Coordination Numbers of Glass Formers – Composition-dependence

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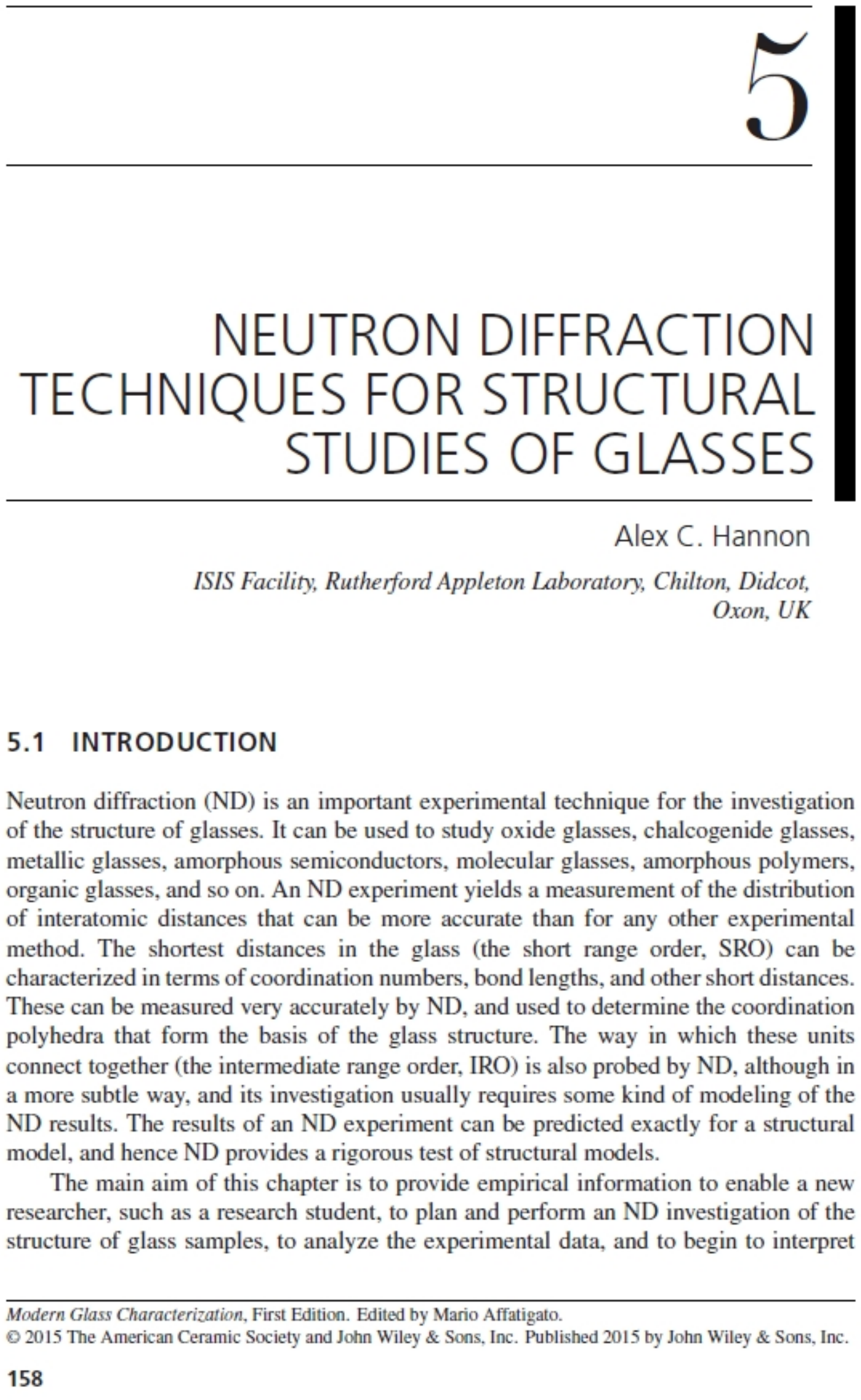
Overview

1. Neutron diffraction
2. Pure GeO_2 glass
3. Cs_2O-GeO_2 glasses
4. Charge avoidance model
5. Li_2O-GeO_2 glasses
6. CaO-GeO_2 glasses
7. Pure amorphous TeO_2
8. K_2O-TeO_2 glasses

Please also see this long (83 pages) book chapter



5

NEUTRON DIFFRACTION TECHNIQUES FOR STRUCTURAL STUDIES OF GLASSES

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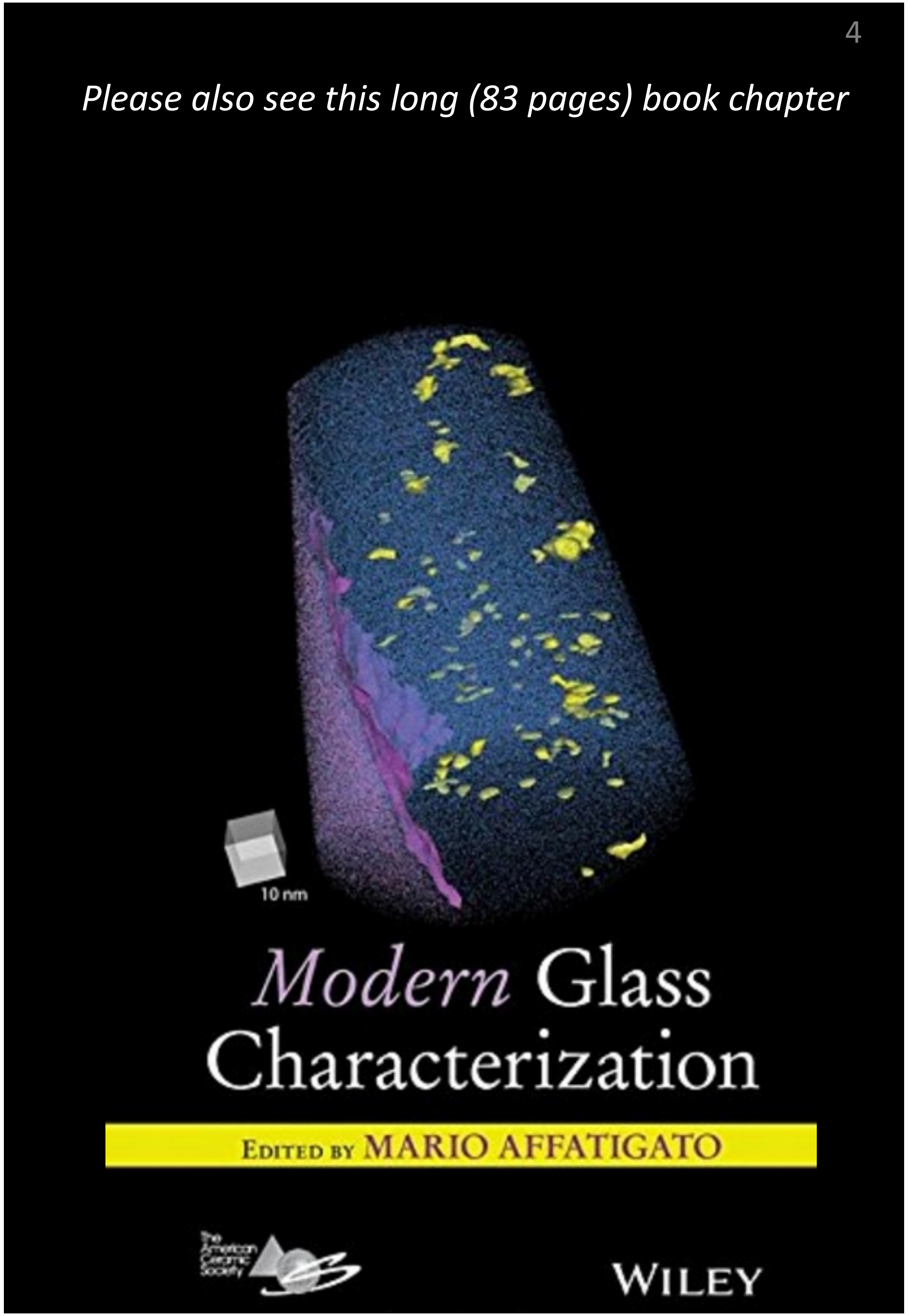
5.1 INTRODUCTION

Neutron diffraction (ND) is an important experimental technique for the investigation of the structure of glasses. It can be used to study oxide glasses, chalcogenide glasses, metallic glasses, amorphous semiconductors, molecular glasses, amorphous polymers, organic glasses, and so on. An ND experiment yields a measurement of the distribution of interatomic distances that can be more accurate than for any other experimental method. The shortest distances in the glass (the short range order, SRO) can be characterized in terms of coordination numbers, bond lengths, and other short distances. These can be measured very accurately by ND, and used to determine the coordination polyhedra that form the basis of the glass structure. The way in which these units connect together (the intermediate range order, IRO) is also probed by ND, although in a more subtle way, and its investigation usually requires some kind of modeling of the ND results. The results of an ND experiment can be predicted exactly for a structural model, and hence ND provides a rigorous test of structural models.

The main aim of this chapter is to provide empirical information to enable a new researcher, such as a research student, to plan and perform an ND investigation of the structure of glass samples, to analyze the experimental data, and to begin to interpret

Modern Glass Characterization, First Edition. Edited by Mario Affatigato.



