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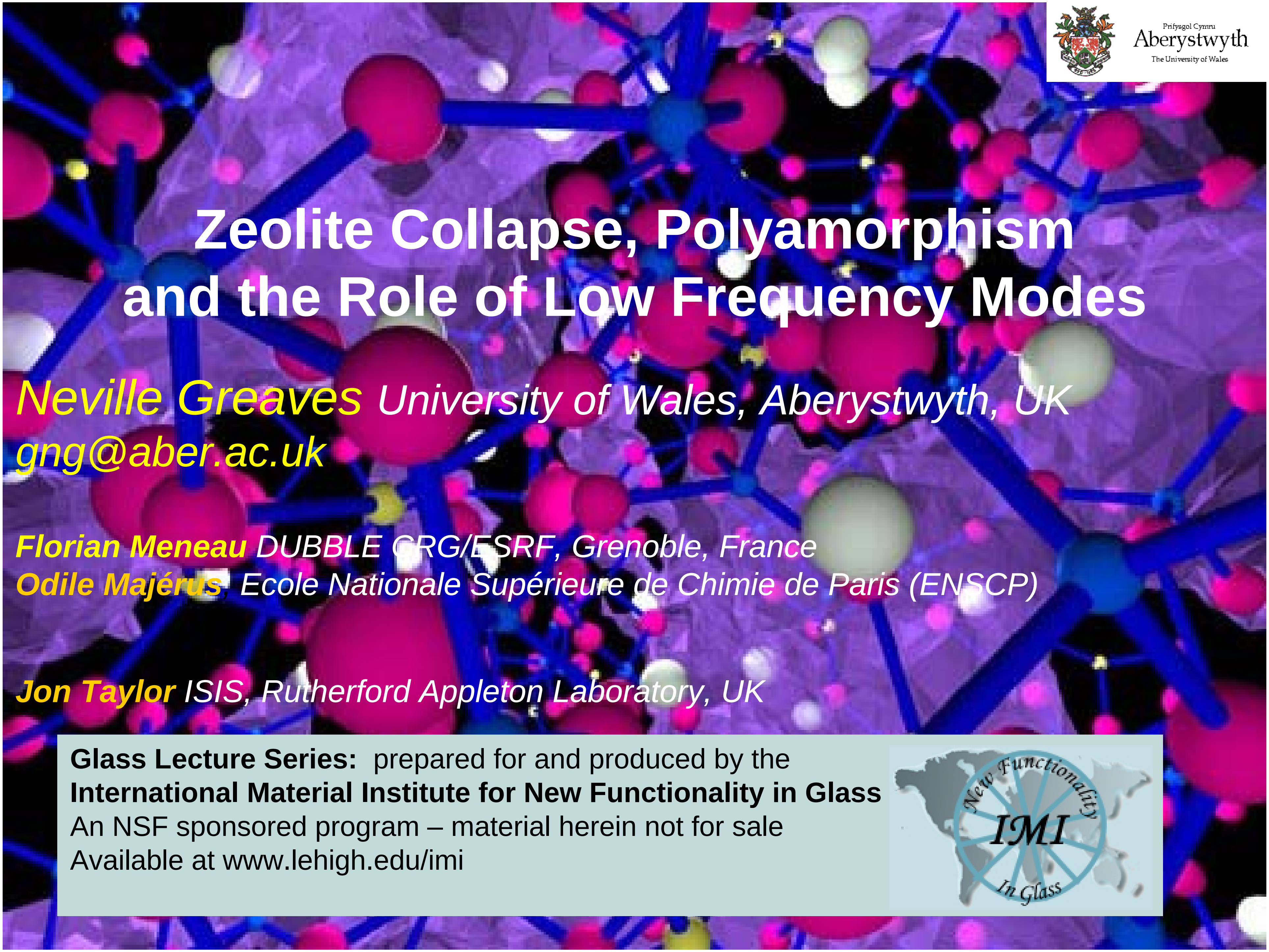

Zeolite Collapse, Polyamorphism and the Role of Low Frequency Modes

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Jon Taylor *ISIS, Rutherford Appleton Laboratory, UK*

Glass Lecture Series: prepared for and produced by the
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Low temperature dynamics

Anomalous C_P, Boson Peak, TLS

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Structure, Collapse, SAXS/WAXS

Low Frequency Modes

Inelastic Neutron Scattering, Boson Peak, Librational Modes, Anharmonicity, LDA-HDA transition

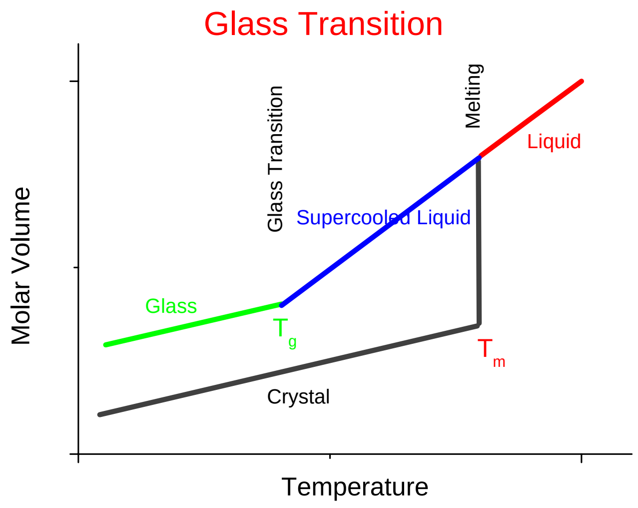
Rheology of collapsing zeolites amorphised by temperature and pressure
GN Greaves,
F Meneau, A Sapelkin, LM Colyer, I ap Gwynn, S Wade, G Sankar
Nature Materials, 2, 622-629 (2003)

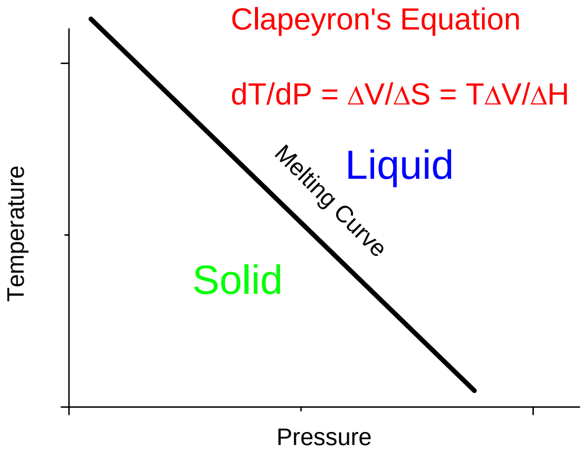
also *Nature Materials News and Views*, 2, 571-572 (2003)

Identifying the vibrations that destabilize crystals and that characterize the glassy state
GN Greaves, F Meneau, O. Majérus, D.G. Jones, J. Taylor
Science, 308, 1299-1302 (2005)

Amorphisation

Normal Melting v Pressure induced Melting


Glass Transition

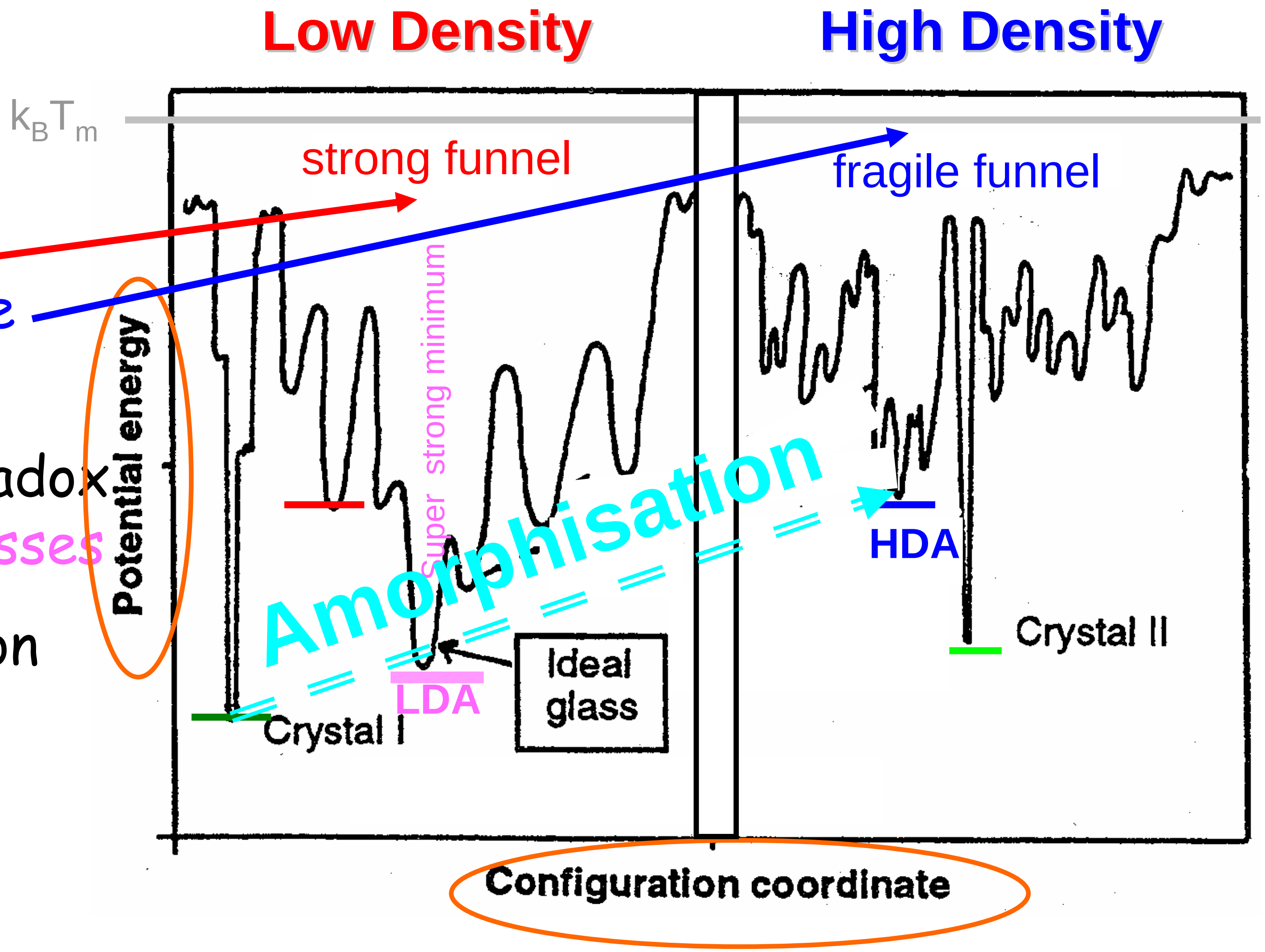

Clapeyron's Equation

$dT/dP = \Delta V/\Delta S = T\Delta V/\Delta H$

…….amorphisation results from instabilities, usually volume decreases and entropy increases

Potential energy landscape

- Strong/fragile liquid behaviour
- Kauzmann paradox and perfect glasses
- Glass transition

