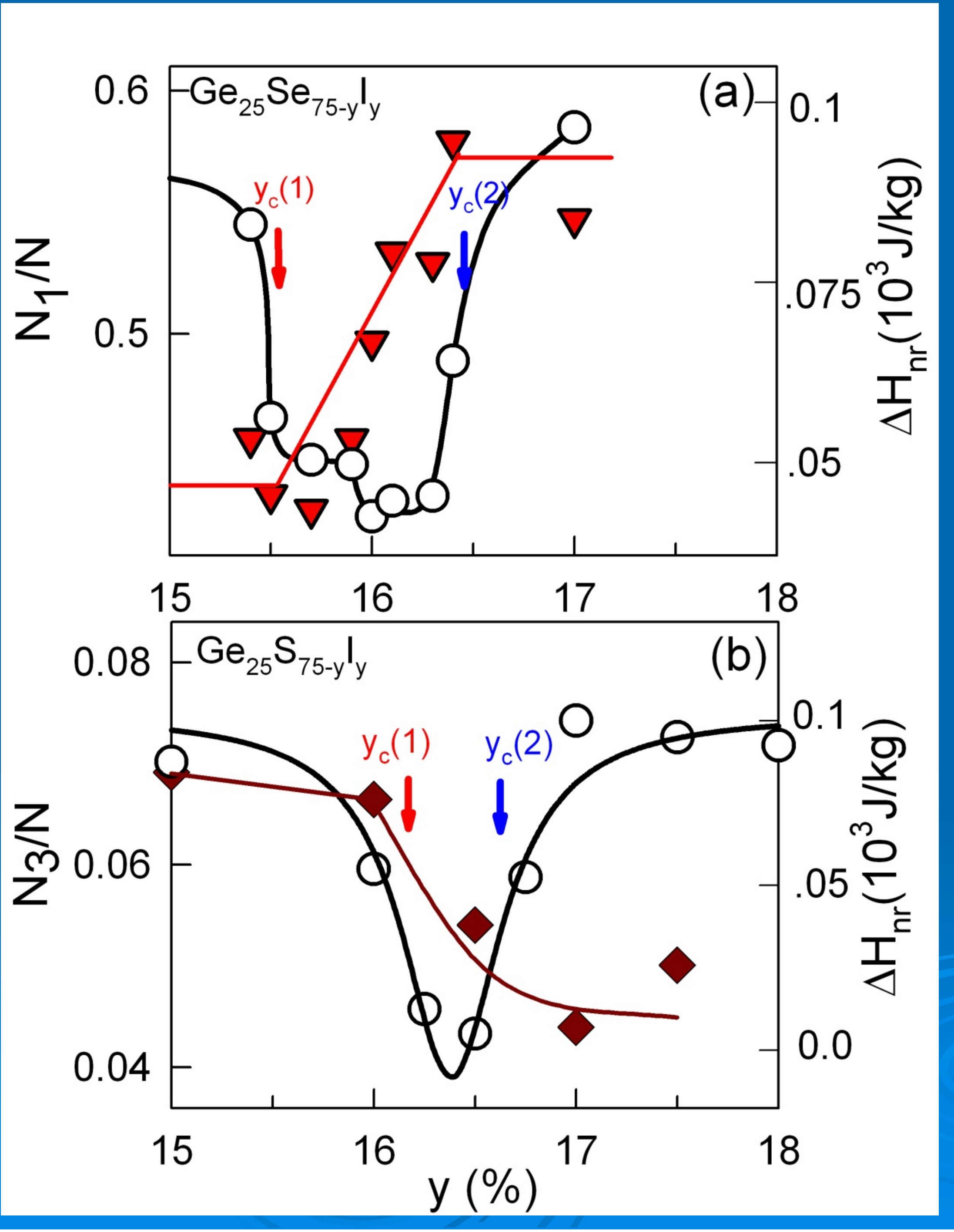
$P(m, y) = [4!\, y^m (1-y)^{4-m}] / [m!\,(4-m)!]$ $\quad 0 < m < 4 \;,\; 0 < y < 1$