Modern Glass Characterization

EDITED BY MARIO AFFATIGATO

The American Ceramic Society

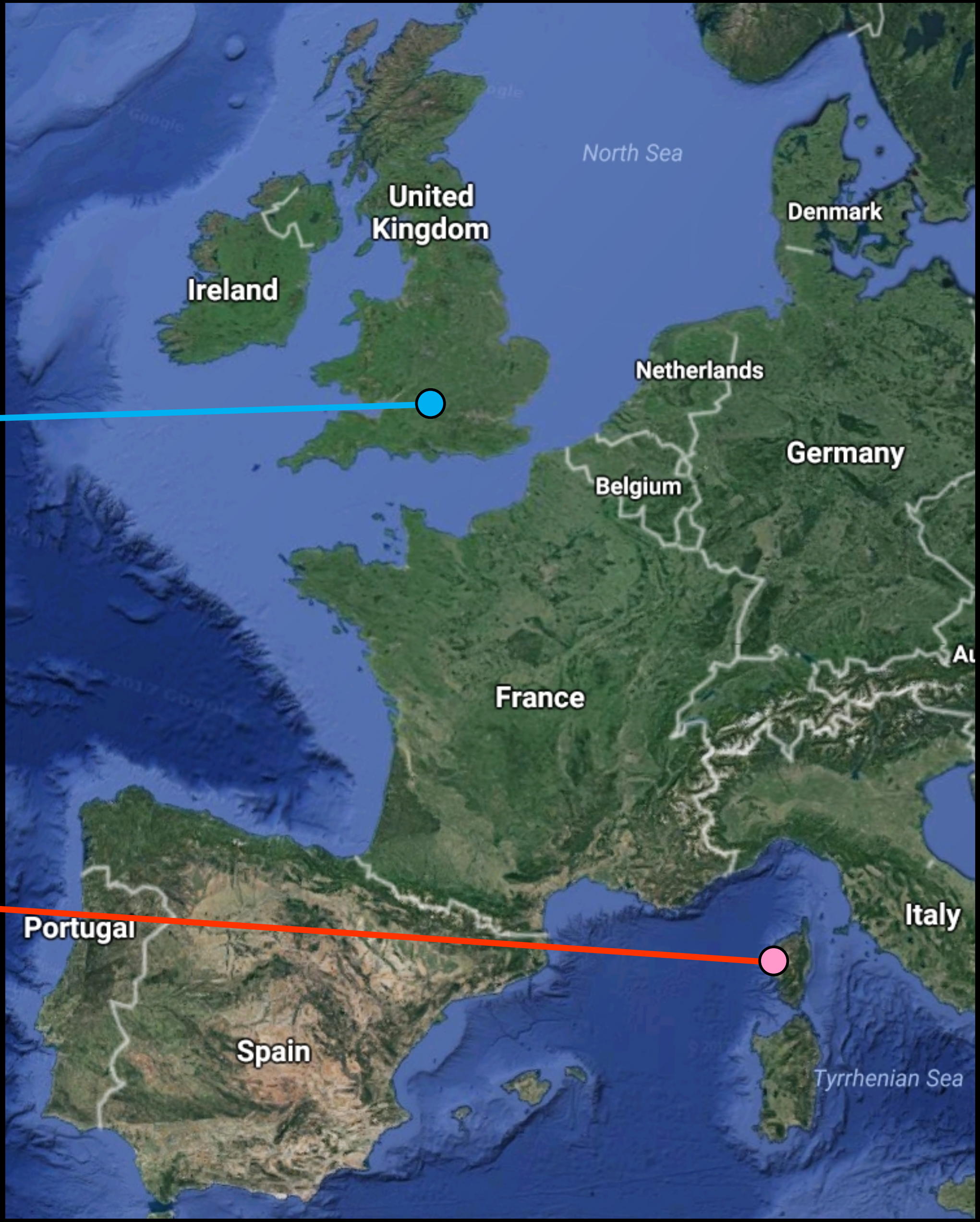
WILEY

The ISIS Facility

ISIS

The world's leading pulsed neutron and muon source

Nous sommes ici



ISIS Facility, Neutron Source

Rutherford Appleton Laboratory

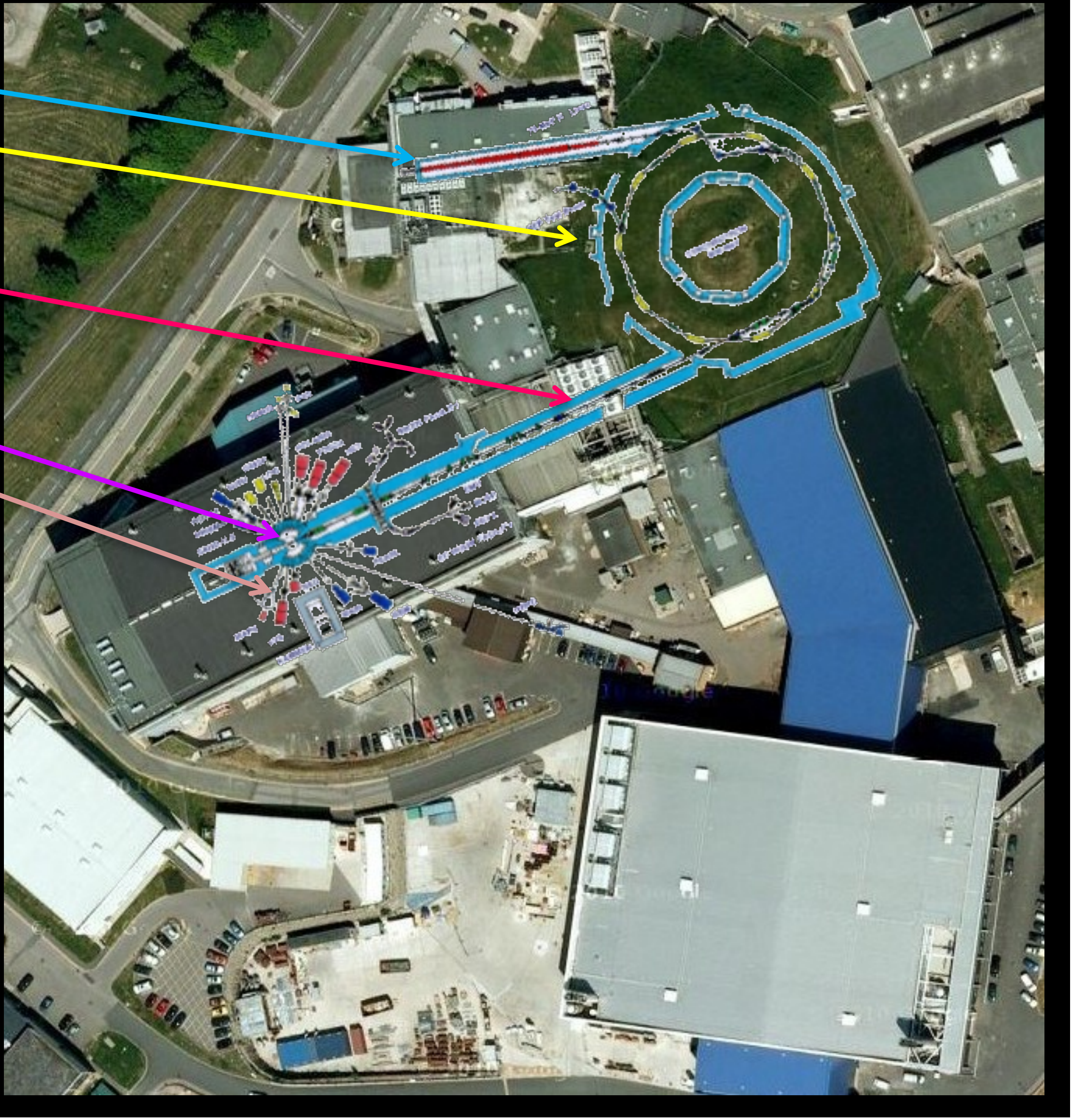
ISIS – the name

- ISIS is not an acronym (Intense Safety Instruction Seminary?)
- ISIS is not involved in Syria or Iraq
- ISIS is the Egyptian goddess of rebirth

Isis was the wife of the god Osiris.
His brother, Seth, slew Osiris and dropped
his body into the Nile.
Isis rescued the body of her husband.
Seth stole the body and hacked it into fourteen pieces.
Isis gathered together his pieces and bound
him together to make him whole.

- The ISIS accelerator was constructed from the parts of a previous nuclear physics accelerator.

ISIS Neutron Source from Above



H- Linac

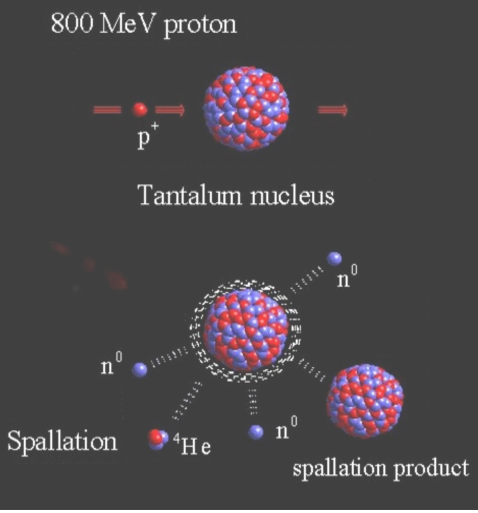
Proton synchrotron

Proton beam

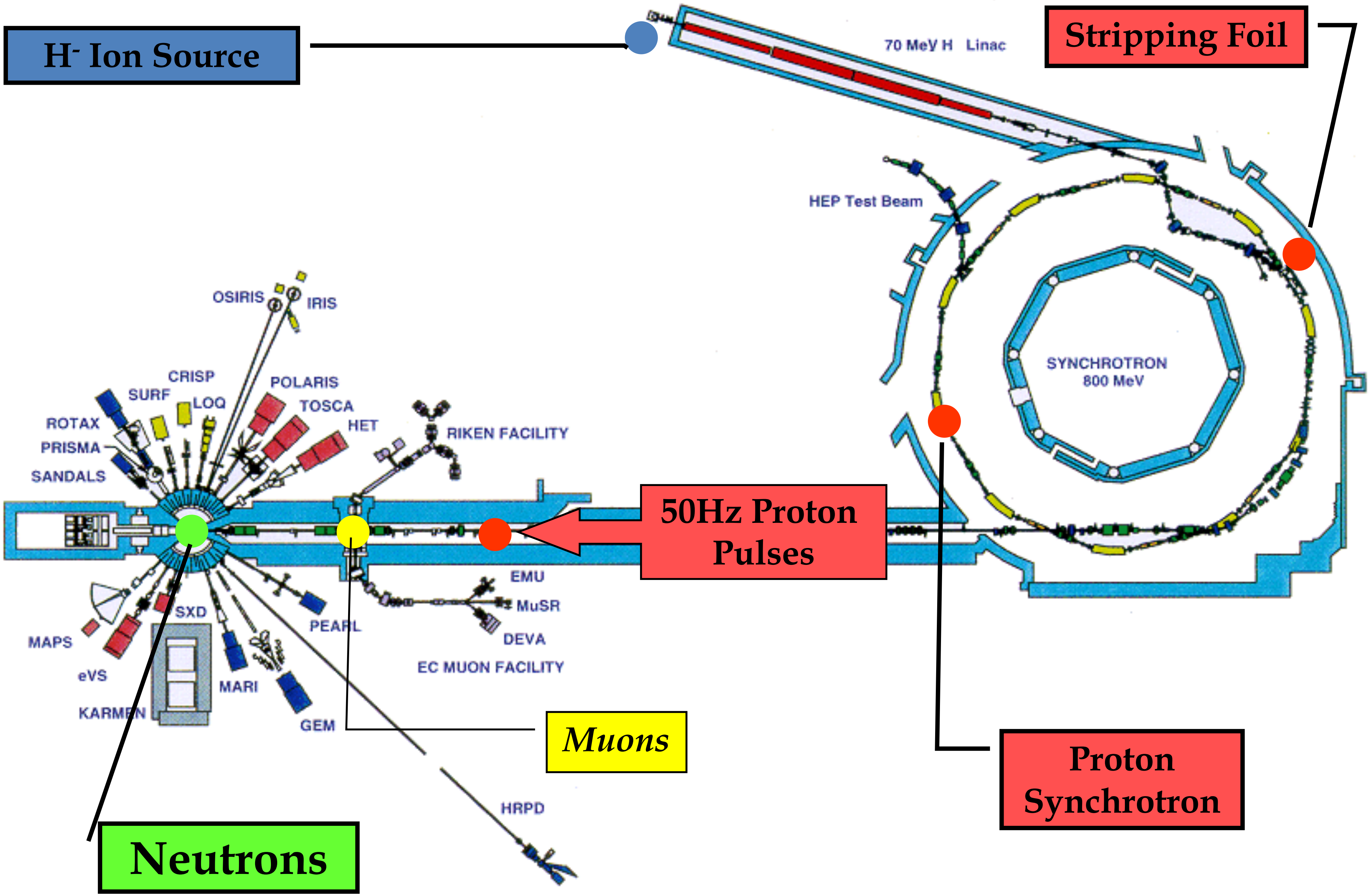
Neutron target

Neutron scattering instruments

Spallation: Energetic proton → heavy nucleus → neutrons + lighter nucleus



The ISIS Spallation Neutron Source



H^- Ion Source

Stripping Foil

50Hz Proton Pulses

Muons

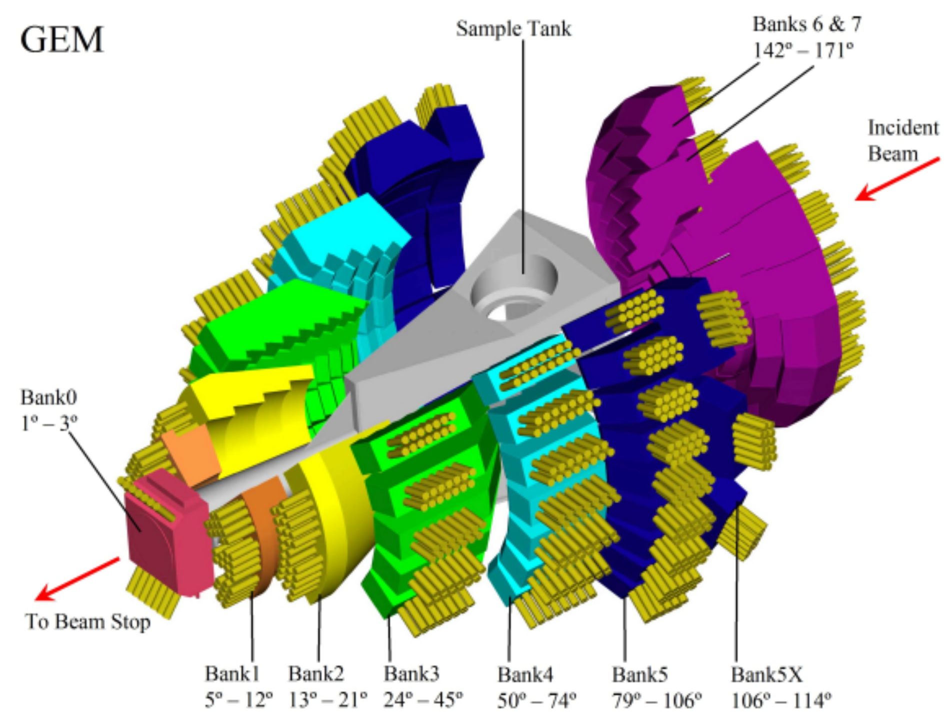
Proton Synchrotron

Neutrons

GEM (GEneral Materials Diffractometer)

funded by EPSRC + Riken
(total cost ~ £4-5 million)