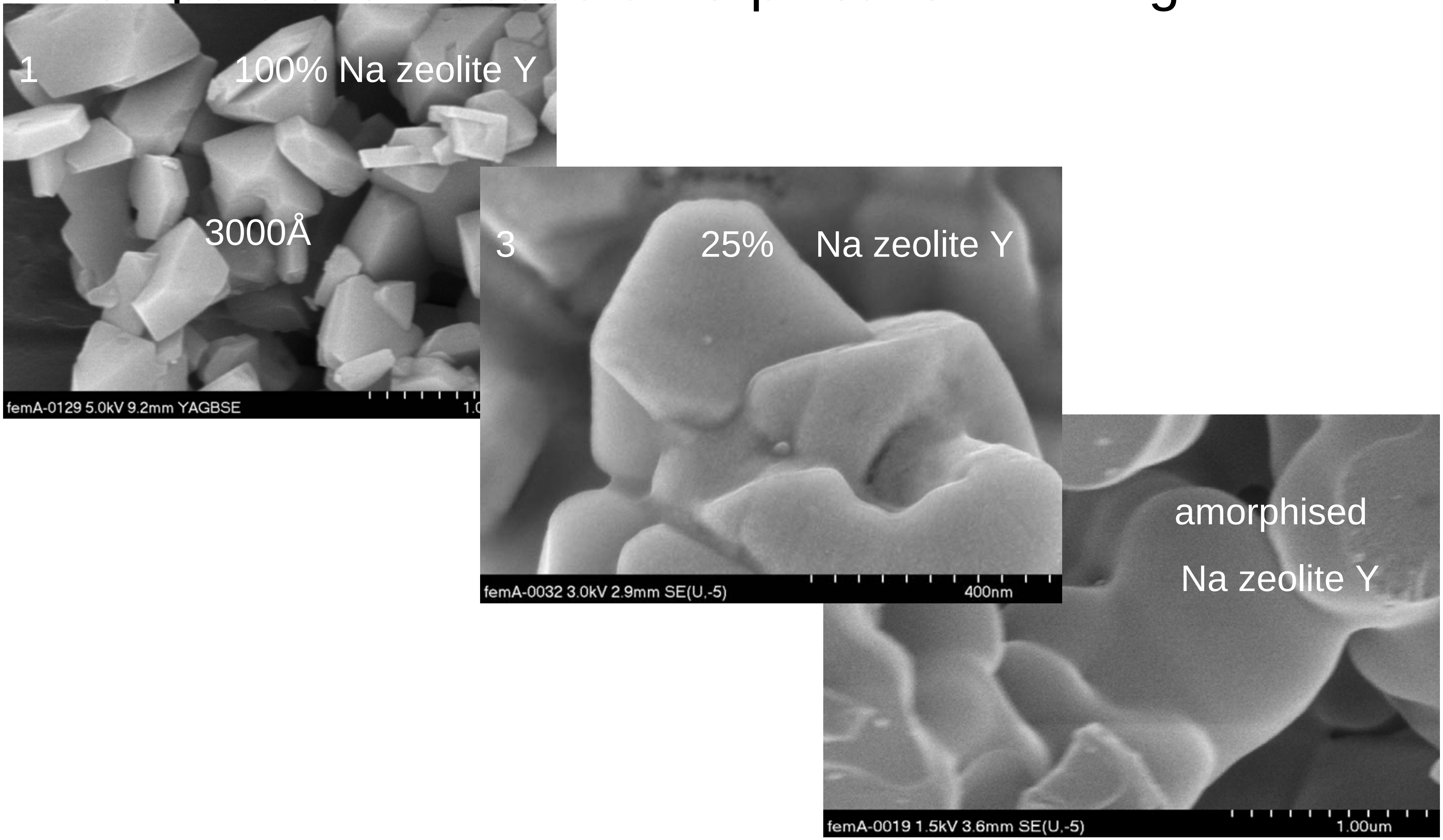


Formation of Glasses from Liquids and Biopolymers
C.A. Angell, Science 267, 1924-1935

Introduction

Zeolite Collapse - **Microscopy**

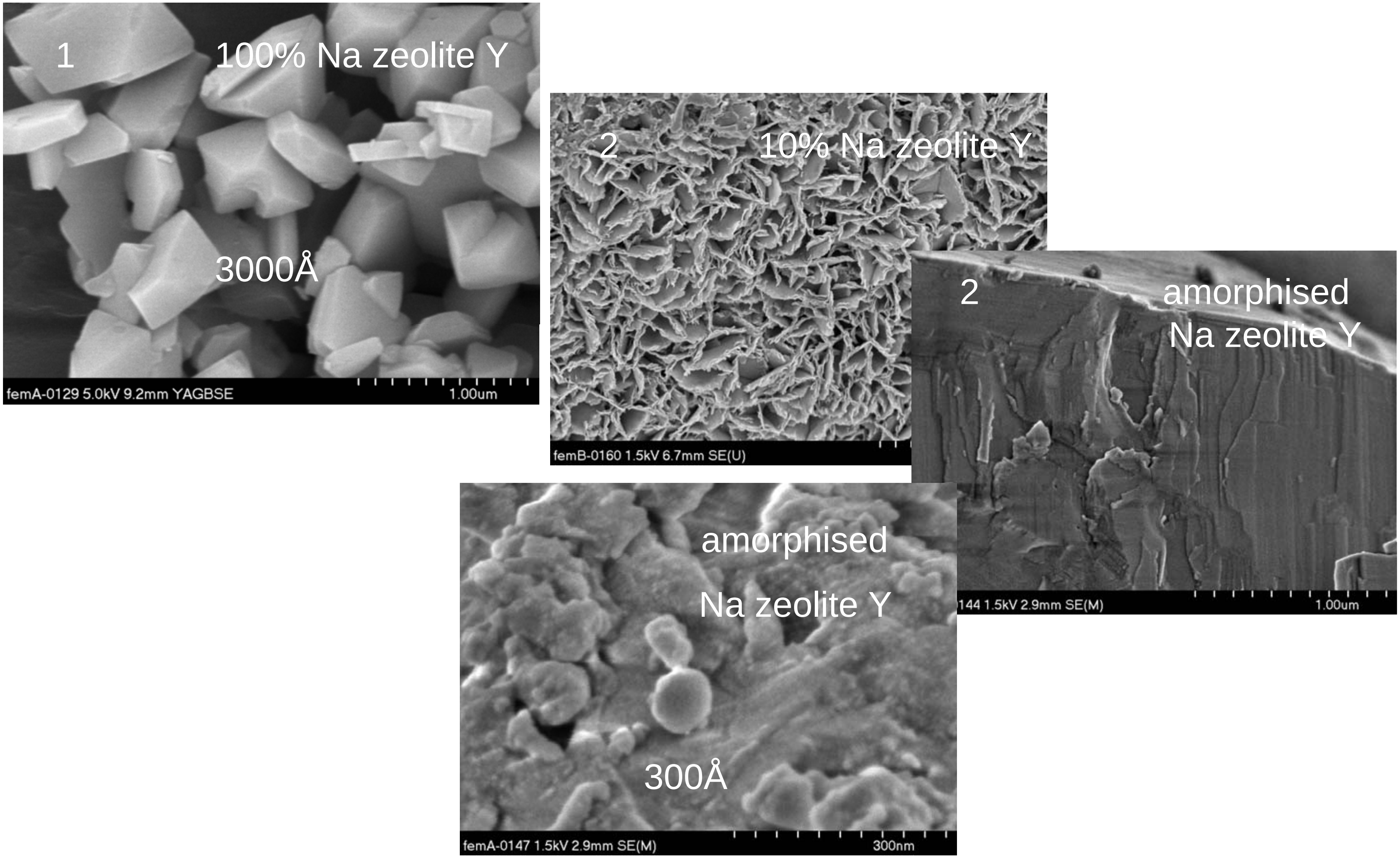
temperature induced amorphisation – T<Tg



Zeolite Collapse – **Microscopy**

Zeolites & Amorphisation

pressure amorphisation



polyamorphism & amorphisation

Ponyatovsky Model

EG Ponyatovsky and OI Barkolov, Pressure-induced amorphous phases, Materials Science Reports 8, 147-191 (1992)

❖Instabilities triggering amorphisation relate to the presence of two amorphous phases: a high density amorphous phase (HDA) and a low density amorphous phase (LDA).

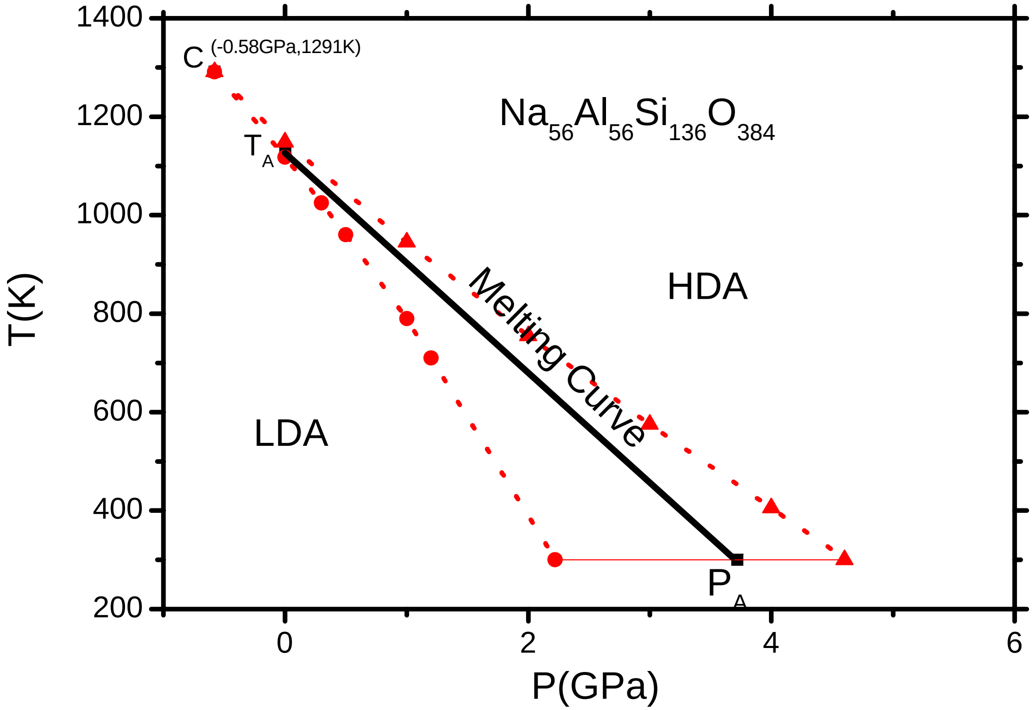
❖Clapeyron crystalline melting curve replaced by free energy maximum for 50/50 mixture, with boundaries determined by the spinodal turning points.

$G(c) = (\Delta U - T\Delta S + P\Delta V).c + U_{mix}.c.(1-c) + RT[c.\ln c + (1-c).\ln(1-c)]$

ΔS is difference in configurational entropy between HDA and LDA phases

polyamorphism and zeolite collapse

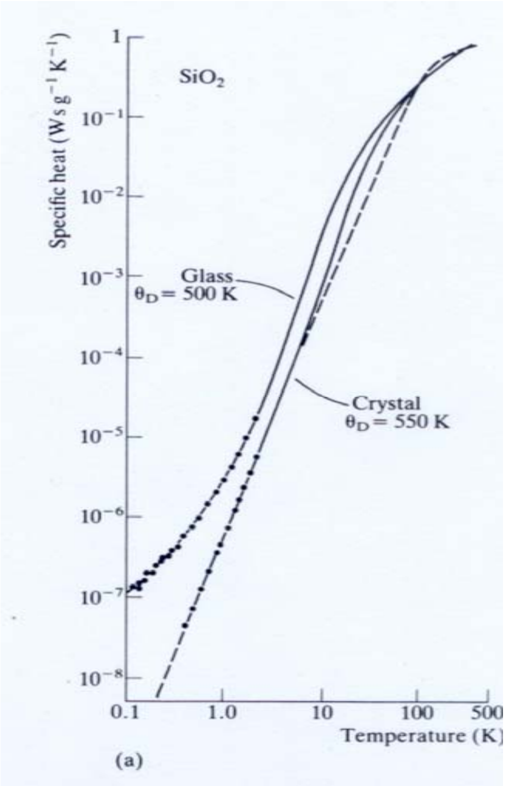
Which vibrations promote polyamorphism and trigger zeolite collapse?