Ge25Se75-yIy
(a)
yc(1)
yc(2)
m=0
m=1
m=2
m=3
m=4
m-Unit Concentrations (Nm/N)
I content y (%)
Ge25S75-yIy
(b)
yc(1)
yc(2)
m=0
m=1
m=2
m=3
m=4
m-Unit Concentrations (Nm/N)
I content y (%)


Ge
Se
I
m=0
n_c = 3.67
<r> = 2.67
m=1
n_c = 3.00
<r> = 2.14
m=2
n_c = 2.50
<r> = 1.75
m=3
n_c = 2.11
<r> = 1.44
n_c = 1.80
<r> = 1.40
m=4



Ge25Se75-yIy
(a)
yc(1)
yc(2)
N1/N
ΔHnr(10^3 J/kg)
0.6
0.5
0.1
.075
.05
15
16
17
18
Ge25S75-yIy
(b)
yc(1)
yc(2)
N3/N
0.08
0.06
0.04
0.1
.05
0.0
y (%)

Structural re-organization in the IP

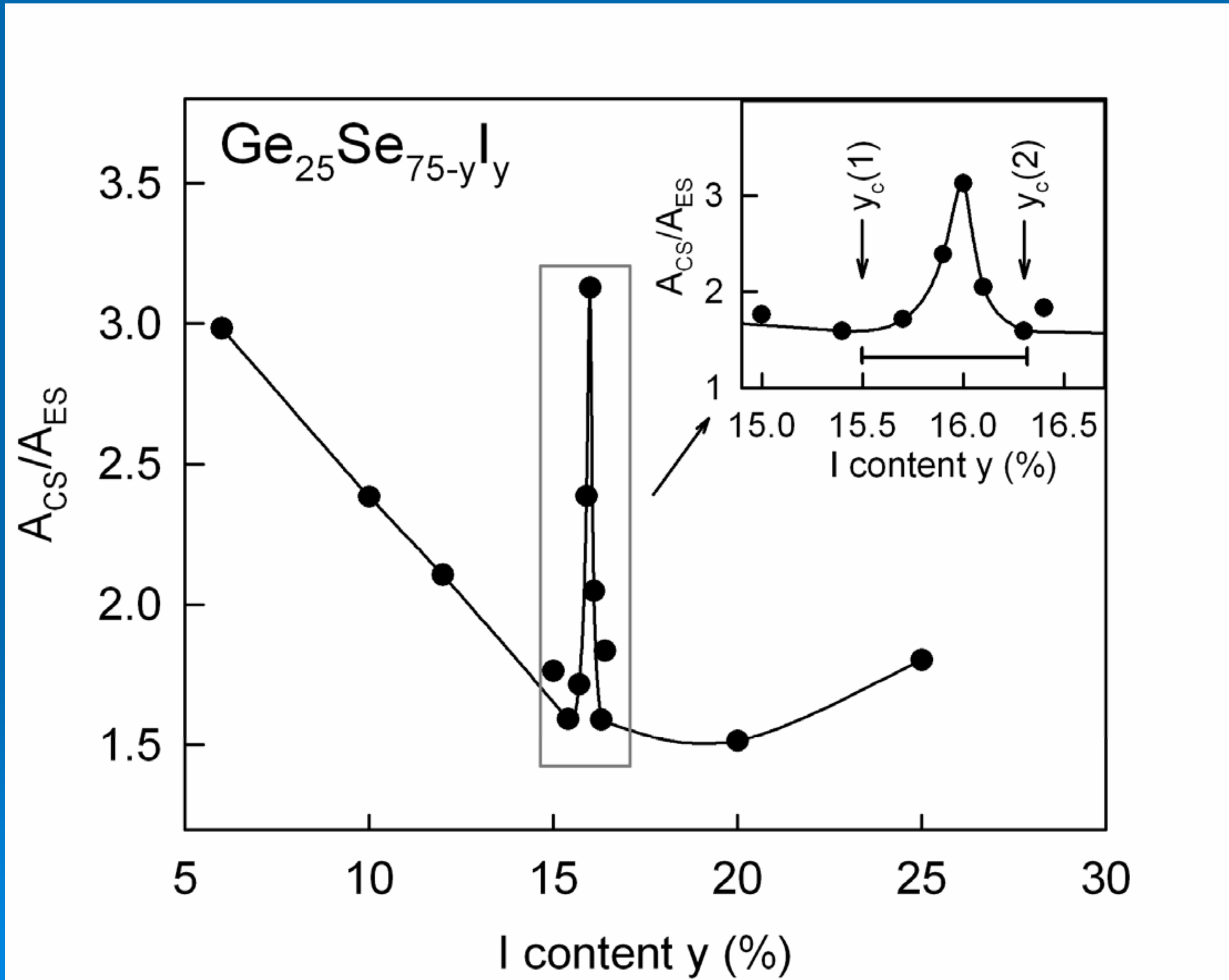
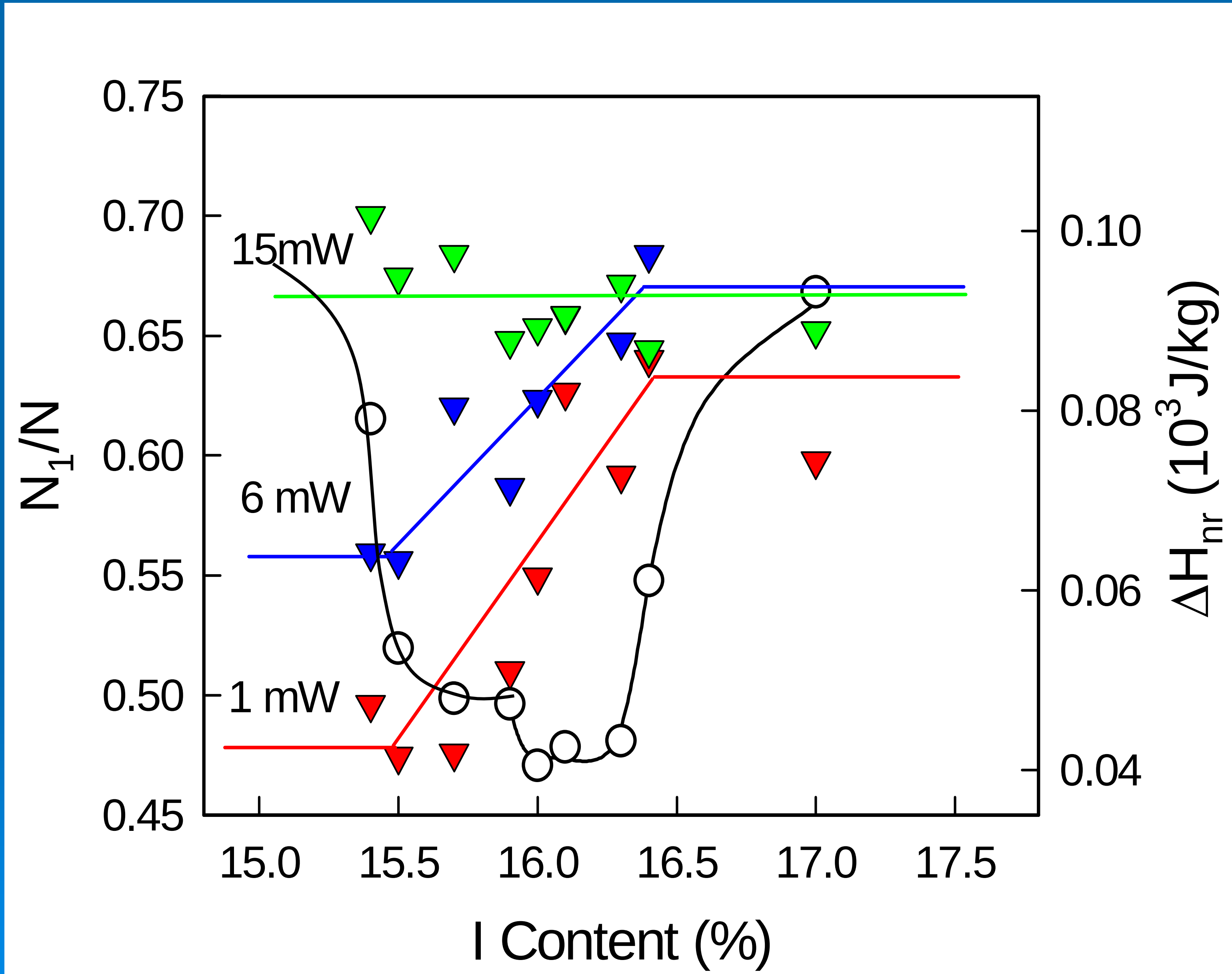