GEM diffractometer *(Hannon, Nucl Inst Meth A 2005)*



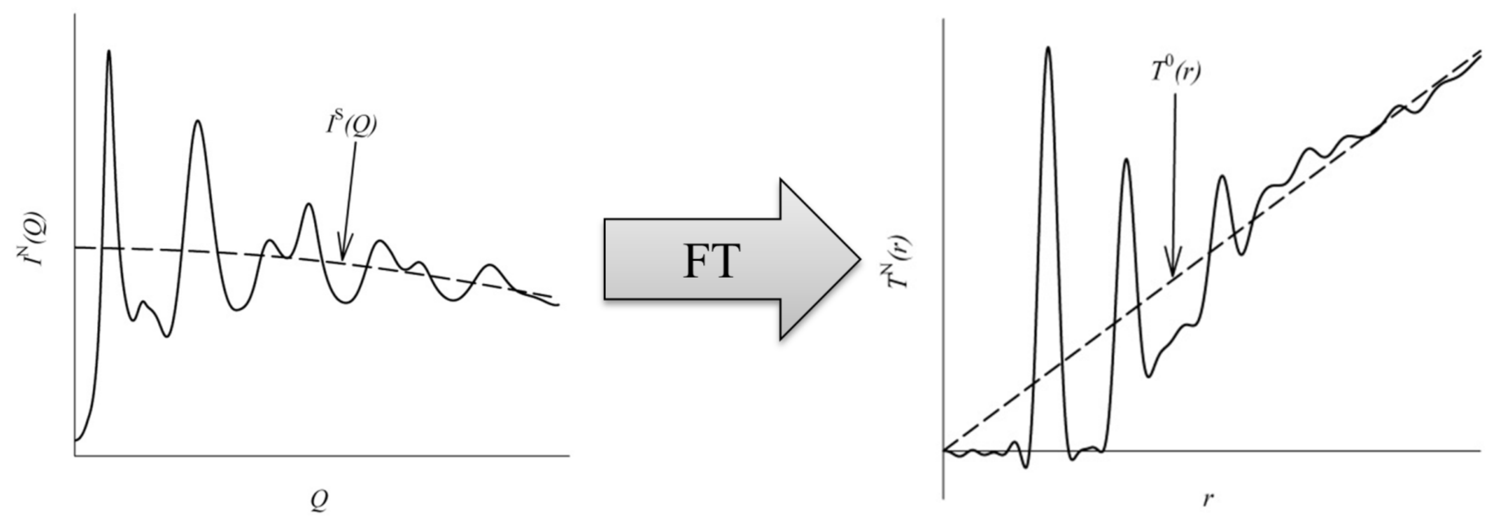
7290 detectors
construction from 1999 to 2004

- State of the art neutron diffractometer for glass and powder diffraction at the ISIS Facility

Glass Diffraction

$$T(r) = T^0(r) + \frac{2}{\pi}\int_0^\infty Q i(Q) M(Q) \sin(rQ)\, dQ$$

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



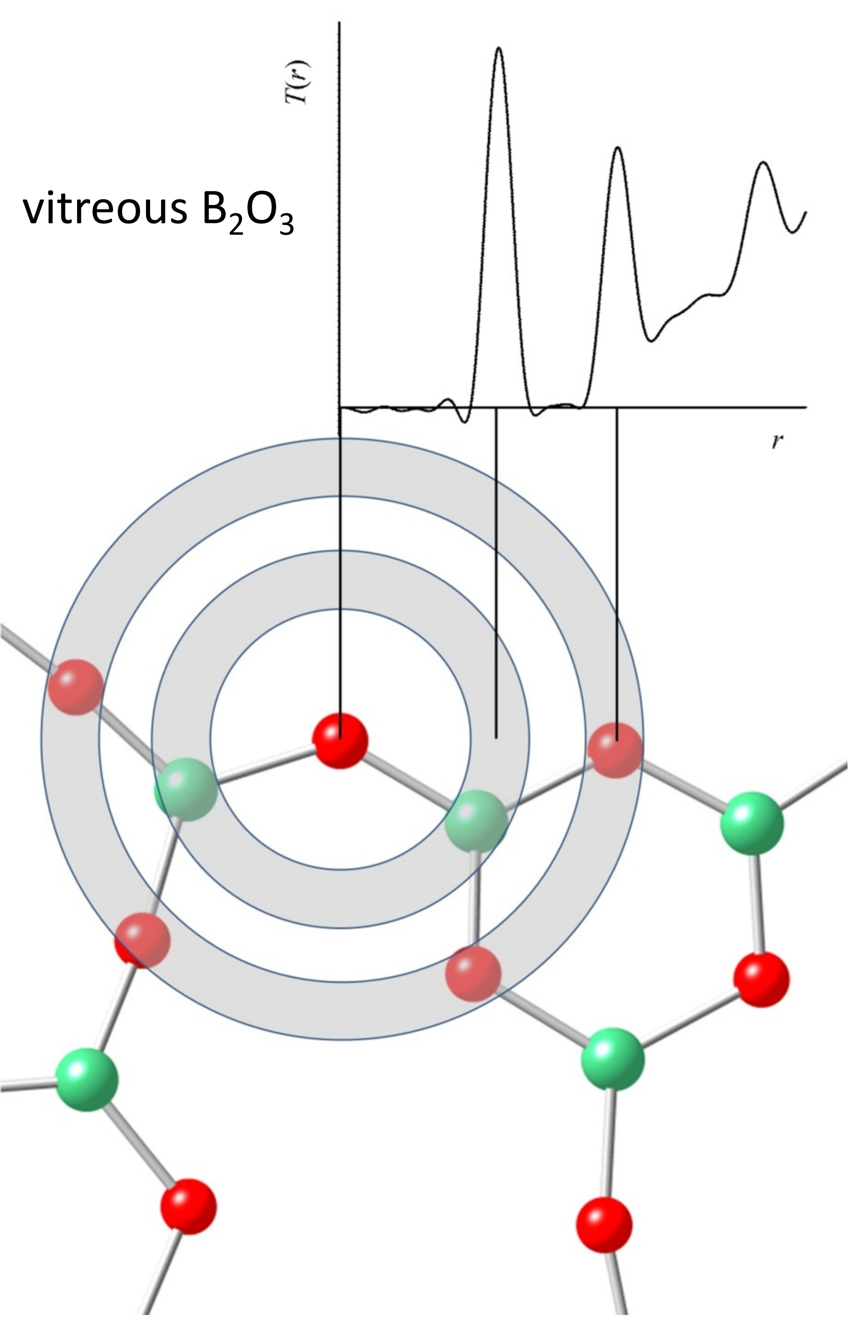
Diffraction pattern I(Q)

Total correlation function T(r)

- Glass diffraction pattern, *I(Q)*, consists of broad peaks, similar to a damped sine wave
- Fourier transformation leads to a real-space correlation function
- Pulsed neutrons give high *Q*, leading to good real-space resolution

What does the correlation function mean?

- A peak in $T(r)$ indicates an interatomic distance that occurs frequently in the sample
- Peak area gives the coordination number n_{jk}
- Peak position r_{jk} gives the bond length
- Peak width/shape gives distribution of distances



Correlation Function Peak

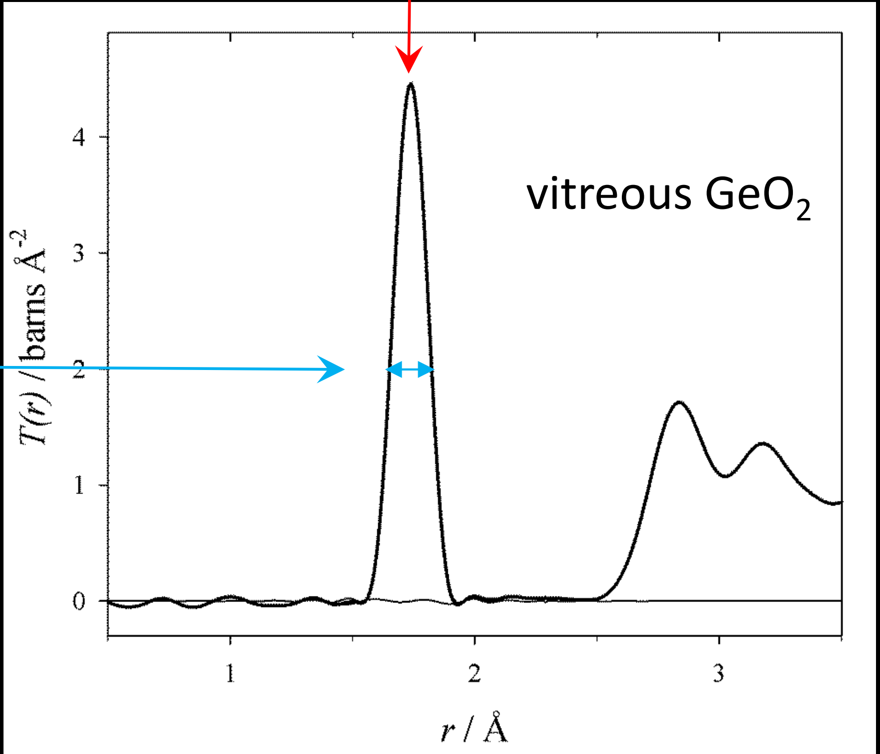
- Peak area A_{jk} gives coordination number n_{jk}
- Peak position r_{jk} gives bond length
- Peak width σ arises from:
  - r-space resolution (Q_{max})
  - thermal motion
  - static disorder

$$\boxed{n_{jk} = \frac{r_{jk} A_{jk}}{\left(2 - \delta_{jk}\right) c_j \bar{b}_j \bar{b}_k}}$$

area A_{GeO}

position r_{GeO}

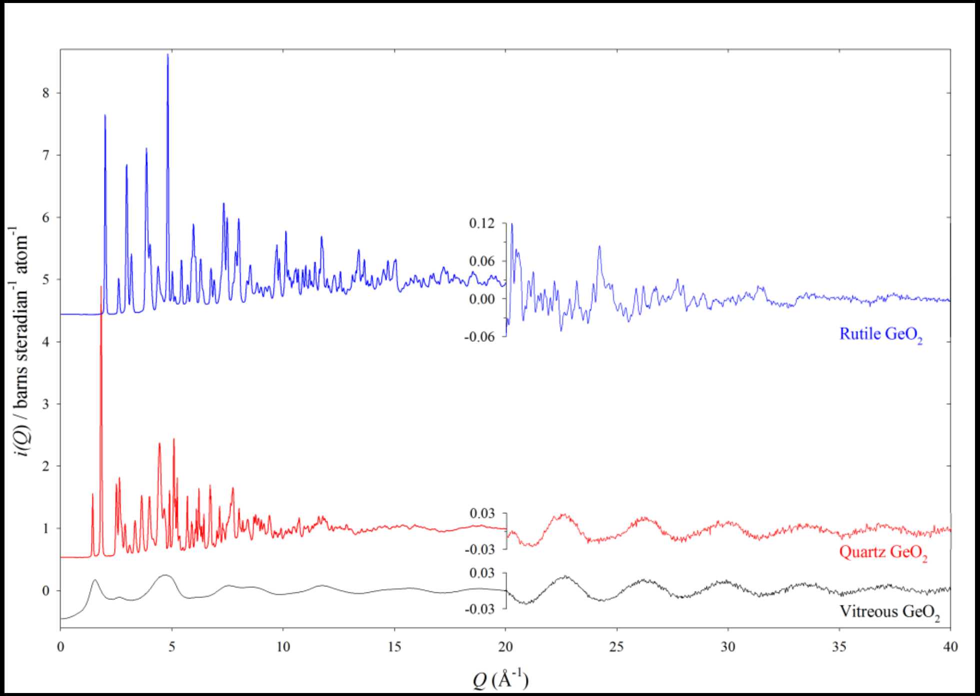
width σ



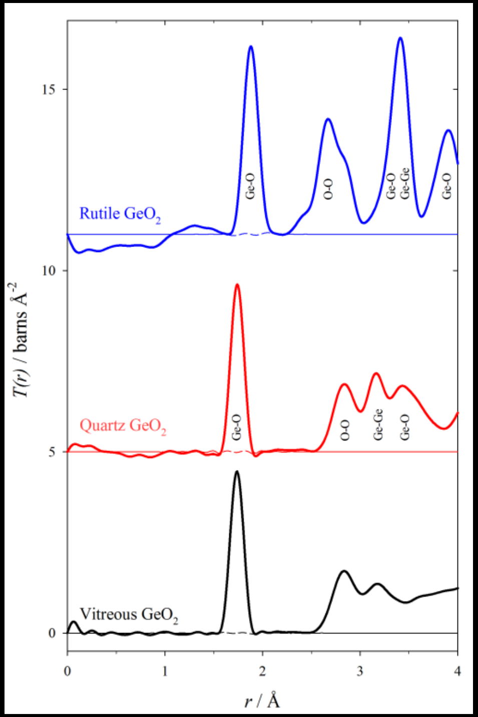
(Hannon, J Phys Chem B 2007)