T-P diagram: ΔU, ΔS, ΔV and Umix parameterised from experimental T-P results

E. Rapoport, J. Chem.Phys. **46**, 2891 (1967); ibid **48**, 1433 (1968)

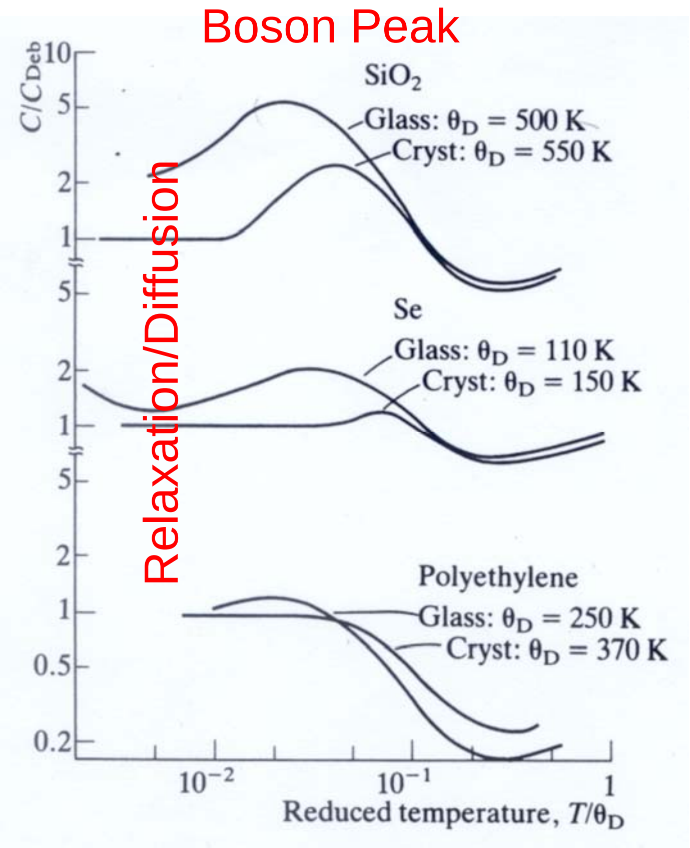
Anomalous Specific Heat



Enhancement over Debye T^3 behaviour

Boson Peak

Relaxation/Diffusion



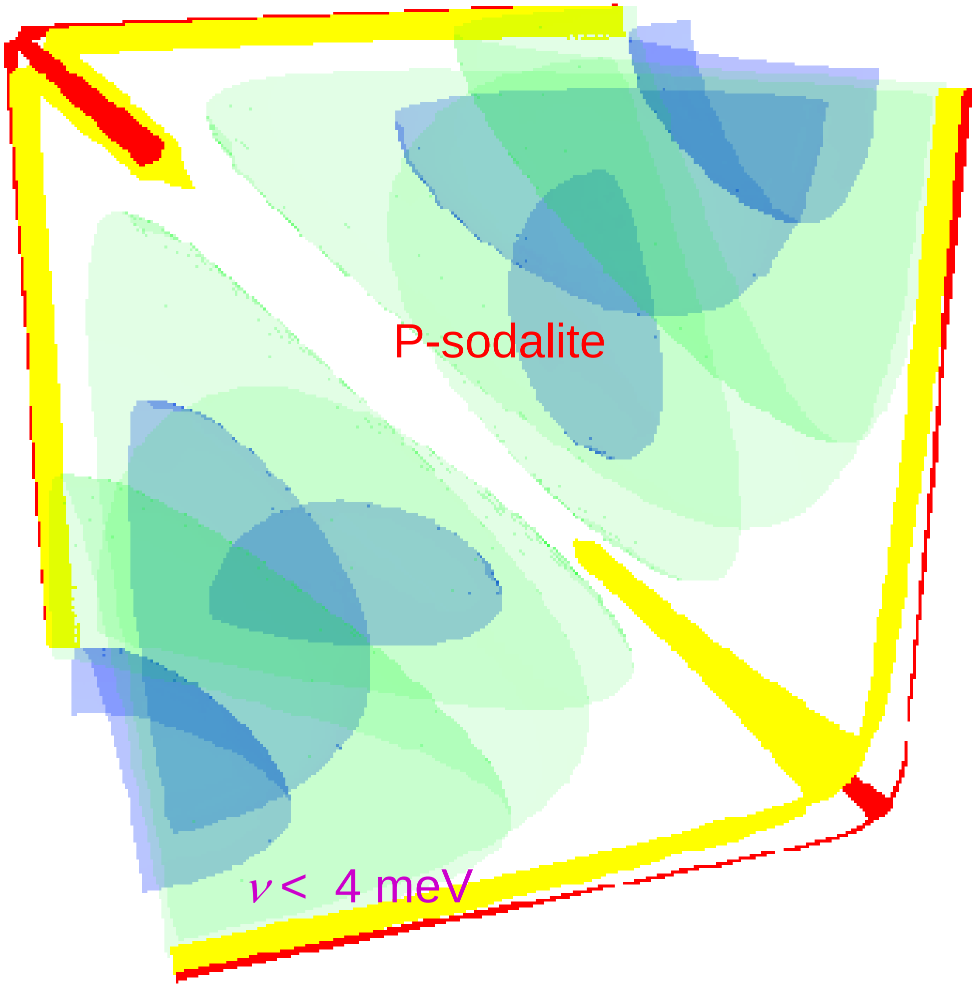
Strength

Low frequency Modes in crystals and glasses

S.R. Elliott, *Physics of Amorphous Materials* (Longman, New York, 1990)

Floppy Modes

Rigid Unit Modes

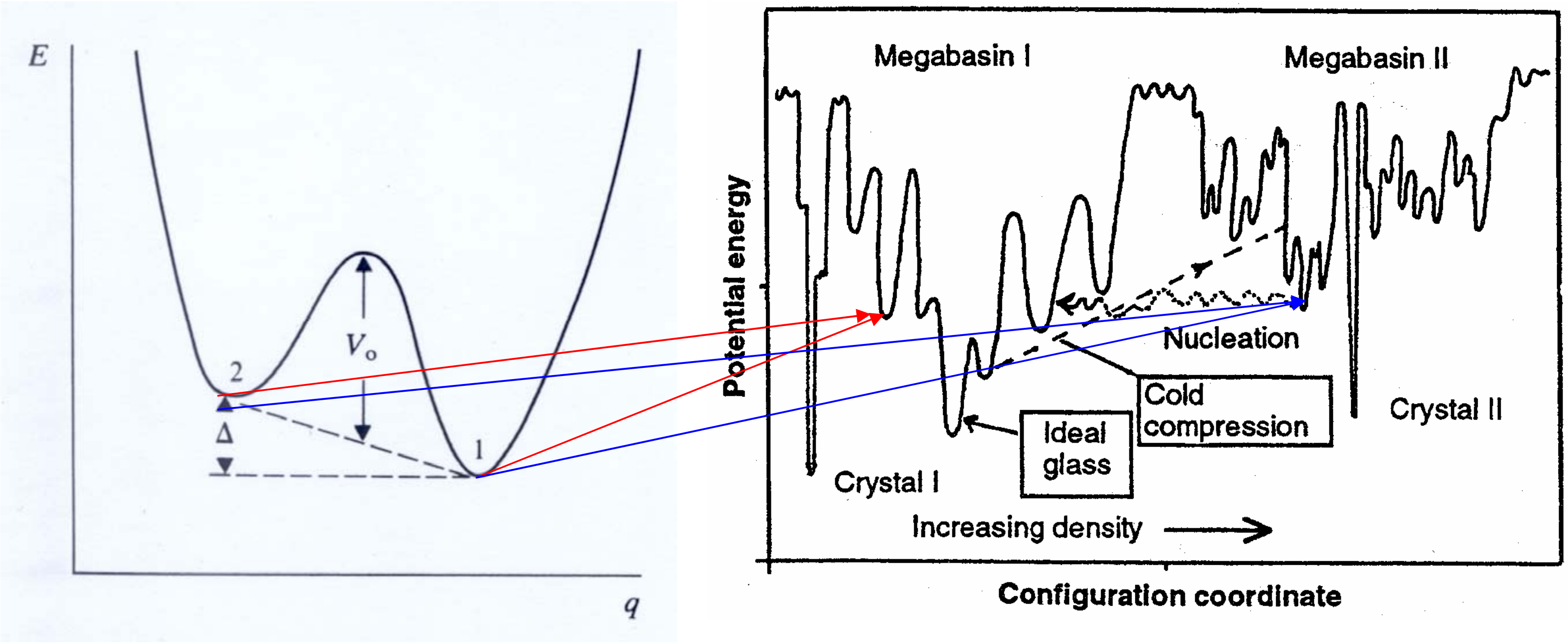


M.T. Dove, *et* al, *Phys. Rev. Lett.* **78**, 1070 (1997)

K.D. Hammonds, H. Dong, V.Heine and M.T.Dove, *Phys.Rev. Lett.* **78**, 3701 (1997)

Low temperature dynamics

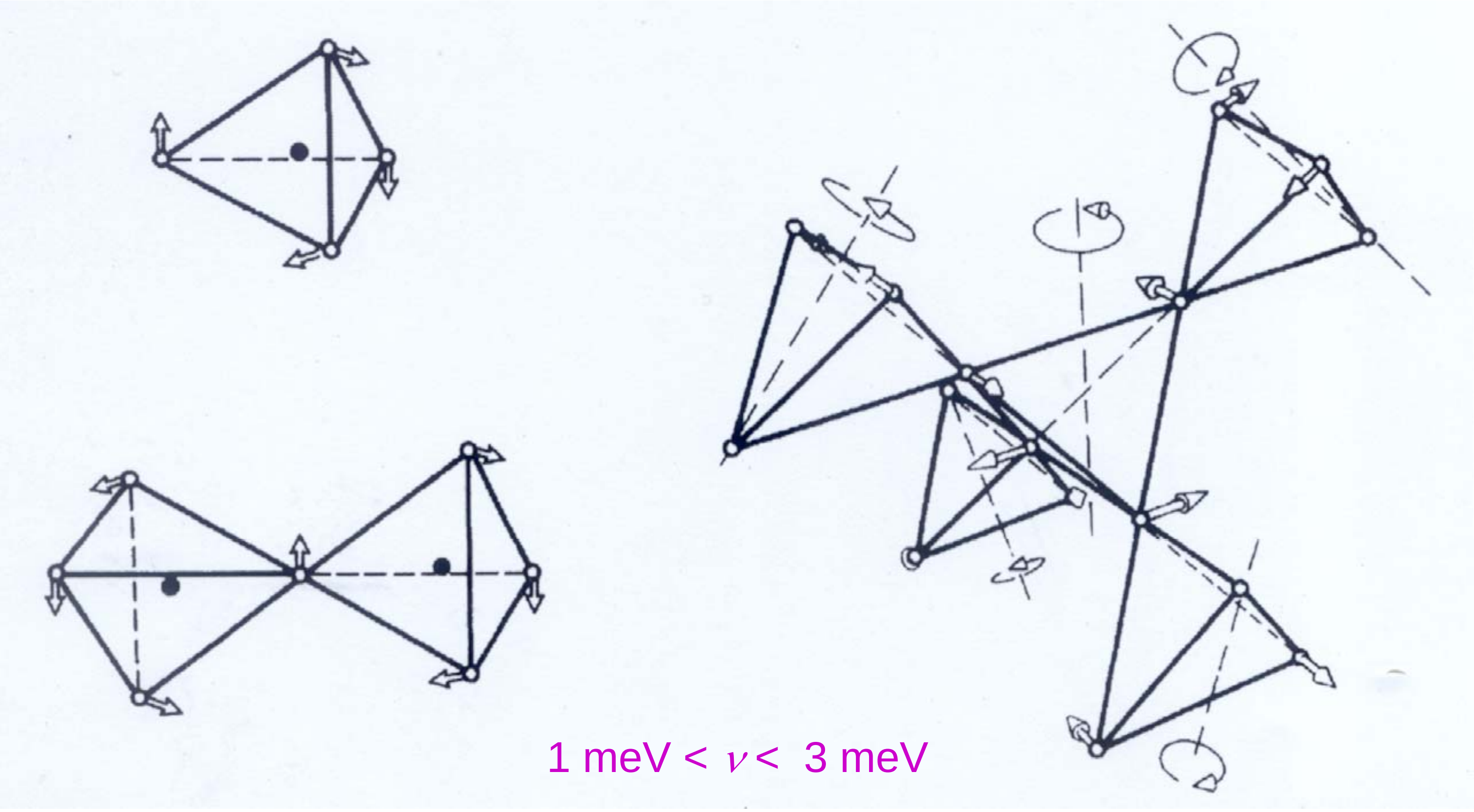
Two Level Systems



W.A. Phillips, *Amorphous Solids: Low Temperature Properties* (Springer-Verlag, Berlin, 1981)

Angell cartoon of Energy Landscape

Librational Modes



1 meV < ν < 3 meV

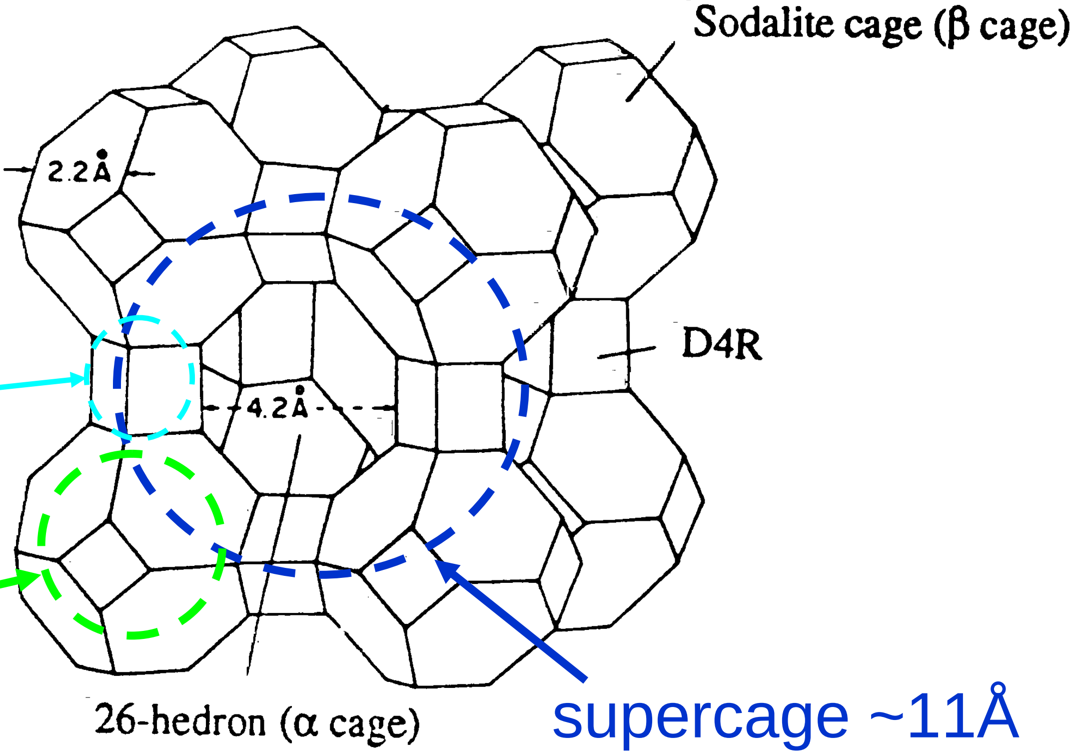
U. Bucheneau, *et al*, *Phys. Rev. B* **34**, 5665 (1986)