Photo-melting of the IP in chalcohalides



Conclusions

- Terminal atoms collapse IPs of base networks rather dramatically. This is a fairly general observation.
- Characteristic rings where isostatic rigidity is nucleated are perhaps cut by terminal atoms.
- In real systems atom size mismatch plays an important role in the way network stress is relieved locally and globally as networks self-organize.

Intermediate phases in glasses

- Chalcogenide glasses (1996- present)

Covalent systems are ideal because ***r*** is estimated directly.

- Chalcohalide glasses (2002-present)

Halogens terminate networks, and collapse IP in a rather striking fashion. Interm. Range order is implicated in IP.

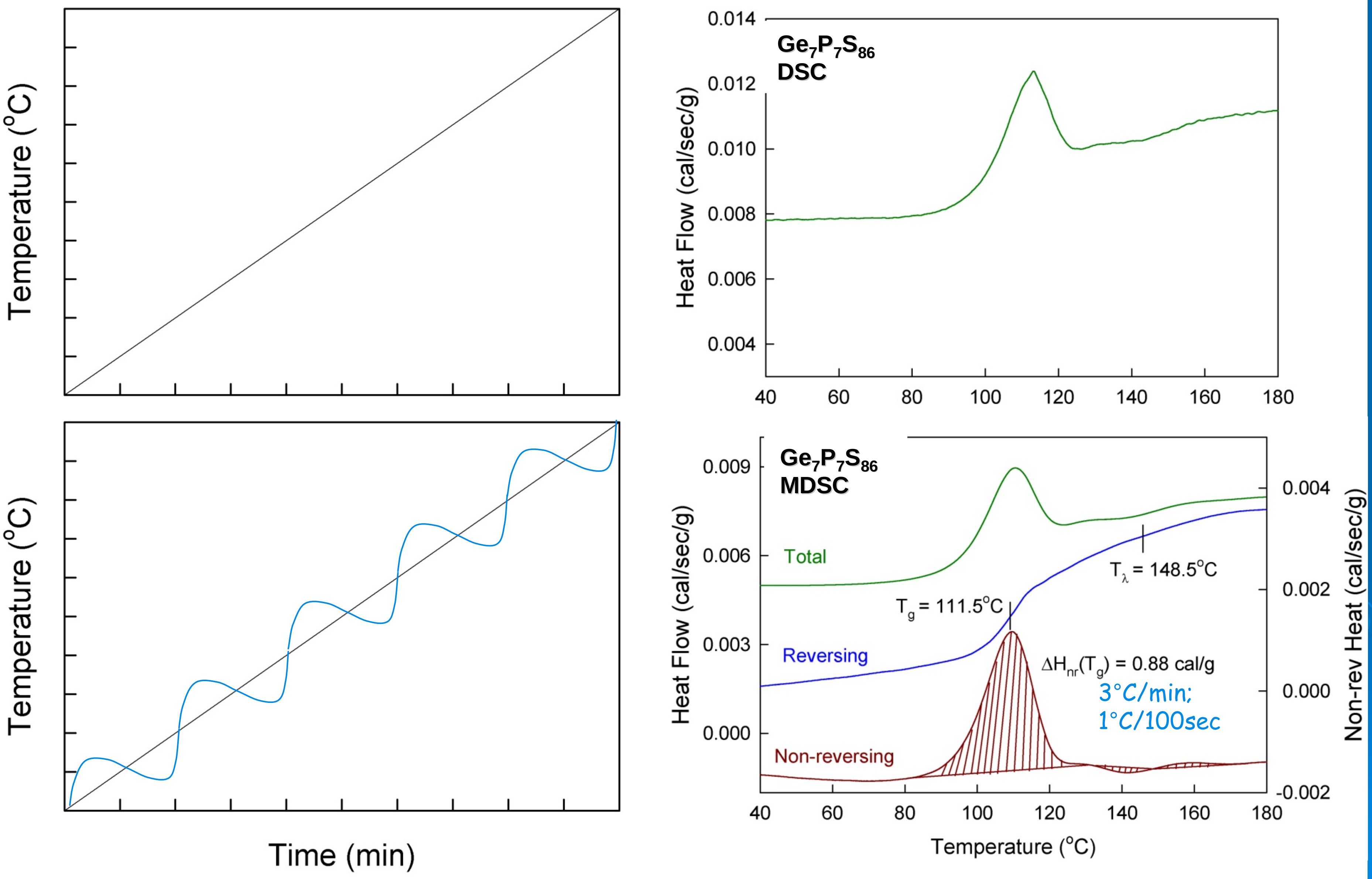
- Alkali- Germanates and – Silicates (2001-present)