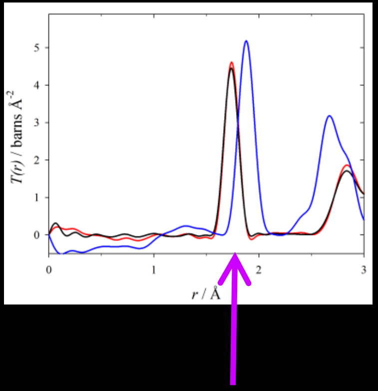
Accurate coordination numbers need:
1. accurate sample composition
2. accurate density
(Alderman, J Non-Cryst Solids 2014)

Pure GeO_2 Neutron Diffraction



(Hannon, J Phys Chem B 2007)



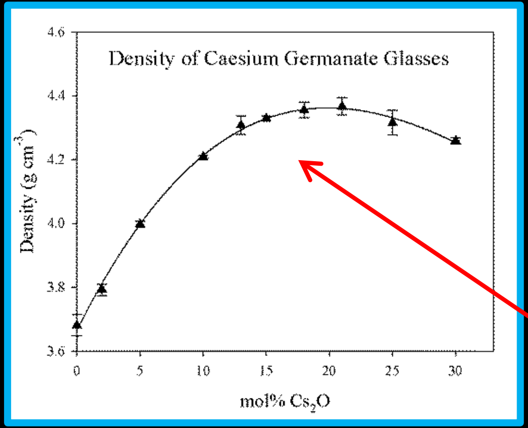


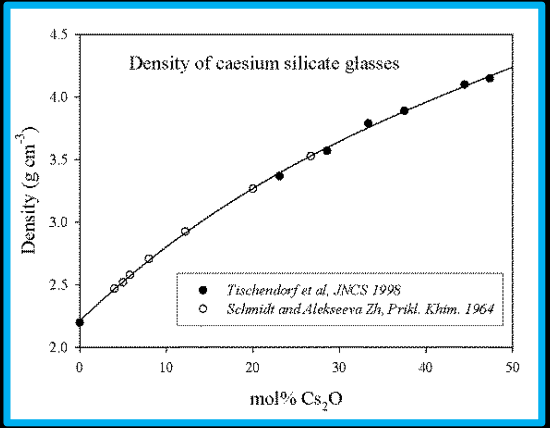
Ge-O
peak

Fits to Ge-O peak			
Rutile GeO_2	n_{GeO}=5.70	Octahedral	r_{GeO}=1.8805Å
Quartz GeO_2	n_{GeO}=4.06	Tetrahedral	r_{GeO}=1.7402Å
GeO_2 Glass	n_{GeO}=4.03	Tetrahedral	r_{GeO}=1.7369Å

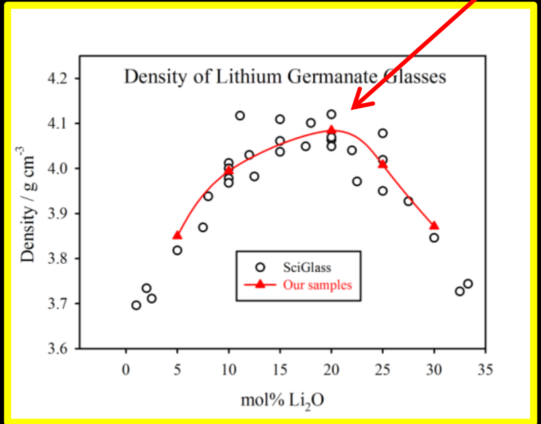
The Germanate Anomaly

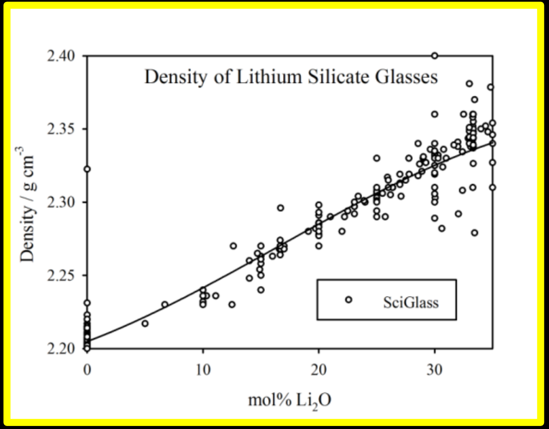
- Thermophysical properties of germanate glasses (e.g. density) show a maximum/minimum as modifier (e.g. Cs_2O or Li_2O) is added – this is the *germanate anomaly*





Density maximum at ~20 mol% Cs_2O or Li_2O for germanate glasses





No such density maximum for silicate glasses

Change in Ge-O Coordination

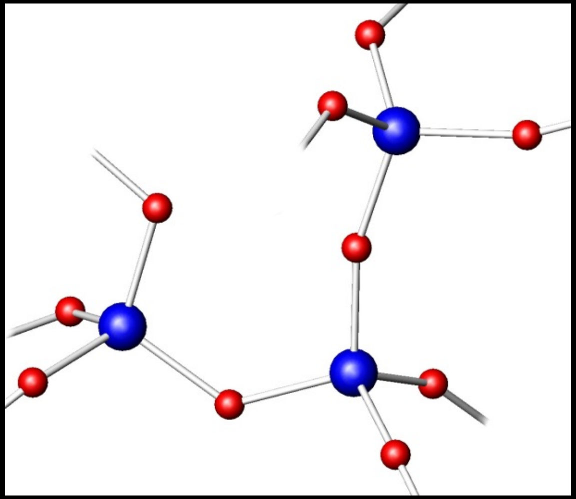
- In 1960s the *germanate anomaly* was ascribed to a growth and decline in number of GeO_6 octahedra in the glass
  (Ivanov & Evstropiev, Dok. Ak. Nauk SSSR 1962; Murthy & Ip, Nature, 1964)

Crystalline forms of GeO_2			
Quartz GeO_2	All GeO_4 tetrahedra	$\rho = 4.28$ g/cm^3	$r_{GeO} = 1.7402$Å
Rutile GeO_2	All GeO_6 octahedra	$\rho = 6.25$ g/cm^3	$r_{GeO} = 1.8805$Å

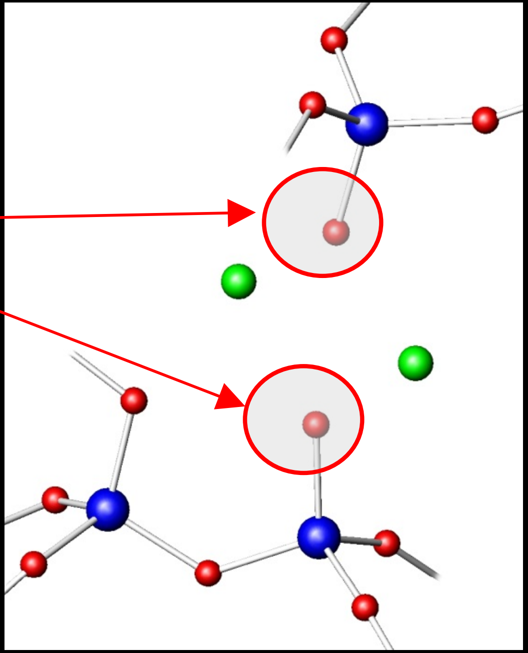
- No direct evidence for Ge-O coordination change in glasses was available in the 1960s.

The creation of GeO_6 Octahedra

Pure GeO_2 glass

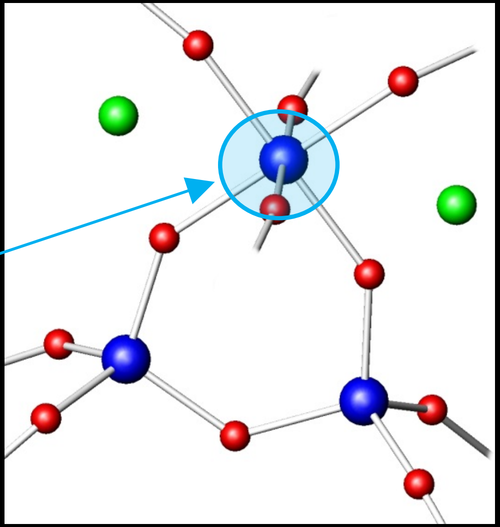


EITHER create two non-bridging oxygens



add Cs_2O

OR create one octahedral germanium



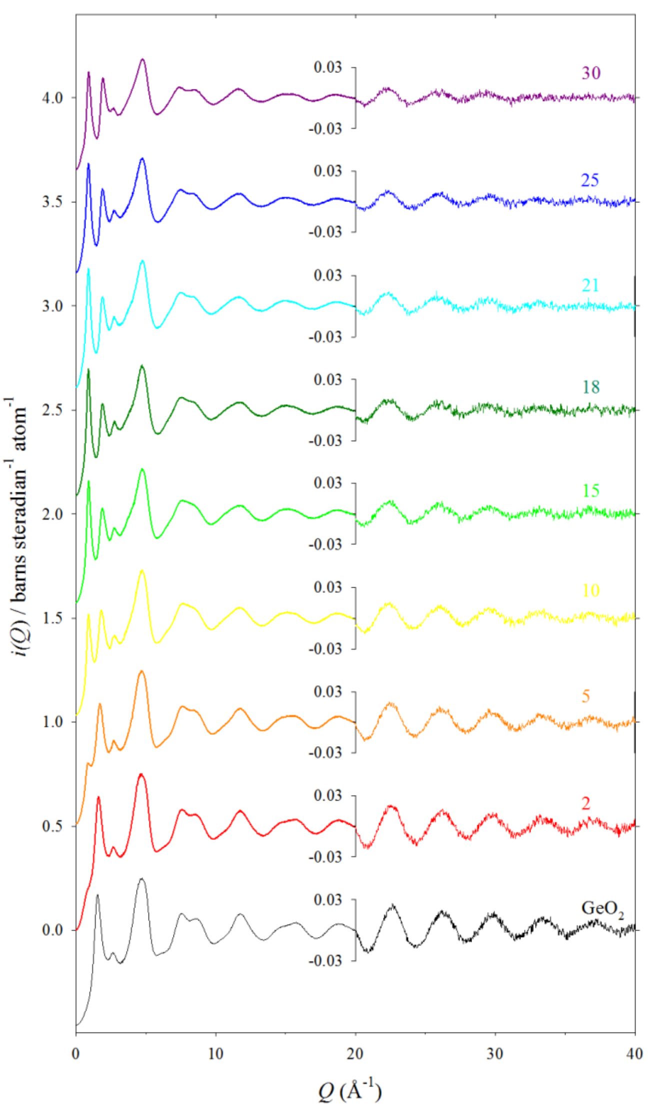
Neutron Diffraction – Caesium Germanate Glasses