Zeolite Structure and Secondary Building Units

density 1.5 $\mathrm{gcm^{-3}}$

NB density of glass 2.5 $\mathrm{gcm^{-3}}$

$\Delta V_A \sim 40\%$



Double ring

~6Å diameter

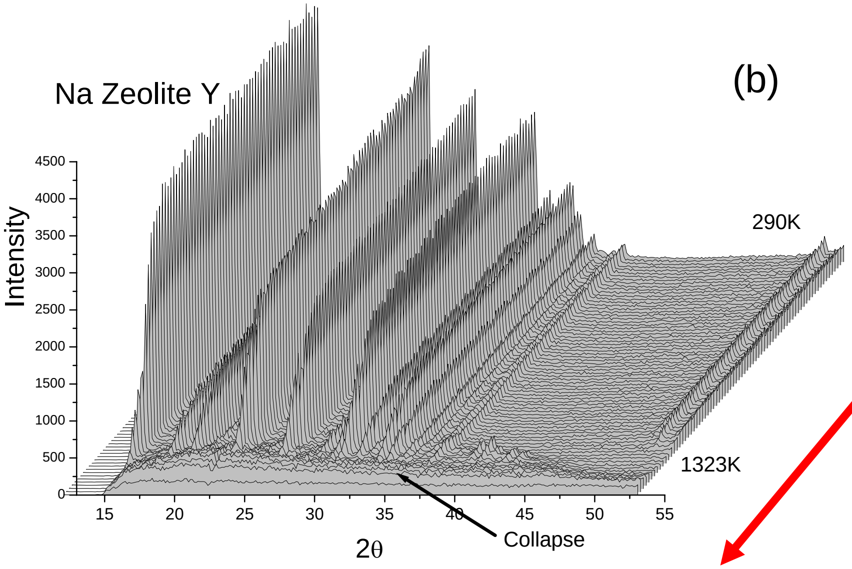
Sodalite cage
~7Å diameter

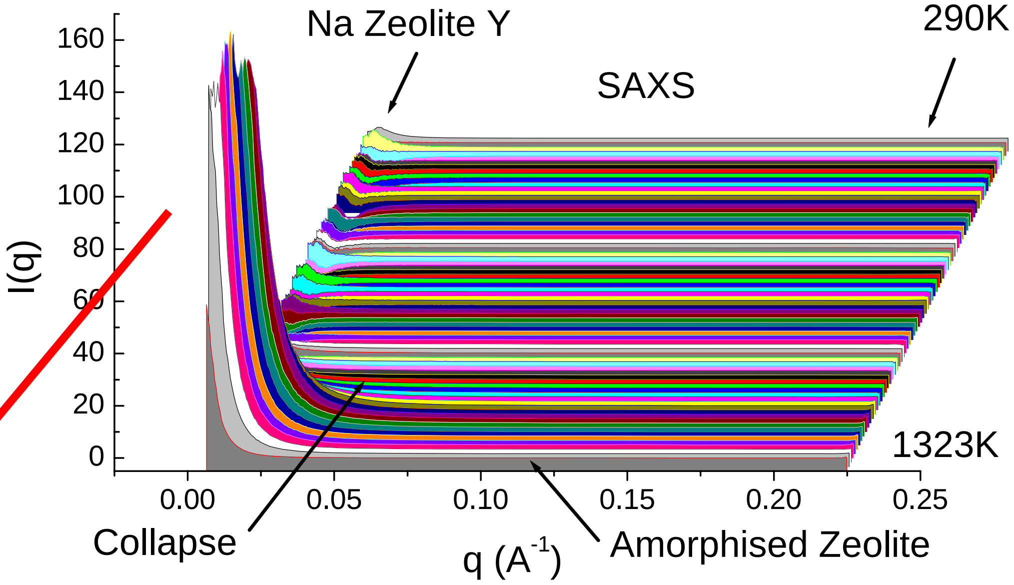
supercage ~11Å diameter

Zeolite A: $Na_{12}Al_{12}Si_{12}O_{48}$

Zeolites and Amorphisation

X-ray Diffraction and Small Angle X-ray Scattering SAXS





Zeolites &
Amorphisation

Evidence for Low and
High Density Phases

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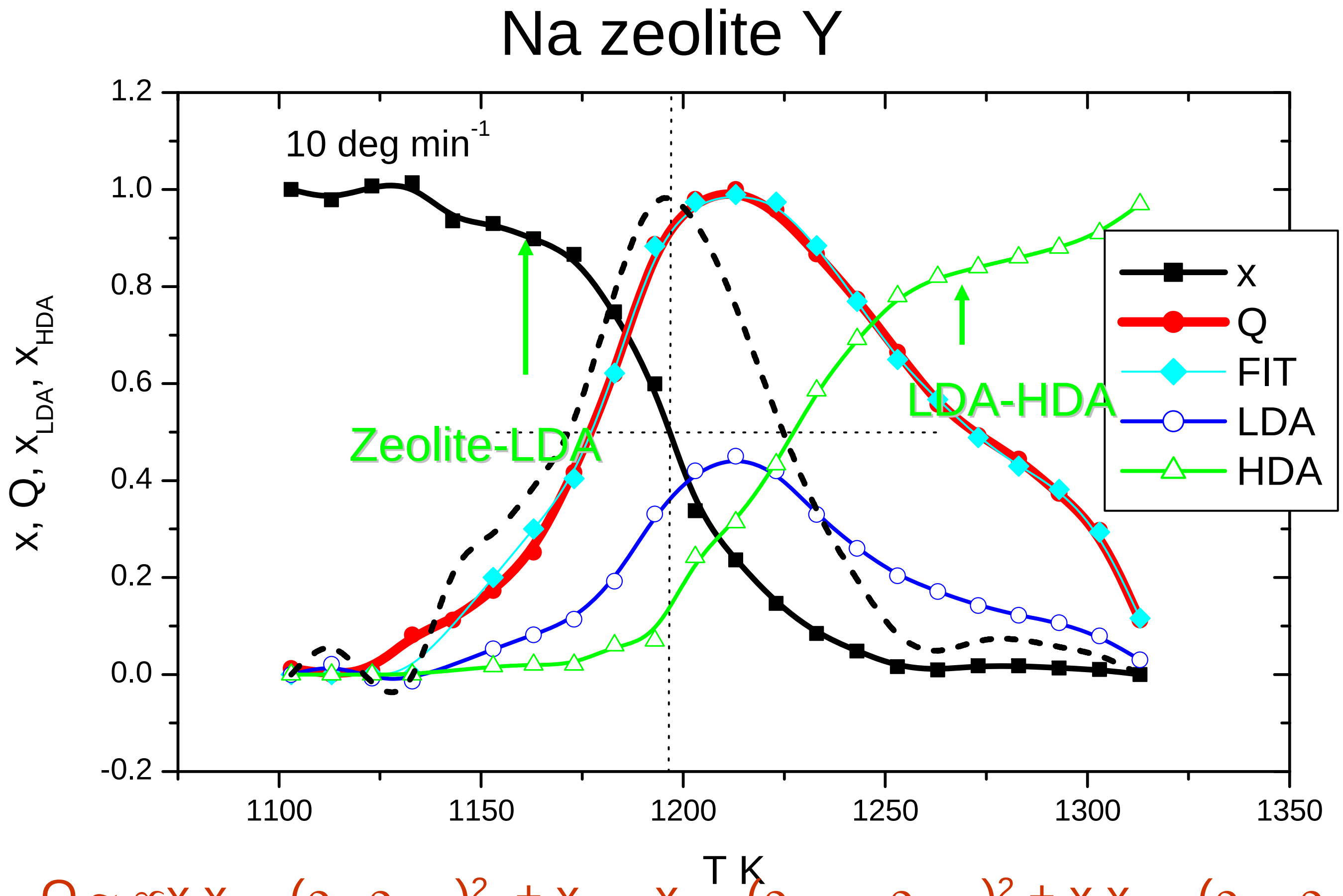
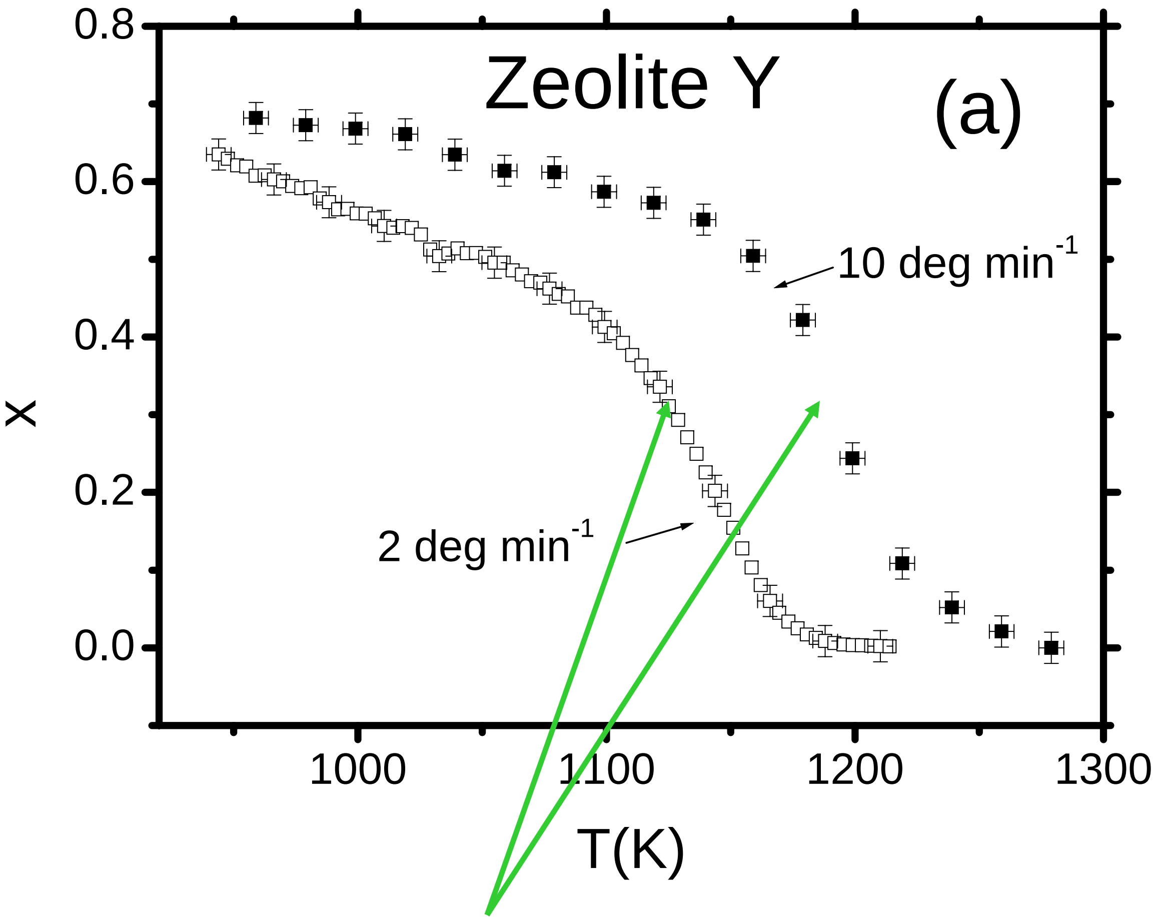
Modelling 3 phases from SAXS & XRD



$Q \sim \propto x.x_{LDA}(\rho_Z-\rho_{LDA})^2 + x_{LDA}.x_{HDA}(\rho_{LDA} - \rho_{HAD})^2 + x.x_{HDA}(\rho_z - \rho_{HDA)})^2$