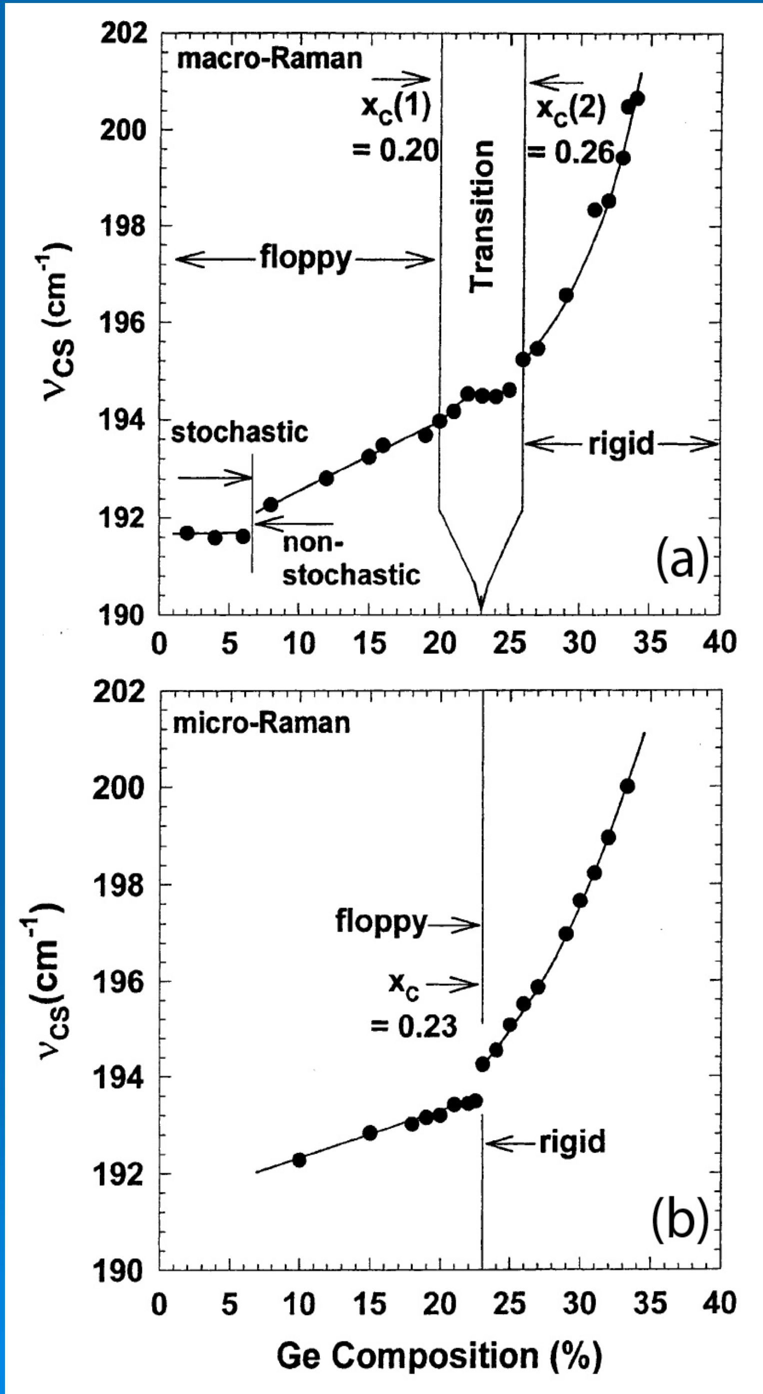
CN of Alkali atoms and effective constraints of networks are less obvious. However, T_gs provide a good guide on network connectivity.