30 mol.% Cs_2O

increasing Cs_2O content

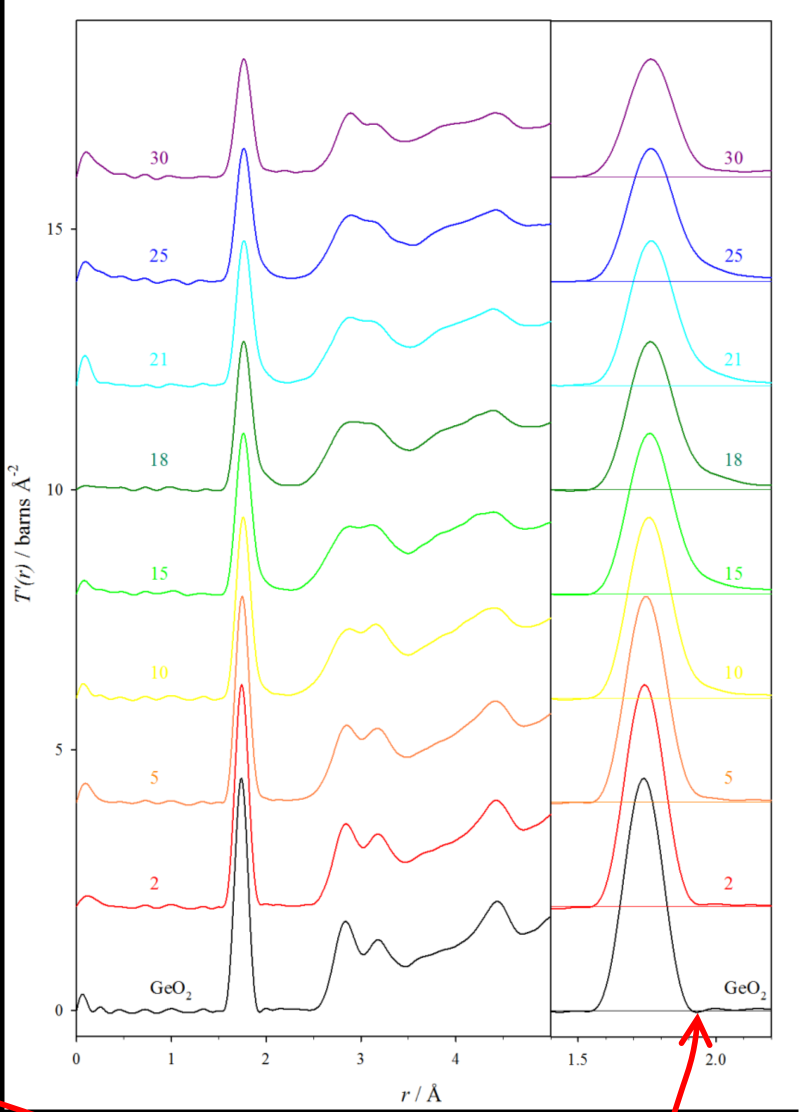
pure GeO_2

Diffraction patterns



Neutron diffraction on glasses with 0, 2, 5, 10, 15, 18, 21, 25 & 30 mol.% Cs_2O

Correlation functions



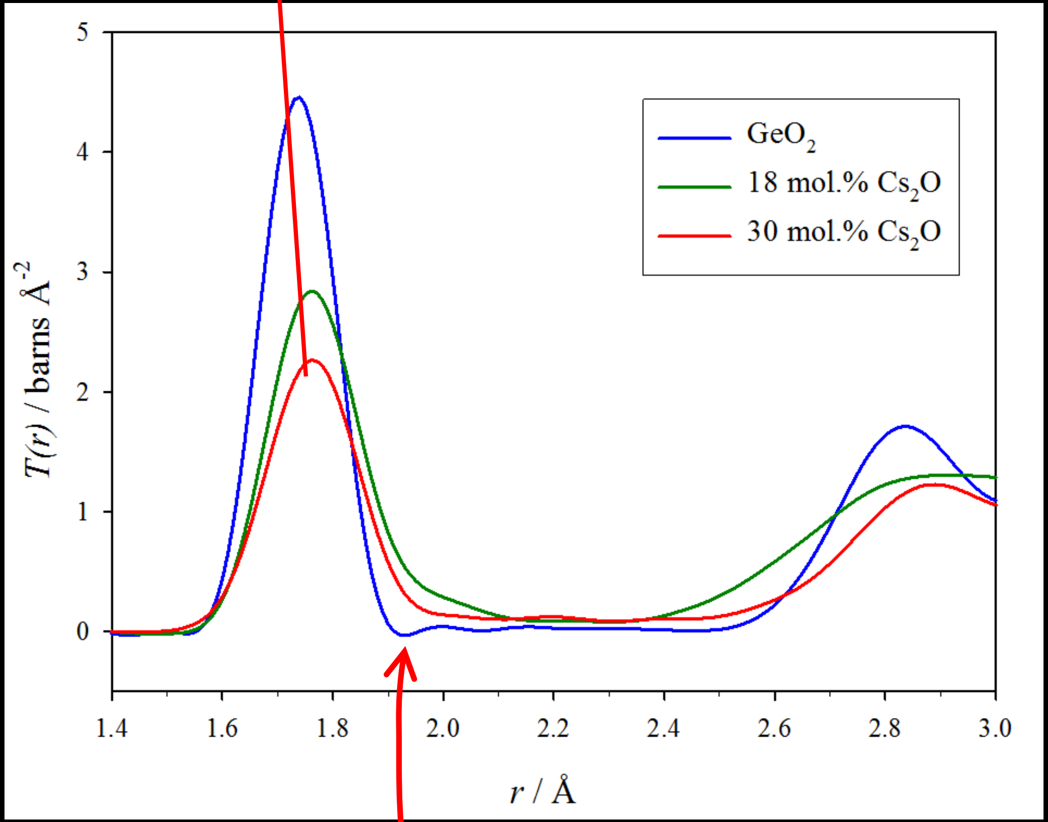
Ge-O peak moves to longer distance and a high-*r* shoulder develops

Cs_2O-GeO_2 glasses

Ge-O peak in correlation functions

Cs_2O-GeO_2 glasses

Ge-O peak moves to longer distance

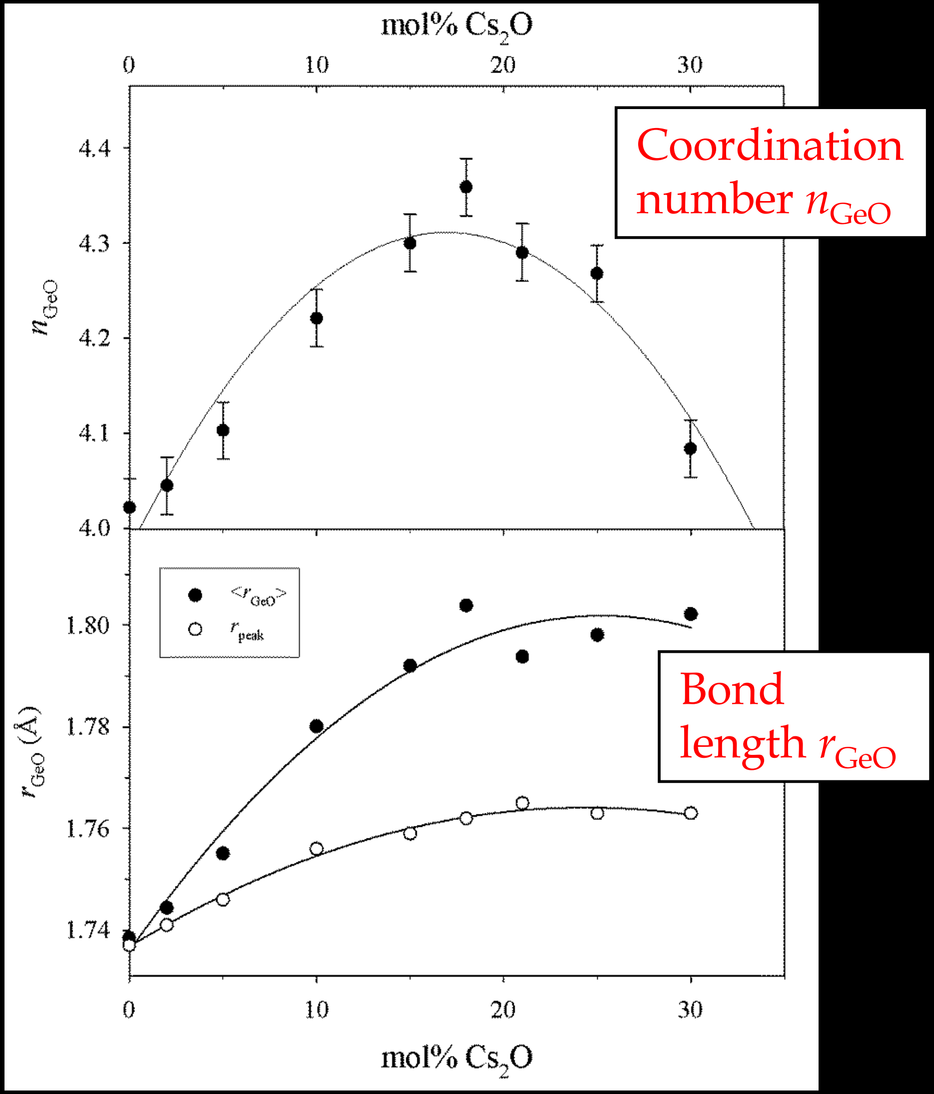


a high-*r* shoulder develops

(Cs-O bond lengths~3.2Å)

Measured Ge-O Coordination

Cs_2O-GeO_2 glasses



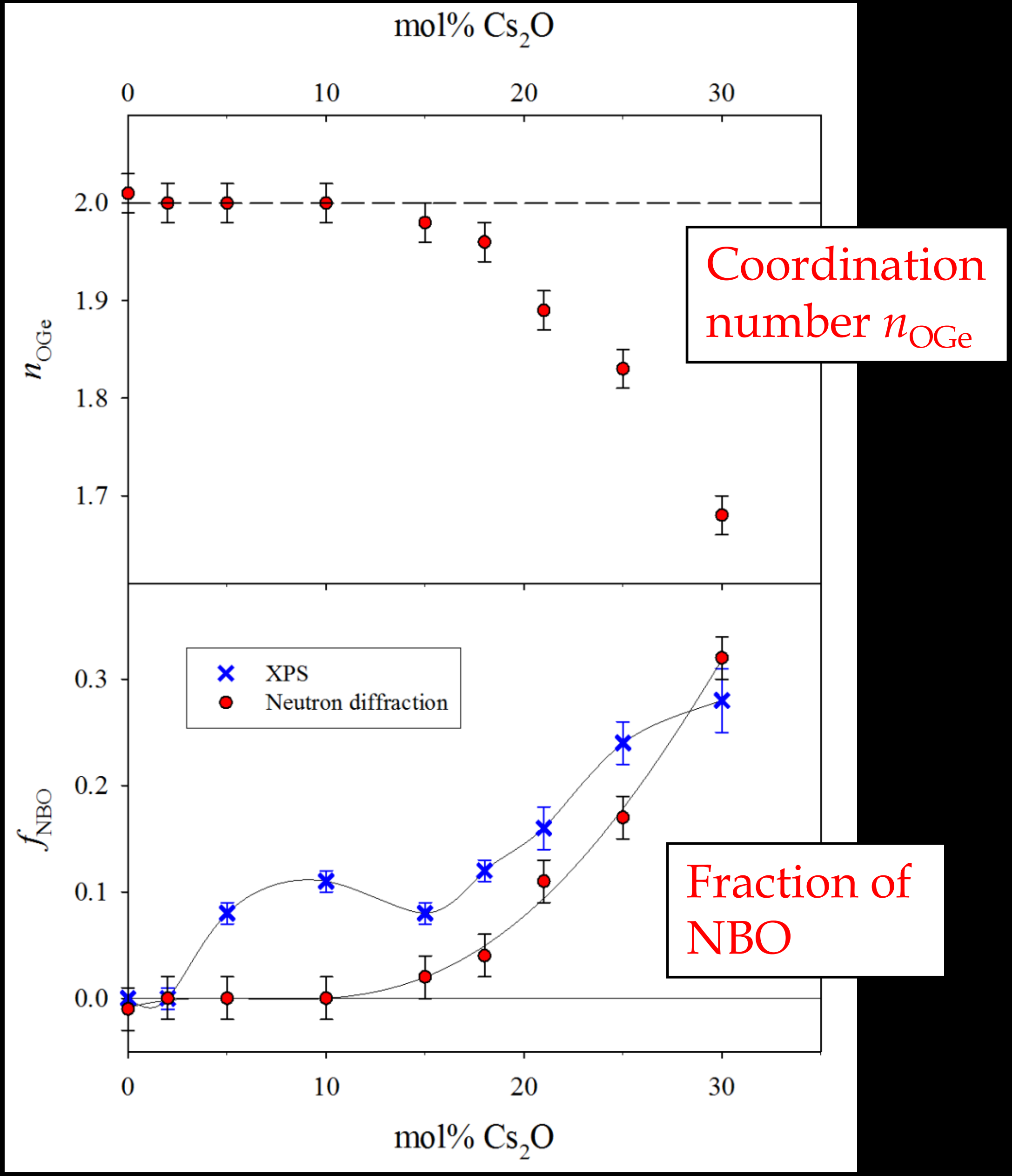
Coordination number n_{GeO}

Bond length r_{GeO}

- Strong evidence for a growth and decline in Ge-O coordination number, n_{GeO}

(Hannon et al, J Phys Chem B, 2007)