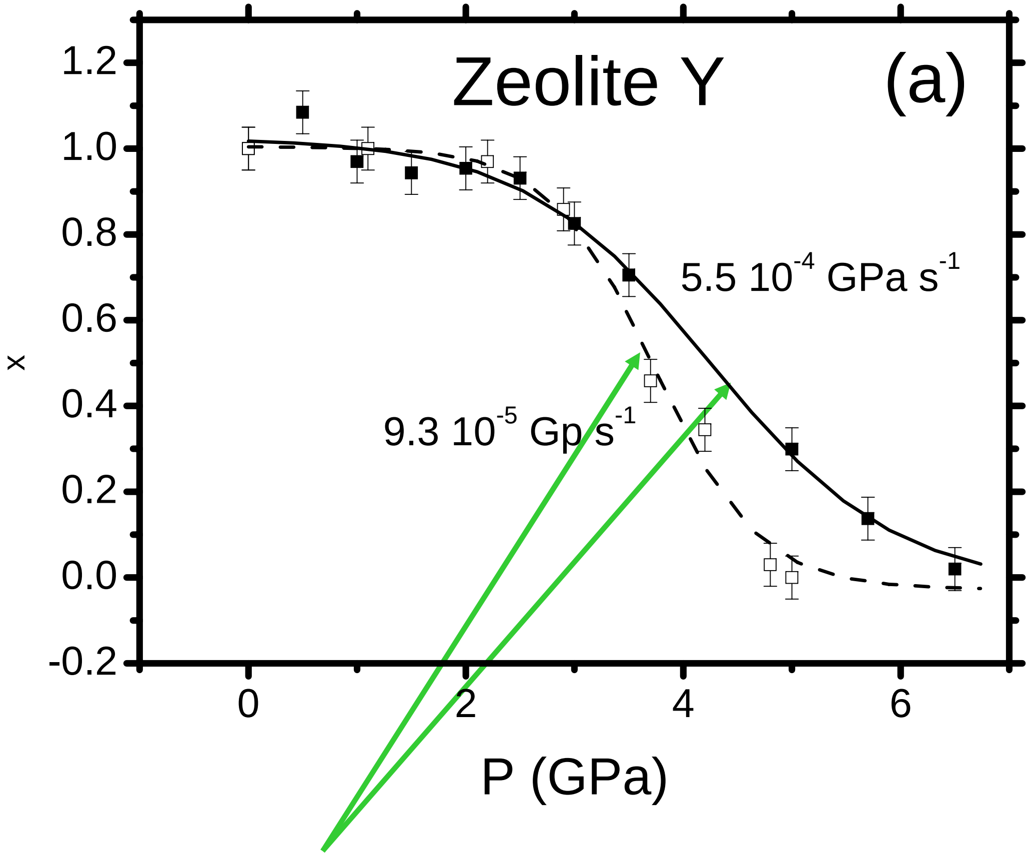
$x + x_{LDA} + x_{HDA} = 1$

Dynamics of T -induced amorphisation



Amorphisation temperature depends on the rate at which temperature is applied

Dynamics of P-induced amorphisation



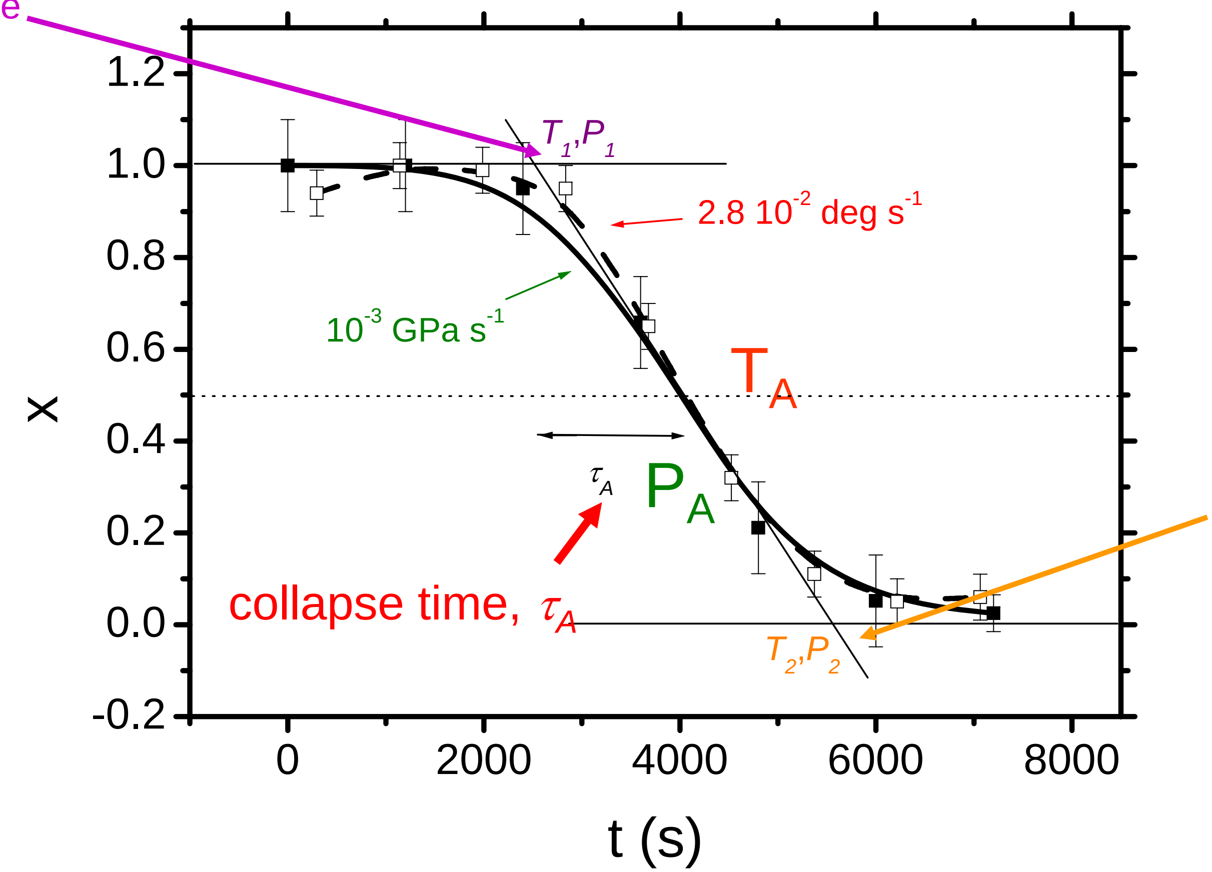
Amorphisation pressure depends on the rate at which the pressure is applied

Zeolite collapse –

T & P –induced amorphisation

Zeolites & Amrophisation

Limits for zeolite stability

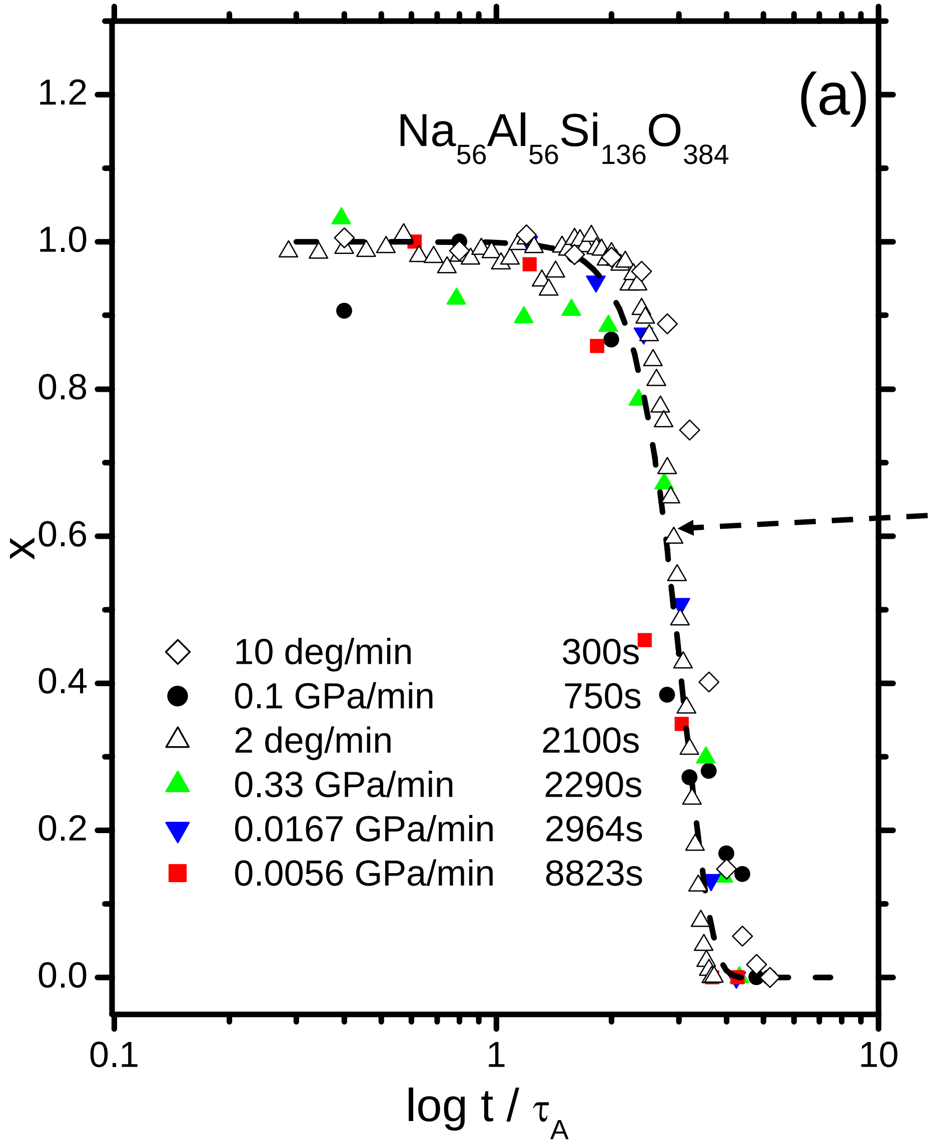


Limits for glass formation

Temperature and Pressure-induced Amorphisation are equivalent

$$P_A \Delta V_A \sim 3RT_A$$

Zeolites and Amorphisation



Universal curve for zeolite collapse

$x = \exp-(t/\tau_A)^n$

Avrami-like n~4

(3D nucleation, 1 process)

temperature and pressure induced amorphisation are equivalent processes

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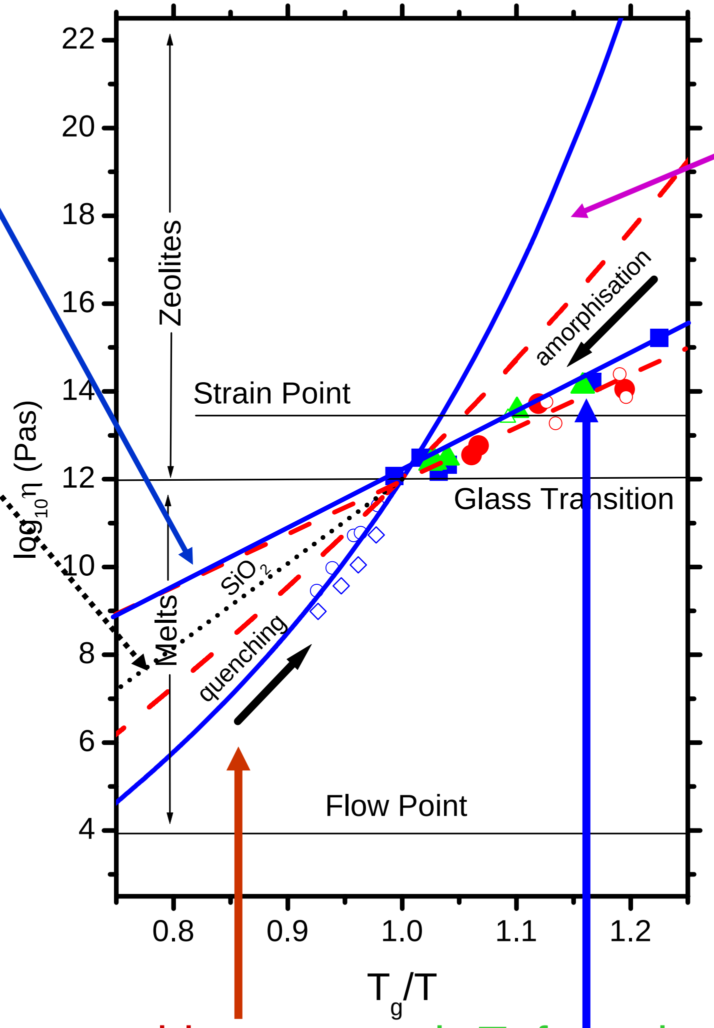
Rheology of Amorphisation