- Solid electrolyte glasses (2005-present)

AgI, Ag_2S, Ag_2Se as additives in base oxide and/or chalcogenide glasses are Fast Ion conductors. Wide IPs are observed and FIC is promoted qualitatively once networks become flexible.

DSC and Modulated-DSC (MDSC)

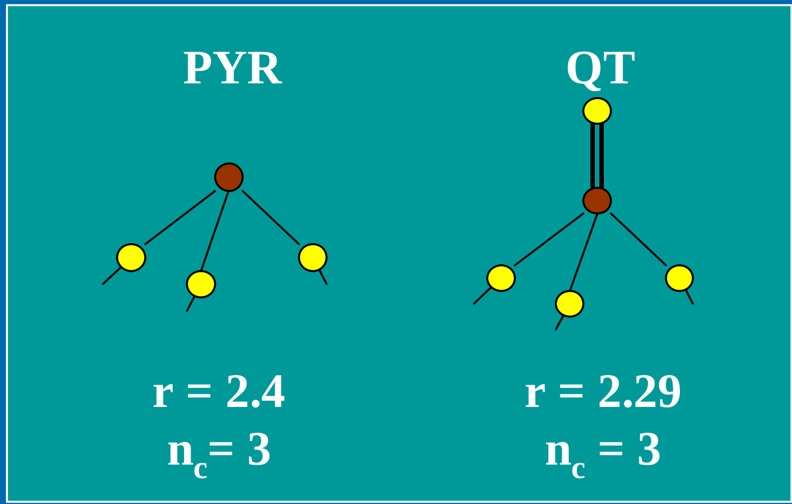




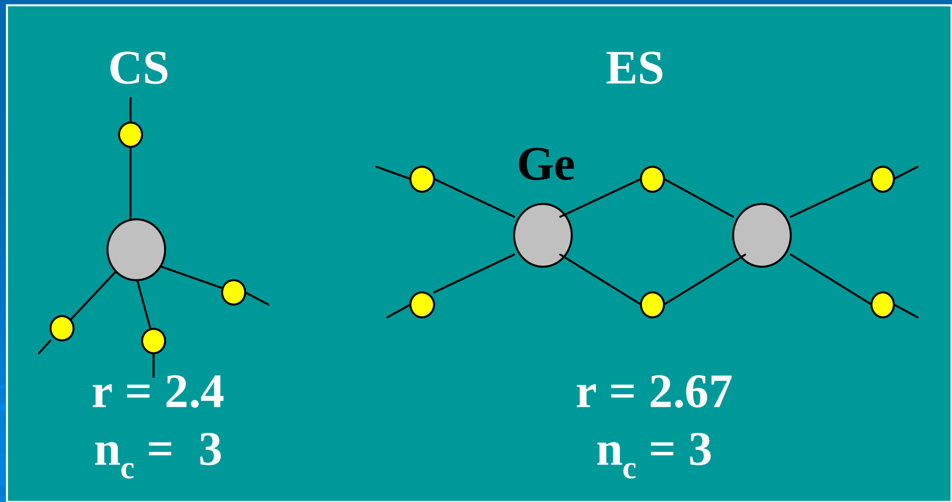
macro-Raman
$x_c(1)$ = 0.20
$x_c(2)$ = 0.26
Transition
floppy
rigid
stochastic
non-stochastic
(a)
ν_{CS} (cm^{-1})
202
200
198
196
194
192
190
0 5 10 15 20 25 30 35 40
micro-Raman
floppy
x_c = 0.23
rigid
(b)
ν_{CS}(cm^{-1})
Ge Composition (%)

Network Forming Units:

Group V centered LS



Group IV centered LS



Intermediate Phase in Ge_xSe_{1-x} glasses

P.B, X.W.Feng and W J.Bresser, J.N.C.S, 293,348 (2001).