Measured O-Ge Coordination



Coordination number n_{OGe}

Fraction of NBO

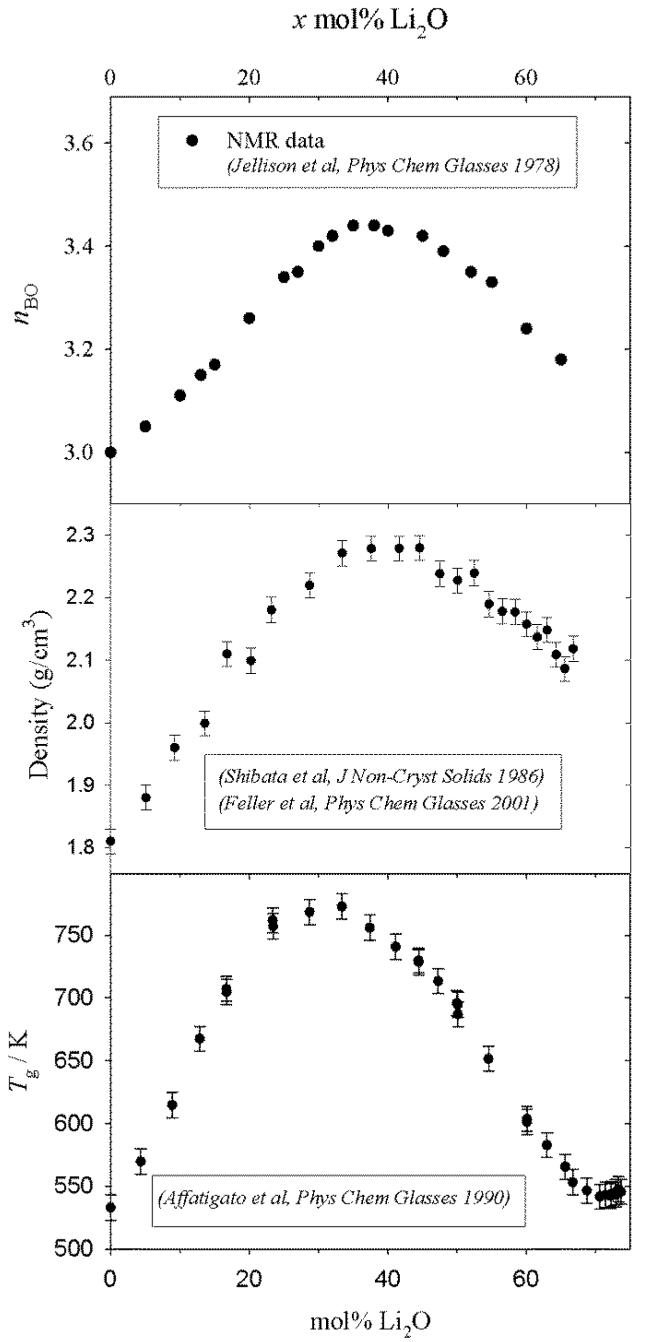
- In rutile GeO_2 and some alkali germanate crystals there are 3-coordinated oxygens, OGe_3, associated with octahedral Ge
- But our results show n_{OGe} does not exceed two → no evidence for 3-coordinated oxygen in these glasses

(NBO=Non-Bridging Oxygen)

Cs_2O-GeO_2 glasses

Borate Glasses

- NMR on ^{73}Ge is difficult and unhelpful
- But ^{11}B NMR is very successful
- Much more is known about the *borate anomaly*
- Widest ranging NMR measurement is for Li borates
- Behaviour of B-O coordination number n_{BO} is similar to physical properties (density, T_g, …)



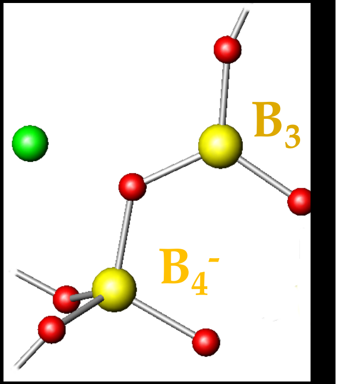
(Jellison et al, Phys Chem Glasses 1978)

(Shibata et al, J Non-Cryst Solids 1986)
(Feller et al, Phys Chem Glasses 2001)

(Affatigato et al, Phys Chem Glasses 1990)

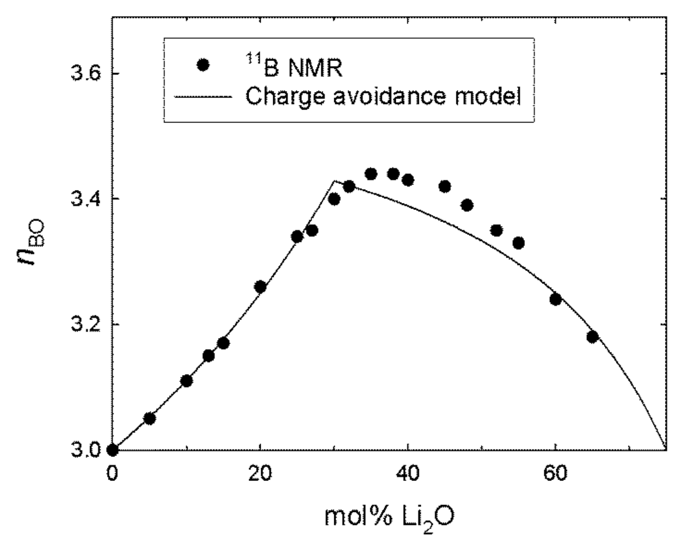
Charge Avoidance Model for Borates

- Assume that centres of negative charge avoid each other…
  1. BO_4^- formation preferred over NBO formation
  2. No bridges between BO_4^-
  3. No BO_4 with NBOs
- No adjustable/fitted parameters
- Predicts…
  - $n_{\mathrm{BO}} = 3 + \frac{x}{1-x}$ for low x
  - alternating BO_3 & BO_4 at x=30 mol% Li2O



(Wright et al, MRS Symp Proc 1997)

(NBO=Non-Bridging Oxygen)



(Hannon & Holland, Phys Chem Glasses 2006)

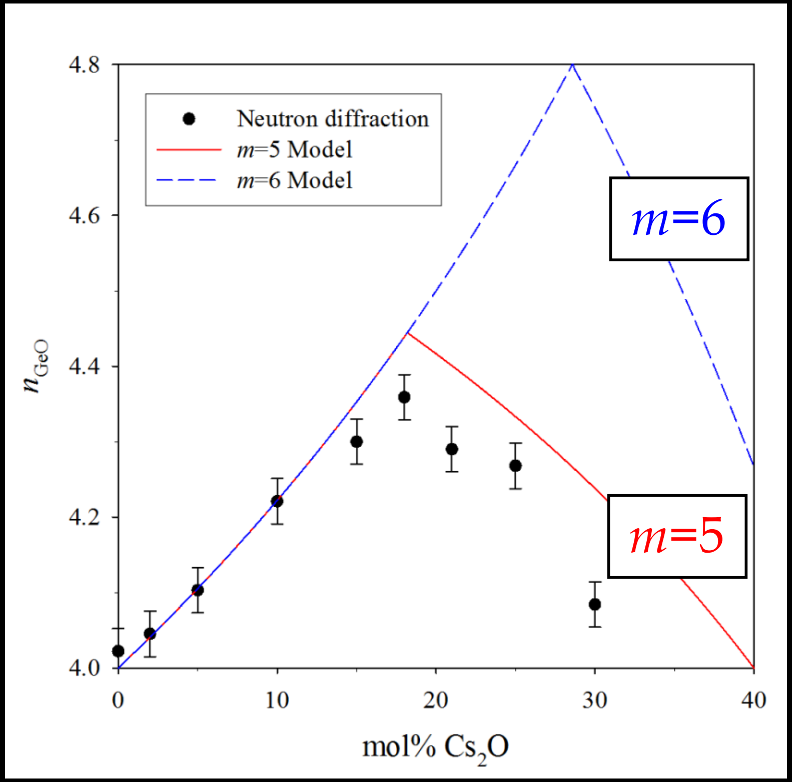
Charge Avoidance Model for Germanates

- GeO_m units cannot be close to other centres of negative charge

- Two possible Ge-O coordinations, either 4 or *m* (either 5 or 6)
- No 3-coordination oxygens, OGe_3
- Number of GeO_m units is maximised, subject to…
  - No bridges between two GeO_m units
  - GeO_m units include no NBOs
  - GeO_4 tetrahedra with more than one NBO cannot exist if GeO_m units are present

(Hannon et al, J Non-Cryst Solids 2007)

Model/Experiment Comparison



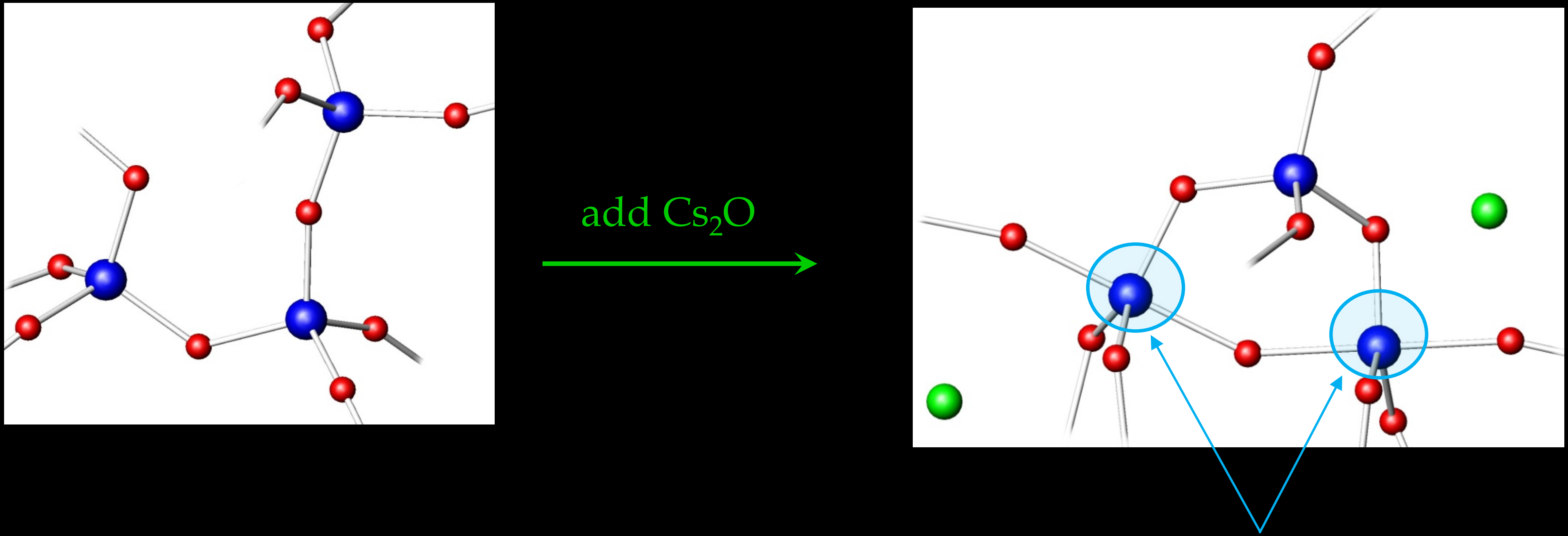
Cs_2O-GeO_2 glasses

- The *m*=5 model agrees much better with experiment
- This indicates the formation of GeO_5 units, not GeO_6 units
- 3-coordinated oxygen occurs more readily for GeO_6 → the lack of OGe_3 also indicates GeO_5 units

(Hannon et al, J Non-Cryst Solids 2007)

GeO_5 Units

Pure GeO_2 glass



add Cs_2O

create two GeO_5 units

GeO_5 units occur in some germanate crystals:

$K_2Ge_8O_{17}$, Bi_2GeO_5, $PbGe_3O_7$, $CaCuGe_2O_6$, $CuNd_2Ge_2O_8$, $BaGe_2O_5$-II (high pressure phase), $La_3AlGe_5O_{16}$, $La_3GaGe_5O_{16}$, $Ce_3AlGe_5O_{16}$, $Y_3GeO_5((OH)_{0.5}F_{0.5})_3$, $YAlGeO_5$, $Ba_3Ge_9O_{20}(OH)_2$, $Dy_3GeO_5(OH)_3$, $Gd_3GeO_5(OH)_3$, $Sm_3GeO_5(OH)_3$, $La_2Ge_3O_9$, $Ce_2Ge_3O_9$, $ErAlGeO_5$.