Different Angell plot

Zeolites & Amorphisation

Slopes of viscosity curves for collapse (LDA) are less even than SiO_2, the classic strong liquid i.e. character of super string liquid

$\eta = G_\infty \tau$



$T < T_g$ collapse is faster than relaxation of equilibrium glass (HDA)

Crystalline chemical order should be retained and a perfect glass formed avoiding Kauzmann Paradox

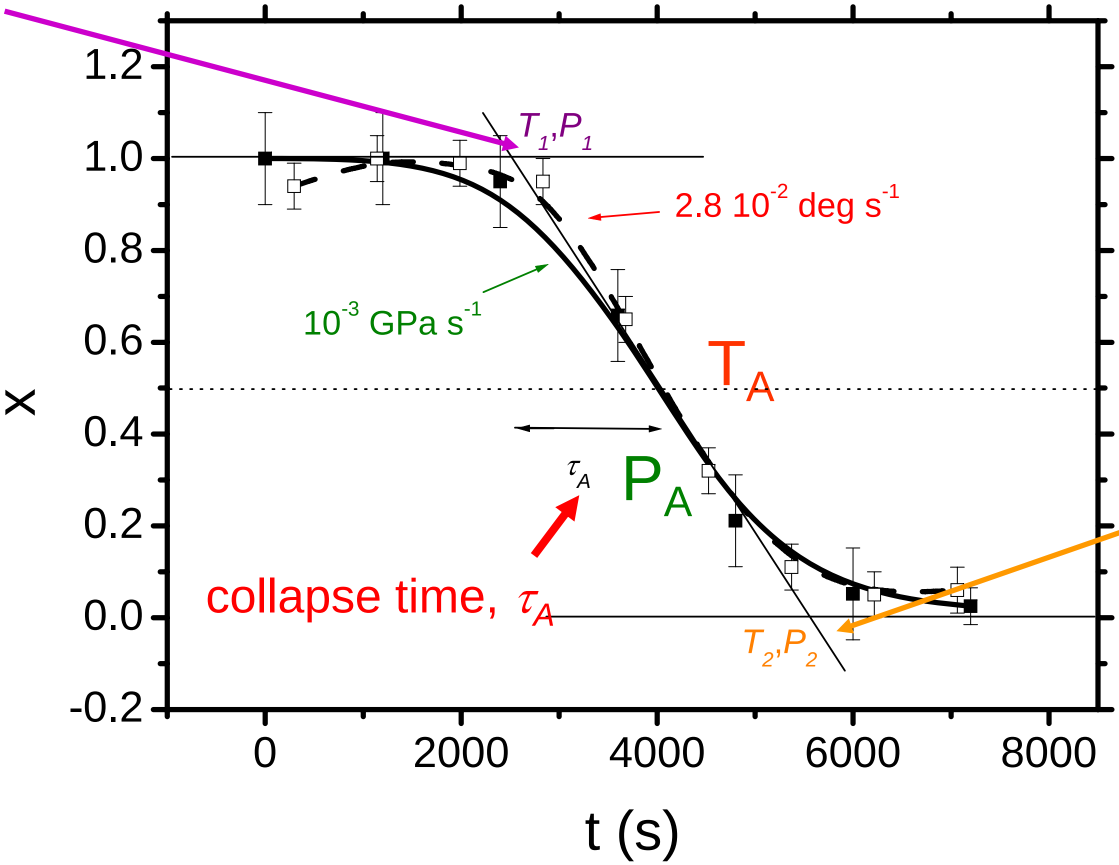
Lowenstein, W. The distribution of aluminium in the tetrahedra of silicates and aluminosilicates. *American Minerologist* **39**, 92-96 (1954)

glasses made by quenching approach T_g from the liquid state
whereas glasses produced by amorphisation approach T_g from the crystalline state

Zeolites & Amrophisation

Zeolite collapse –

T & P –induced amorphisation



Limits for zeolite stability

collapse time, τ_A

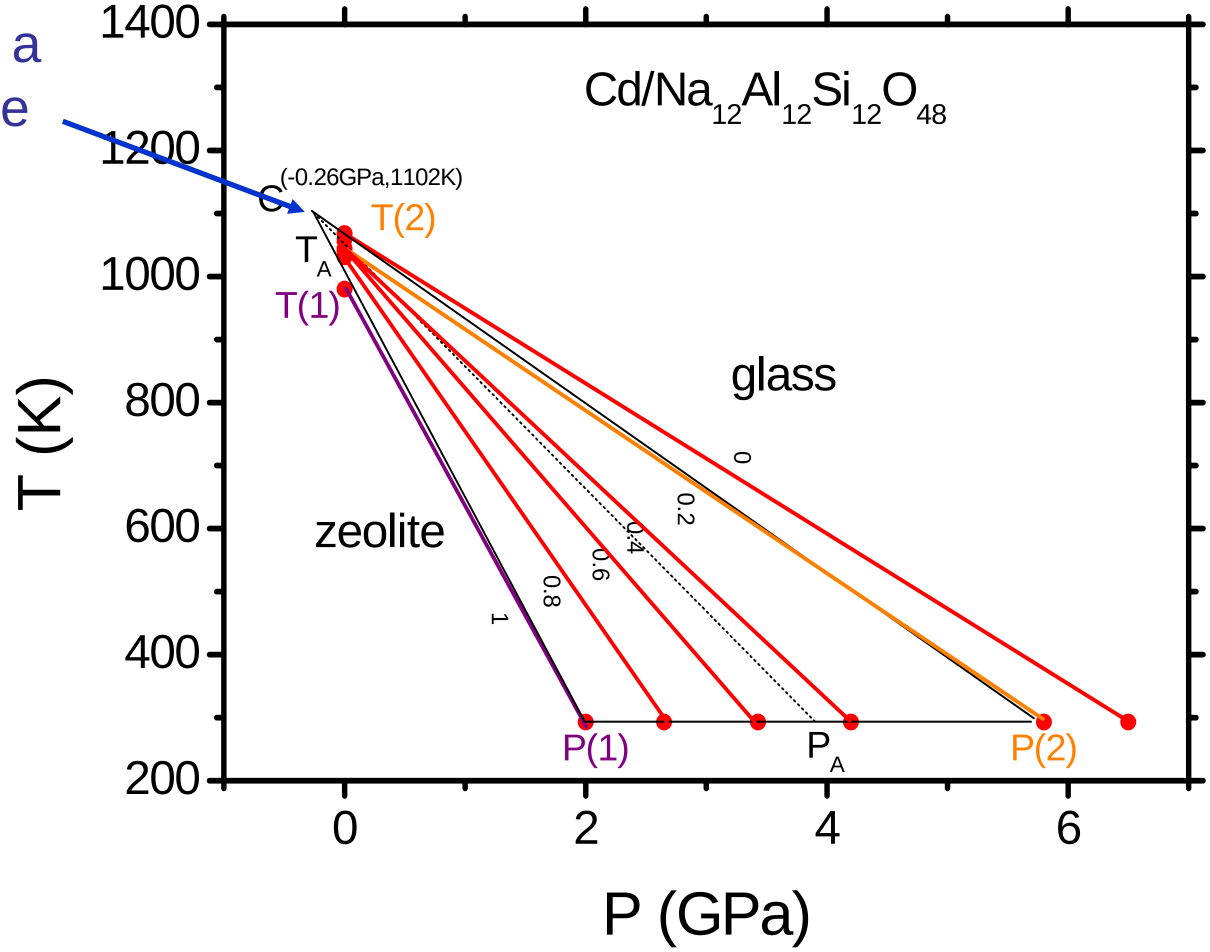
Limits for glass formation

Temperature and Pressure-induced Amorphisation are equivalent

$$P_A \Delta V_A \sim 3RT_A$$

Zeolite Collapse - T-P relationships

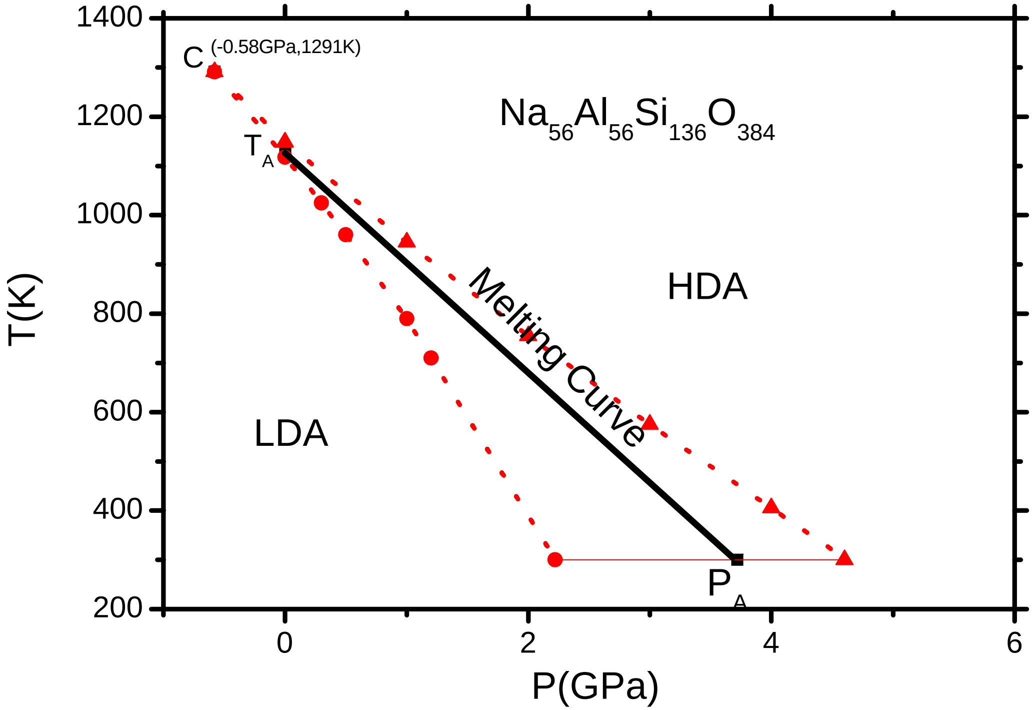
P_1-T_1 and P_2-T_2 point to a Critical Point at negative pressure



Prologue

polyamorphism and zeolite collapse

Which vibrations promote polyamorphism and trigger zeolite collapse?



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E. Rapoport, J. Chem.Phys. **46**, 2891 (1967); ibid **48**, 1433 (1968)

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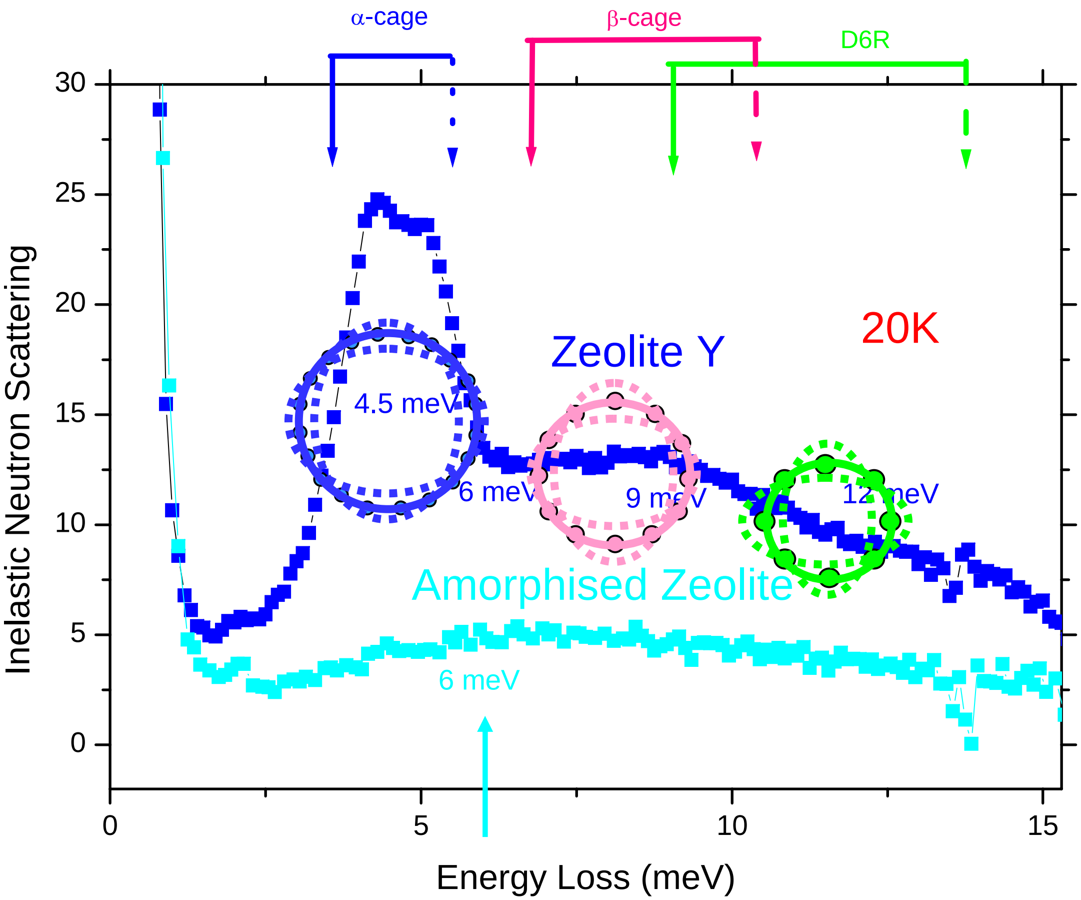
Inelastic neutron scattering

Low frequency modes

Zeolite modes relate to Secondary Building Units SBUs



Boson Peak

low frequency mode

$\nu = v_{t/l}/\lambda$

$V_{t/l}$, speed of sound:

longitudinal 5181 ms^{-1}
transverse 3358 ms^{-1}

λ= circumference of sbus

microporous enhancement

Low Frequency

Modes

Inelastic neutron scattering

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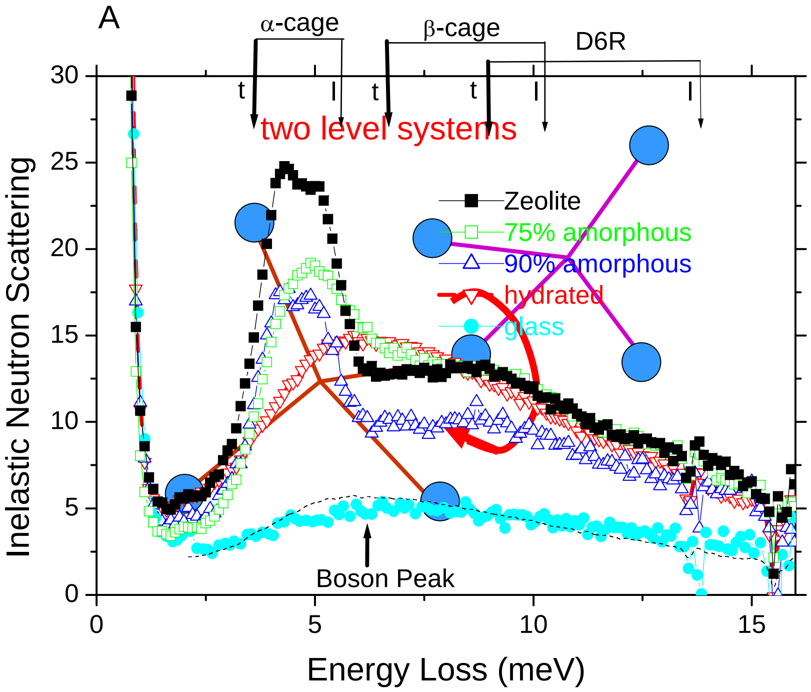

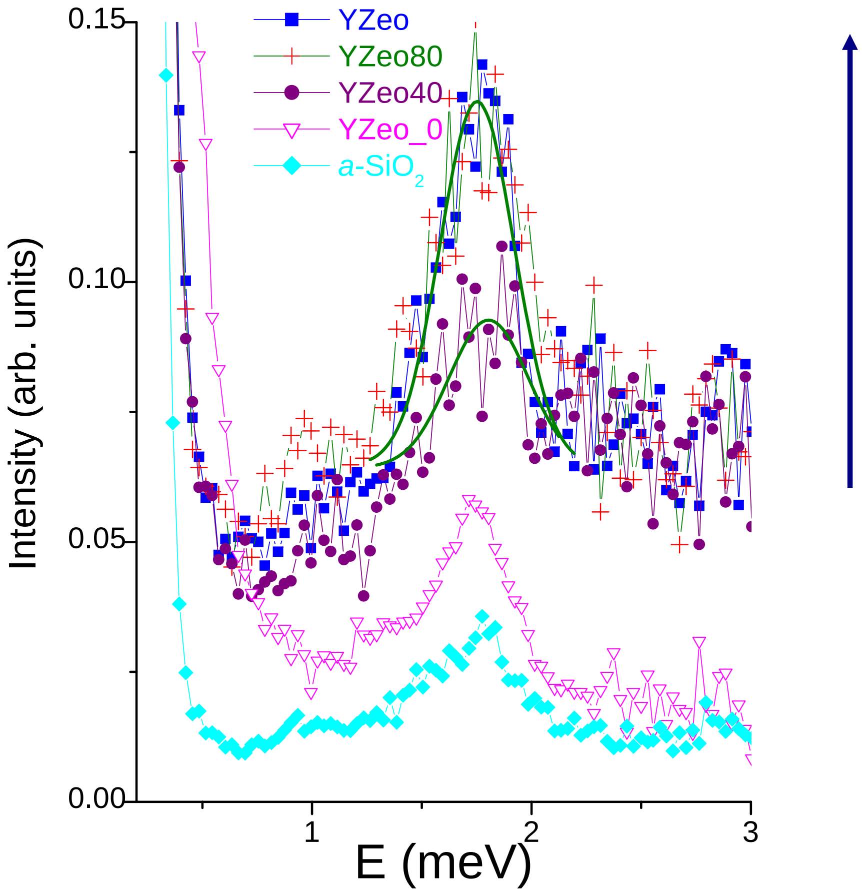

$S(Q,\underline{E}) \propto Q^2$

librational modes

1 – 3 meV

sound propagating
acoustic modes

$S(Q,\underline{E}) \propto Q$

localised modes

microporous enhancement

Temperature Dependence

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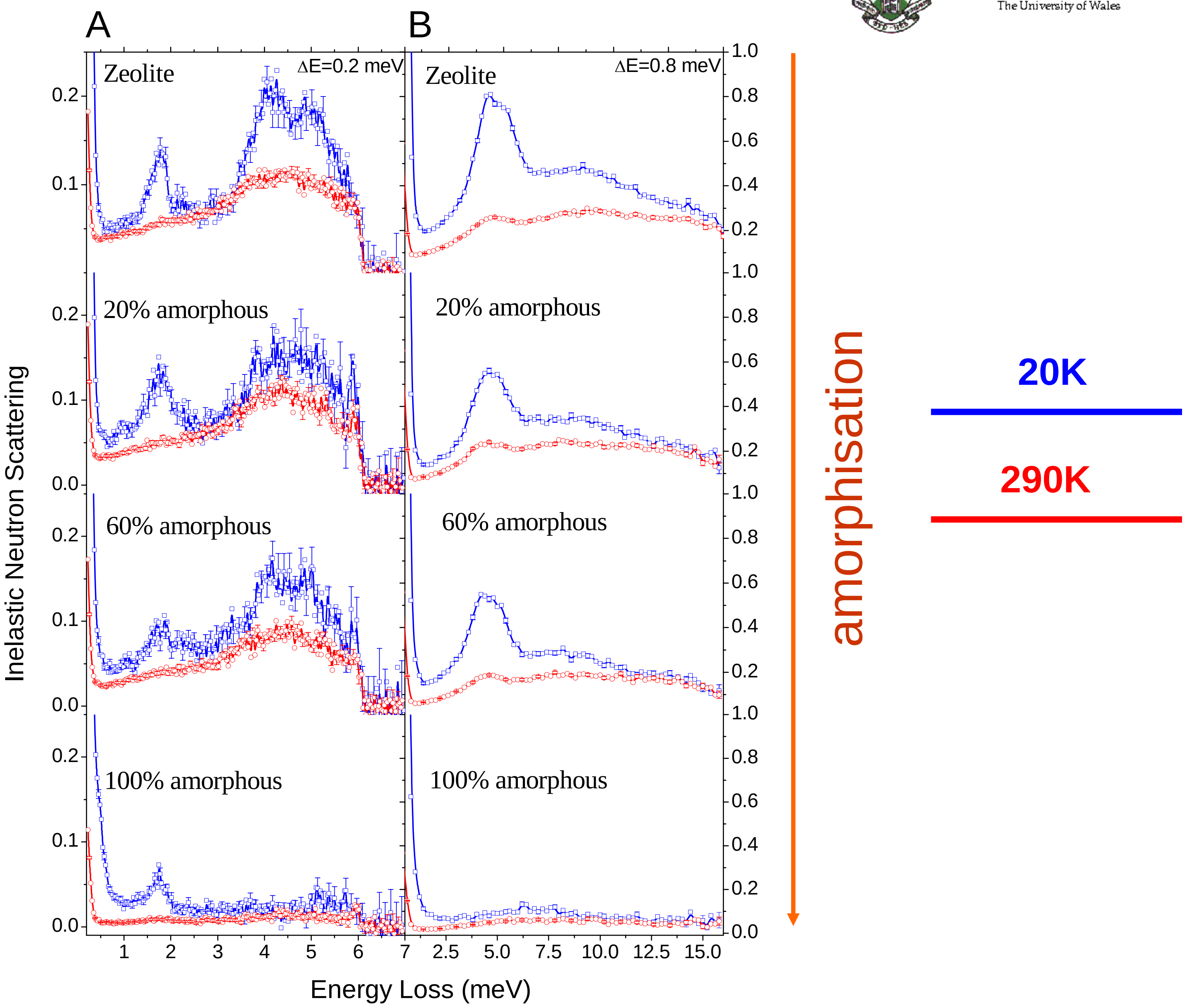
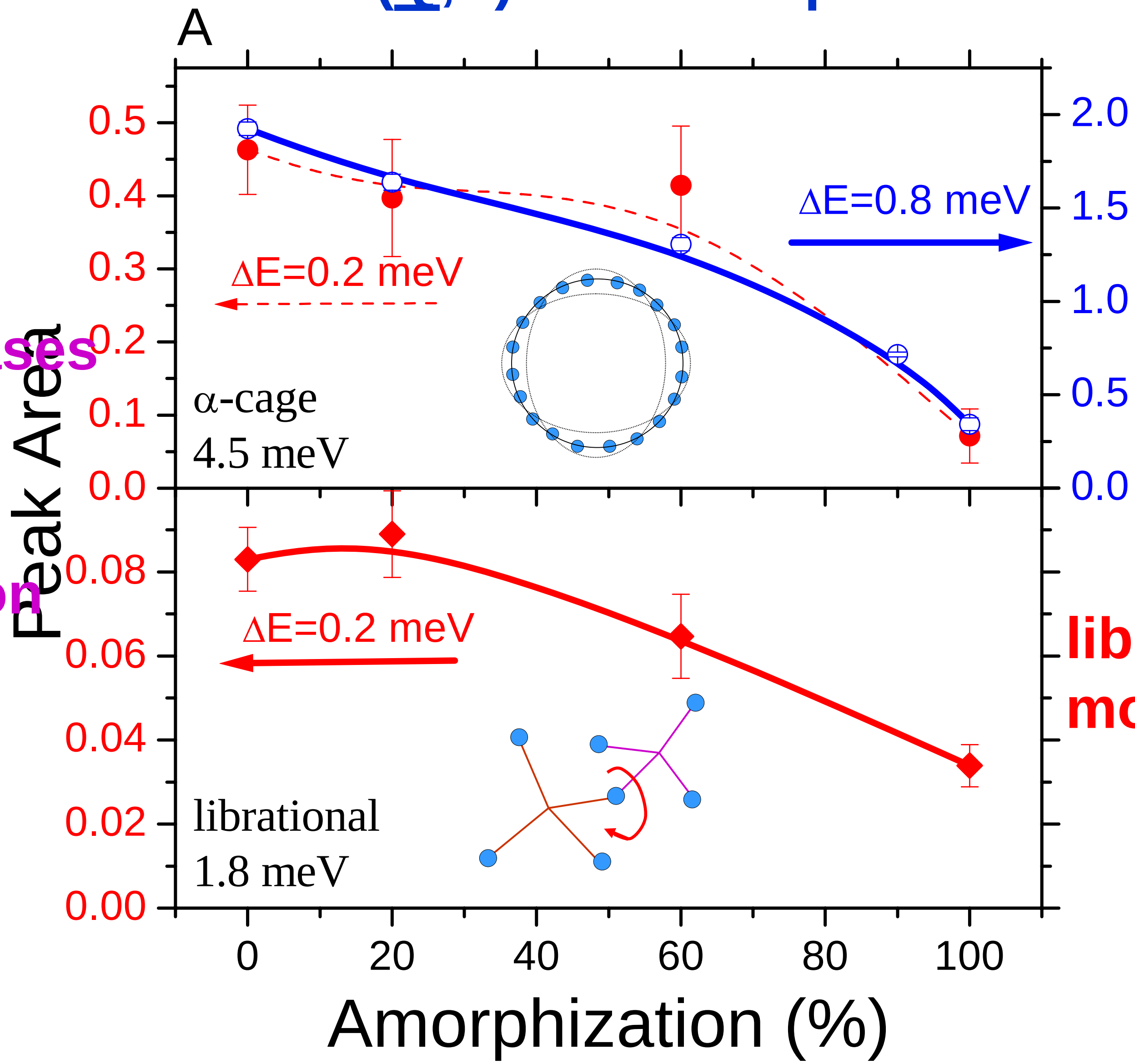
Low frequency modes