Glass studies in support of GeO_5 units:

MD: *(Karthikeyan & Almeida, JNCS 2001; Watanabe & Sakai, Phys Chem Glasses 2017)*

Neutron diffraction: *(Hoppe et al, JNCS 1999)*

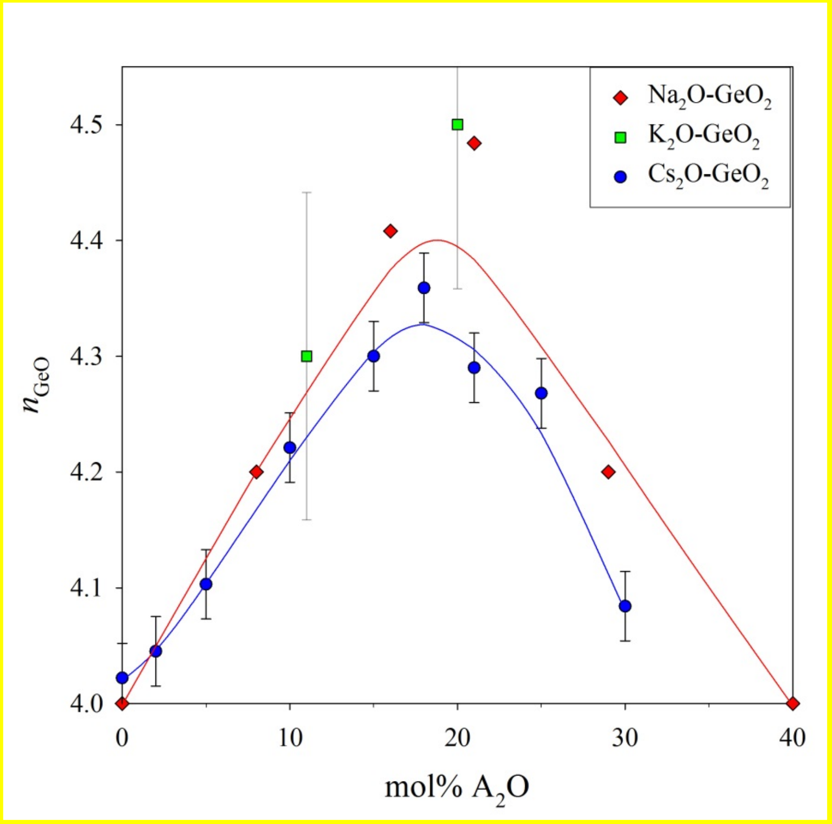
XANES: *(Wang & Henderson, Phys Chem Glasses 2005)*

Raman: *(di Martino et al, JNCS 2001; Henderson & Amos, JNCS 2003)*

NMR: *(Du & Stebbins, J Phys Chem B 2006)*

Ge-O coordination numbers from neutron diffraction

- For alkali germanate glasses, neutron diffraction consistently shows n_{GeO} growth and a maximum



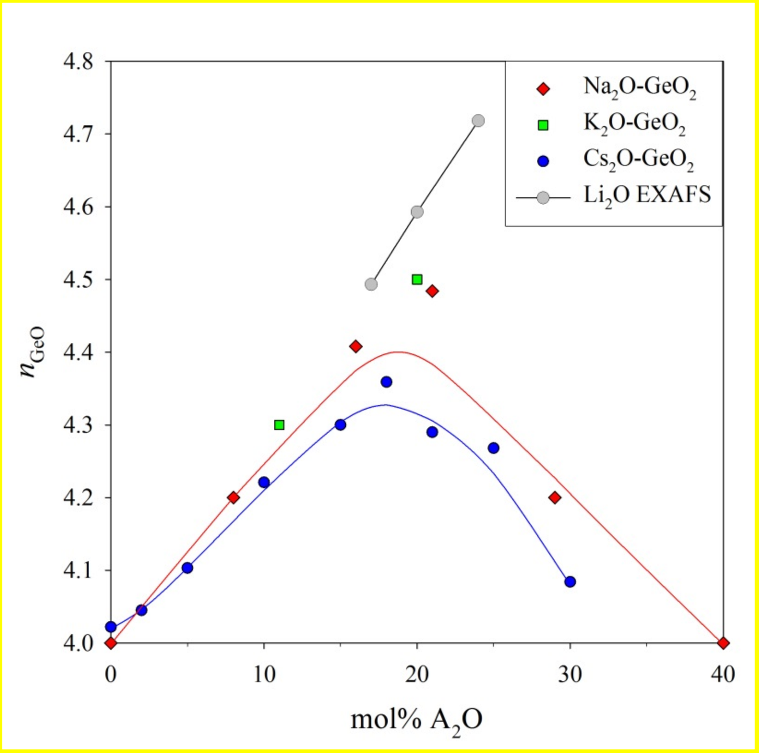
Na_2O: *(Ueno et al, Physica B, 1983)*
K_2O: *(Hoppe et al, J Non-Cryst Sol, 1999)*
Cs_2O: *(Hannon et al, J Phys Chem B, 2007)*

Lithium germanate EXAFS

- Recent EXAFS on Li germanates

  (Arima et al, J Min Pet Sci 2005)

- n_{GeO} larger, no maximum
  - not consistent with ND results for K, Na, Cs germanates



Li_2O: *(Arima et al, J Min Pet Sci, 2005)*

Neutron diffraction with Lithium

Isotope	Scattering length b / fm	Absorption cross-section σ_a / barns
^{Nat}Li	-1.90	70.5
^{6}Li	2.00	940
^{7}Li	-2.22	0.0454
^{null}Li	0	495

- In crystalline GeO_2:
  r_{GeO}=1.73 Å in tetrahedra, r_{GeO}=1.88 Å in octahedra
- Typical $r_{LiO} \approx 1.95$ Å
  → big overlap with Ge-O bond lengths
- Neutron diffraction:
  Use isotopic substitution, absorption is a problem
- Null lithium is made by mixing ^{6}Li and ^{Nat}Li

Isotopic substitution ND

- Neutron correlation function is sum of partial functions for all atom pairs (Ge-Ge, Ge-O, Ge-Li, Li-O, Li-Li, O-O):

$$T^{\mathrm{N}}(r)=\sum_{l,l'} c_l \bar{b}_l \bar{b}_{l'} t_{ll'}(r)$$

- With $^{\mathrm{null}}$Li, Li-X terms are absent:

$$T_{\mathrm{null}}(r)=c_{\mathrm{Ge}}\bar{b}_{\mathrm{Ge}}^{\ 2}t_{\mathrm{GeGe}}(r)+2c_{\mathrm{Ge}}\bar{b}_{\mathrm{Ge}}\bar{b}_{\mathrm{O}}t_{\mathrm{GeO}}(r)+c_{\mathrm{O}}\bar{b}_{\mathrm{O}}^{\ 2}t_{\mathrm{OO}}(r)$$

(only Ge-Ge, Ge-O and O-O terms are present)

- With $^{7/6}$Li, Li-X terms are present, and a difference isolates these terms:

$$T_{^7\mathrm{Li}}(r)=T_{\mathrm{null}}(r)+c_{\mathrm{Li}}\bar{b}_{^7\mathrm{Li}}^{\ 2}t_{\mathrm{LiLi}}(r)+2c_{\mathrm{Li}}\bar{b}_{^7\mathrm{Li}}\bar{b}_{\mathrm{O}}t_{\mathrm{LiO}}(r)+2c_{\mathrm{Li}}\bar{b}_{^7\mathrm{Li}}\bar{b}_{\mathrm{Ge}}t_{\mathrm{LiGe}}(r)$$

$$\begin{aligned}\Delta_{7-0}(r)&=T_{^7\mathrm{Li}}(r)-T_{\mathrm{null}}(r)\\&=c_{\mathrm{Li}}\bar{b}_{^7\mathrm{Li}}^{\ 2}t_{\mathrm{LiLi}}(r)+2c_{\mathrm{Li}}\bar{b}_{^7\mathrm{Li}}\bar{b}_{\mathrm{O}}t_{\mathrm{LiO}}(r)+2c_{\mathrm{Li}}\bar{b}_{^7\mathrm{Li}}\bar{b}_{\mathrm{Ge}}t_{\mathrm{LiGe}}(r)\end{aligned}$$

(Li-O, Li-Ge and Li-Li terms are isolated)

Lithium germanates ND

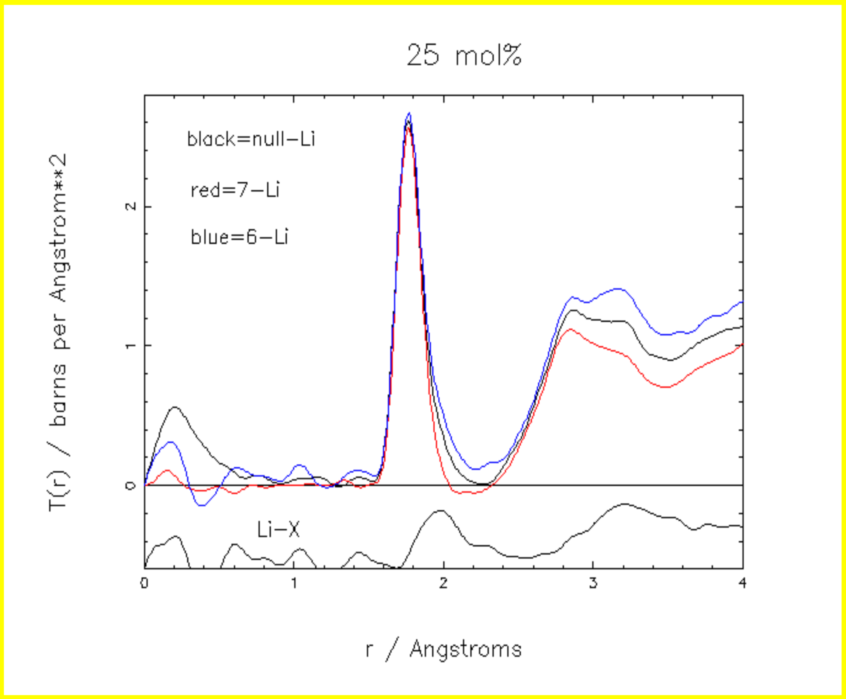
- Li_2O-GeO_2 binary glass samples:

5 mol% Li_2O	10 mol% Li_2O	20 mol% Li_2O	25 mol% Li_2O	30 mol% Li_2O
^{null}Li	^{null}Li	^{null}Li	^{null}Li	^{null}Li
^{7}Li	^{7}Li	^{7}Li	^{7}Li	^{7}Li
	^{6}Li	^{6}Li	^{6}Li	

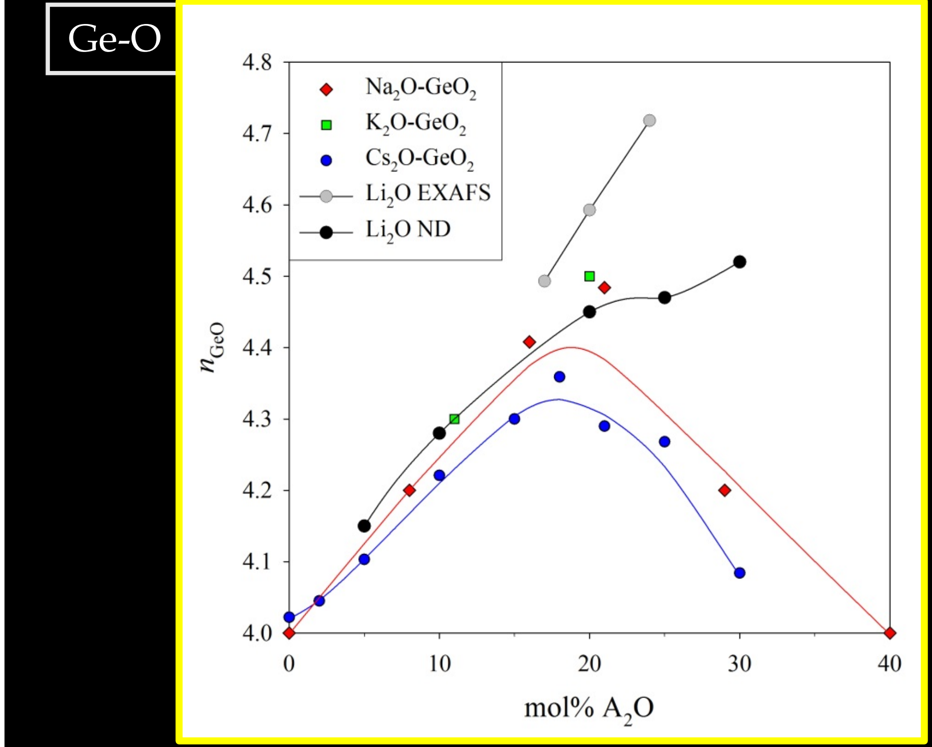
- ^{null}Li samples: Li-X correlations absent (but high absorption).
Measures Ge-O distribution.