both sound propagating and localised modes are anharmonic



Low frequency modes

Decrease in S(Q,E) with amorphisation



S(Q,E) deceases non-linearly

with amorphisation

Boson Peak

librational modes

Amorphous contribution

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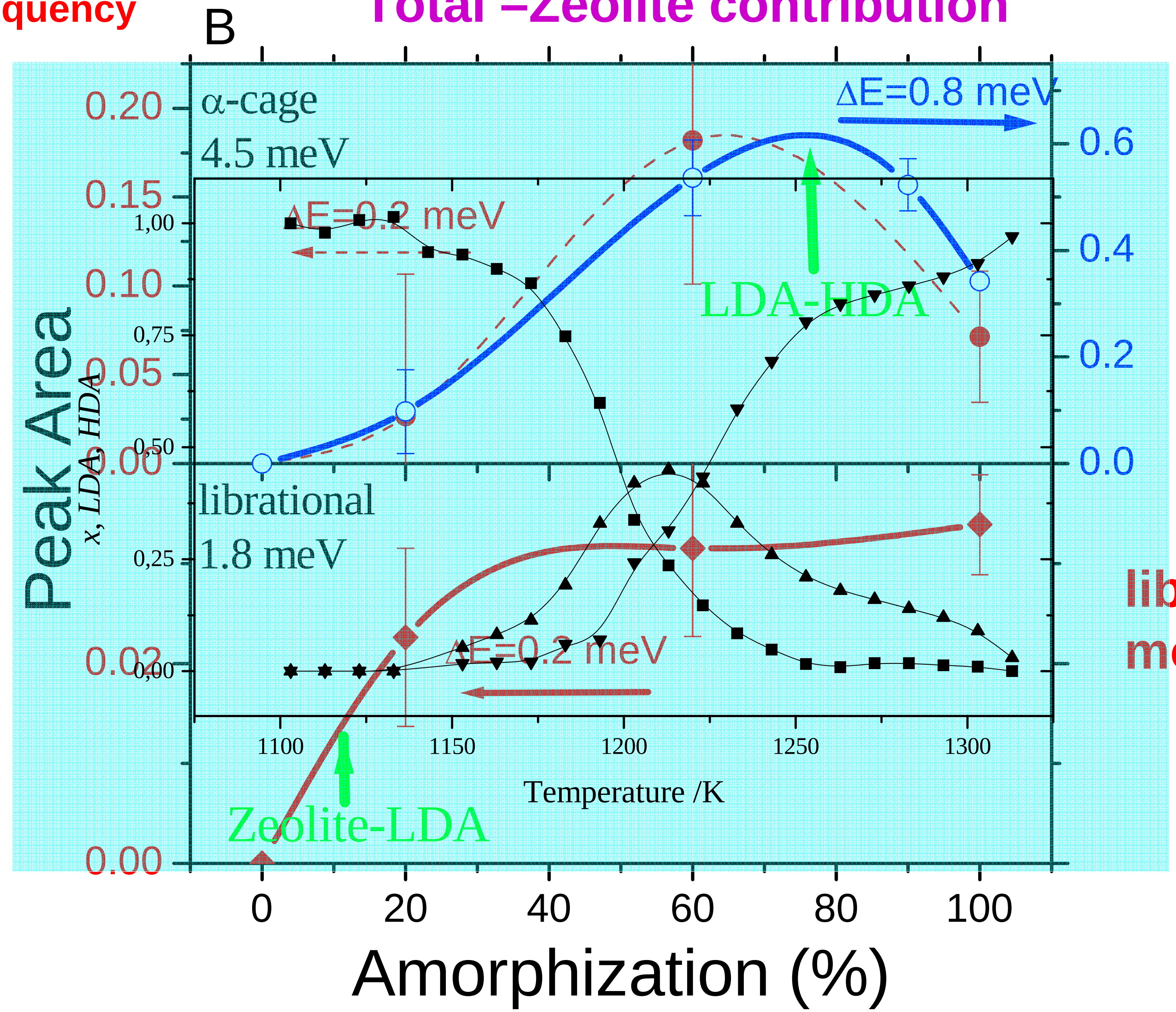
Total –Zeolite contribution

Low frequency modes



Boson Peak

librational modes

S(Q,E) for Amorphous contribution

$S(Q,E)_{Total} - S(Q,E)_{Zeolite}$

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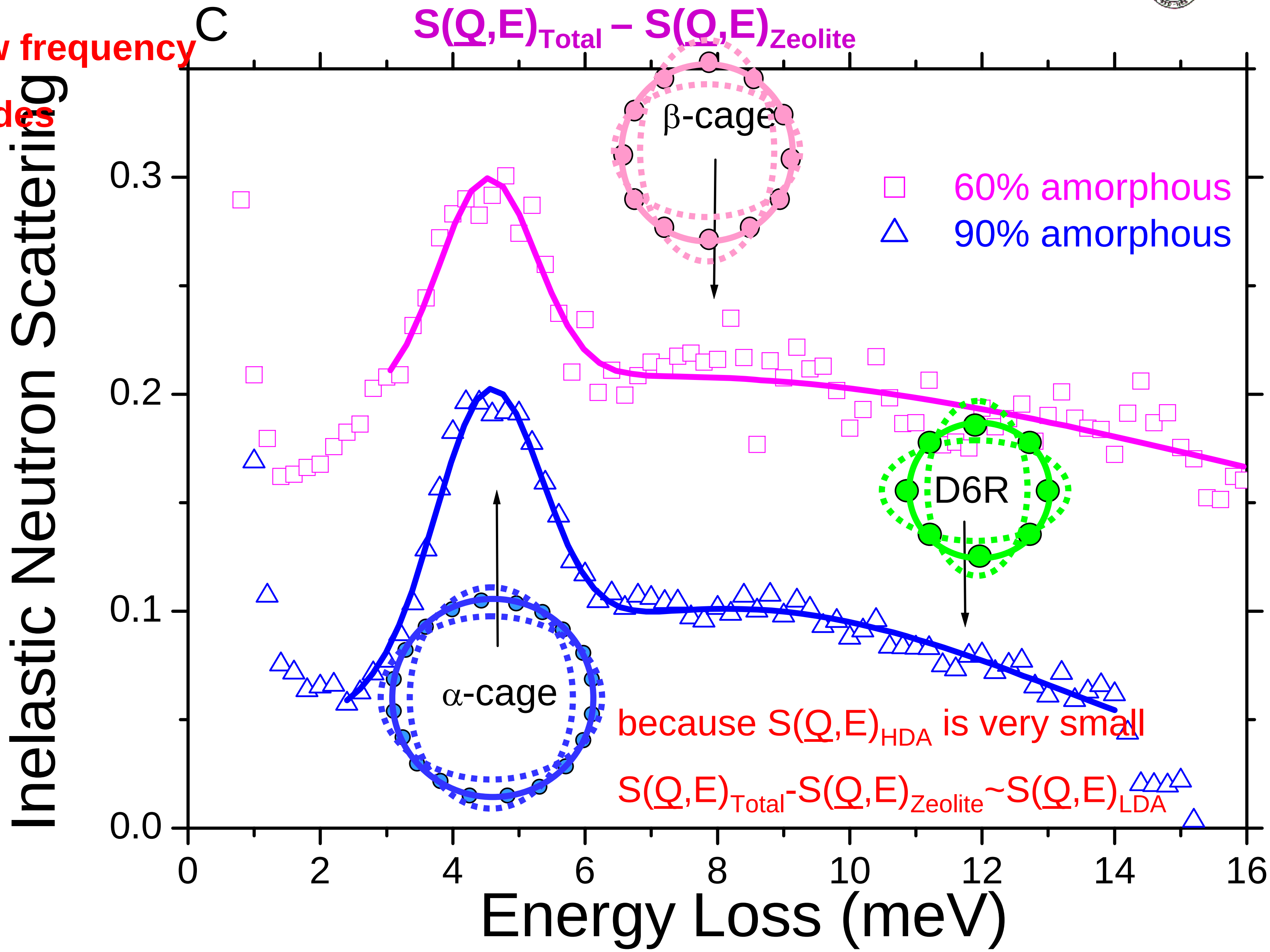
Low frequency modes



because $S(Q,E)_{HDA}$ is very small

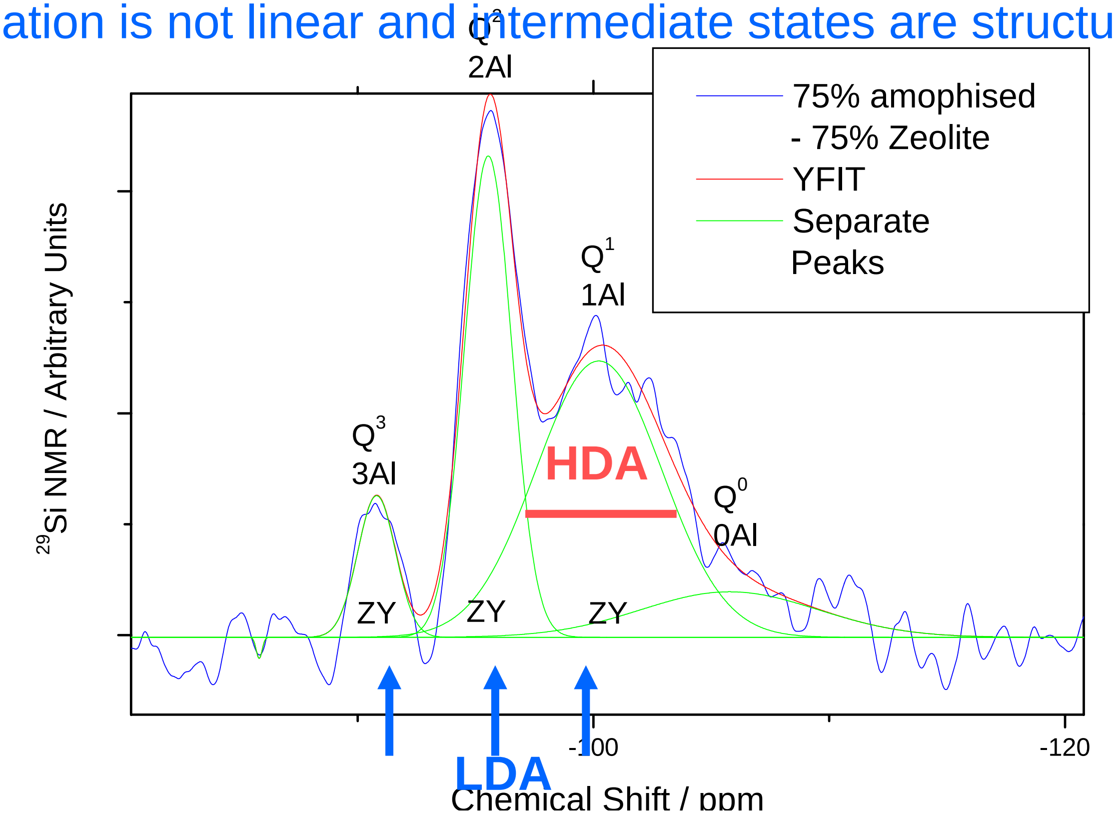
$S(Q,E)_{Total}-S(Q,E)_{Zeolite} \sim S(Q,E)_{LDA}$

^{29}Si NMR

1 Si and Al are ordered in zeolites and Si NMR is structured

2 Si and Al are disordered in HDA glass and Si NMR comprises a single peak

3 Conversion of zeolite spectrum into glass spectrum through amorphisation is not linear and intermediate states are structured



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Conclusions

•Inroduction
Melting v Amorphisation, Microscopy

•Low temperature dynamics
Anomalous CP, TLS, Boson Peak

•Zeolite Collapse
SBUs, SAXS/WAS, Low Density and High Density Phases (LDA, HDA)

•Low frequency Modes -
Boson Peak enhancement, surface modes, anharmonicity, TLS and microporous instability, evidence for LDA


Na Zeolite Y - ambient pressure

Zeolite amorphisation is a catastrophic and irreversible order transition

this is the supercage

Na Zeolite Y - ambient pressure

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this was the supercage

Na Zeolite Y – 3.8 GPa