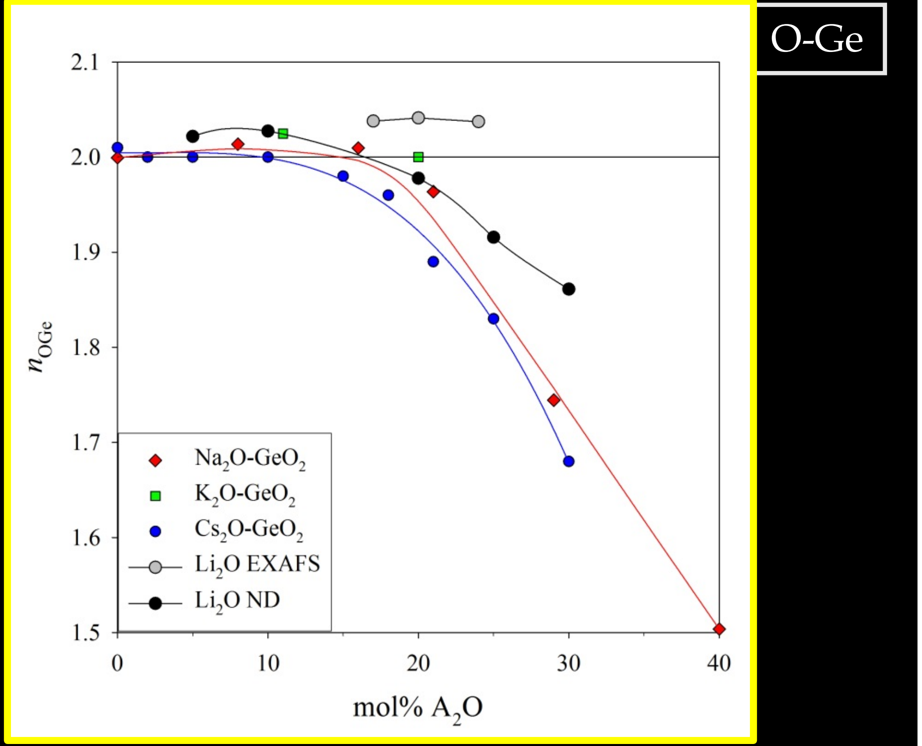
- ^{7}Li samples: Low absorption.
Fixes normalisation of data.
Measures Li-X correlations.

- ^{6}Li samples: Consistency check.
Largest isotope difference.



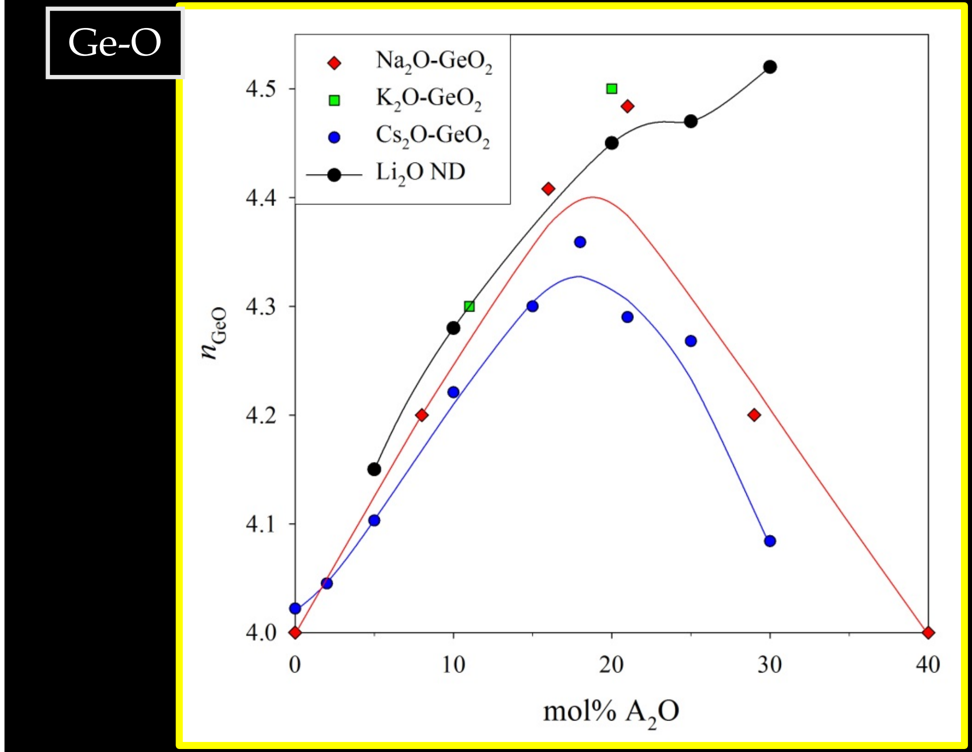
Ge-O coordination numbers

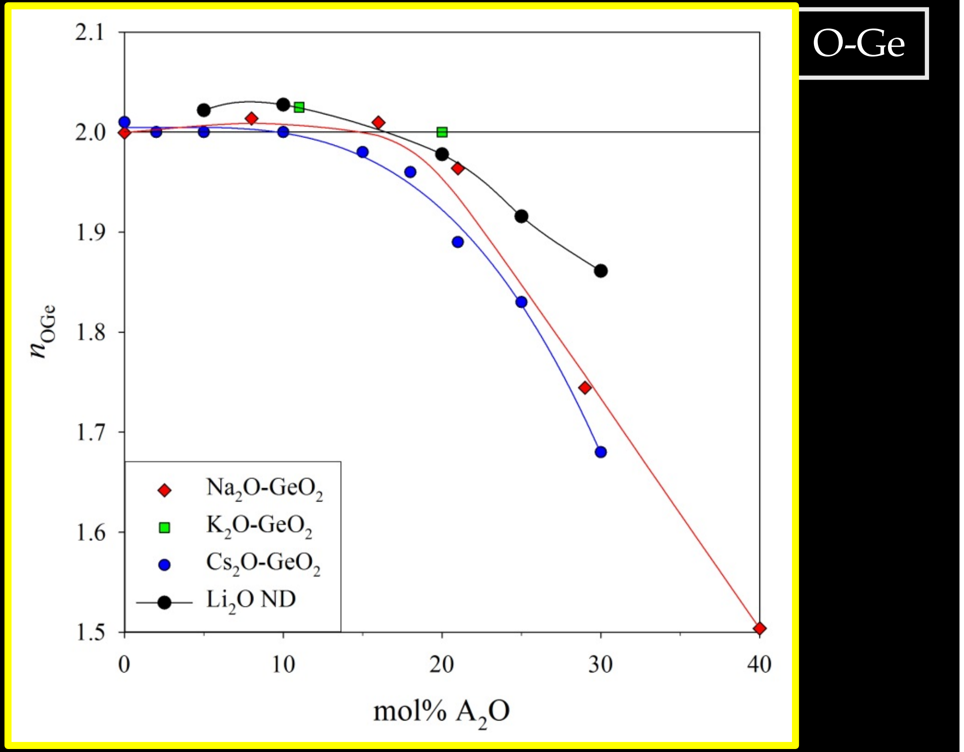




- Clearly EXAFS has over-estimated coordination numbers
- But, coordination number growth does fall
- And the fall is <u>different</u> for each alkali
- NBOs appear at ~20 mol% Li_2O

Dependence on alkali





- Usually increasing alkali field strength *z/r* leads to increase in number of NBOs – we observe the opposite

e.g. (Wu & Stebbins, J Non-Cryst Sol, 2009)

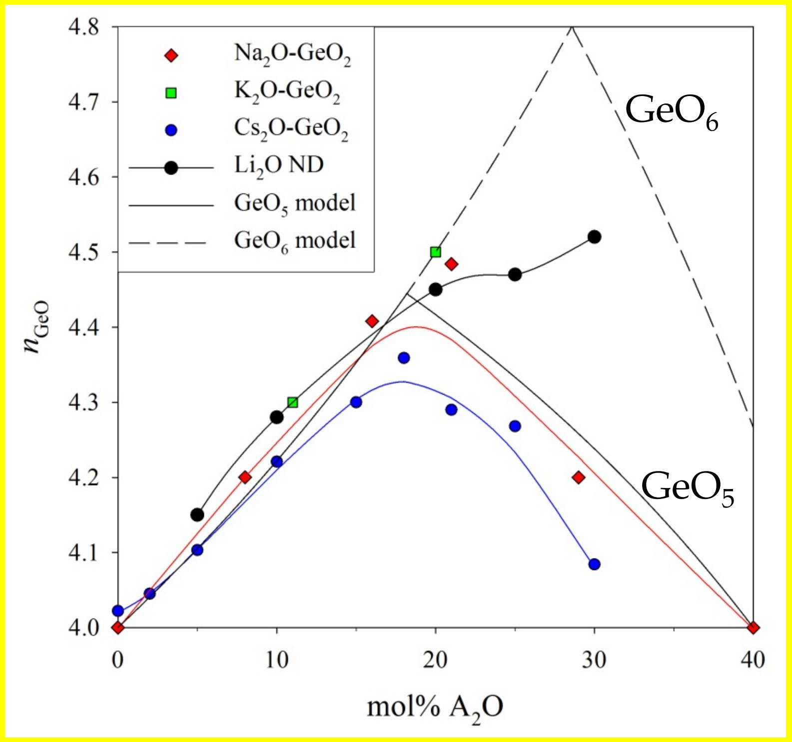
- On the other hand, a similar dependence on alkali is observed for N_4 in borates

(Michaelis et al, J Non-Cryst Sol, 2007)

Charge avoidance model

(Hannon et al, J Non-Cryst Sol, 2007)

Ge-O



(e.g. GeO_6-GeO_6 bridges are forbidden)

- Charge avoidance model predicts n_{GeO} behaviour depends on higher Ge-O coordination number (5 or 6)
- Li germanate results are consistent with mostly GeO_6

(Cs and Na germanate results are consistent with mostly GeO_5)

- Li^+ has larger field strength, and is better able to balance GeO_6^{2-}

Bridging and non-bridging oxygen

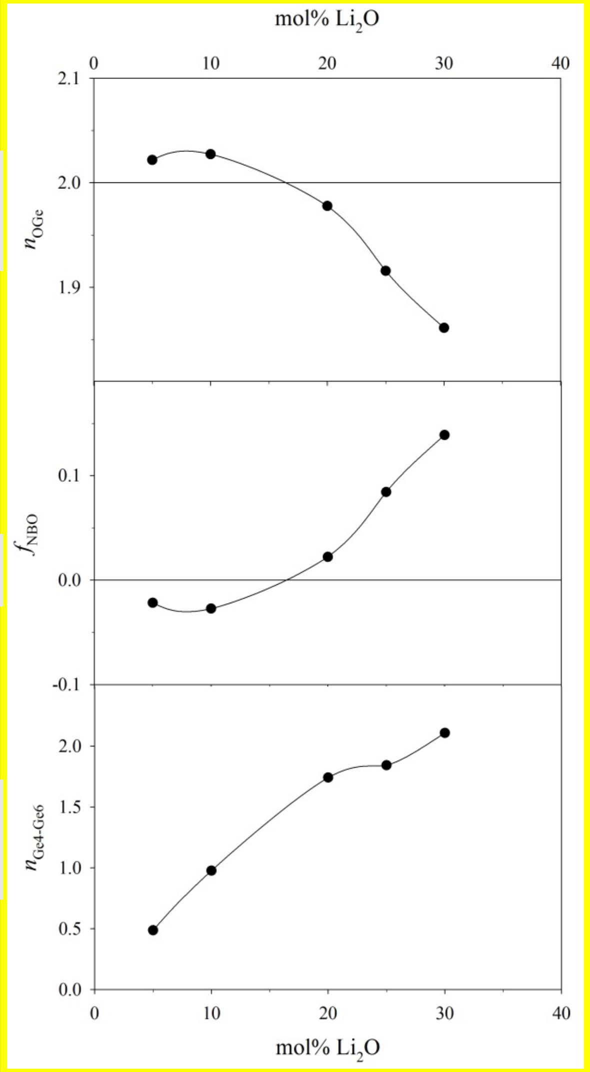
- There are few NBOs

  e.g. for 30 mol% Li_2O,
  14% of oxygen are NBO

- There are many G4-G6 bridges

  (*i.e.* Ge4-O-Ge6)

  e.g. for 30 mol% Li_2O,
  ~half the bridges are G4-G6

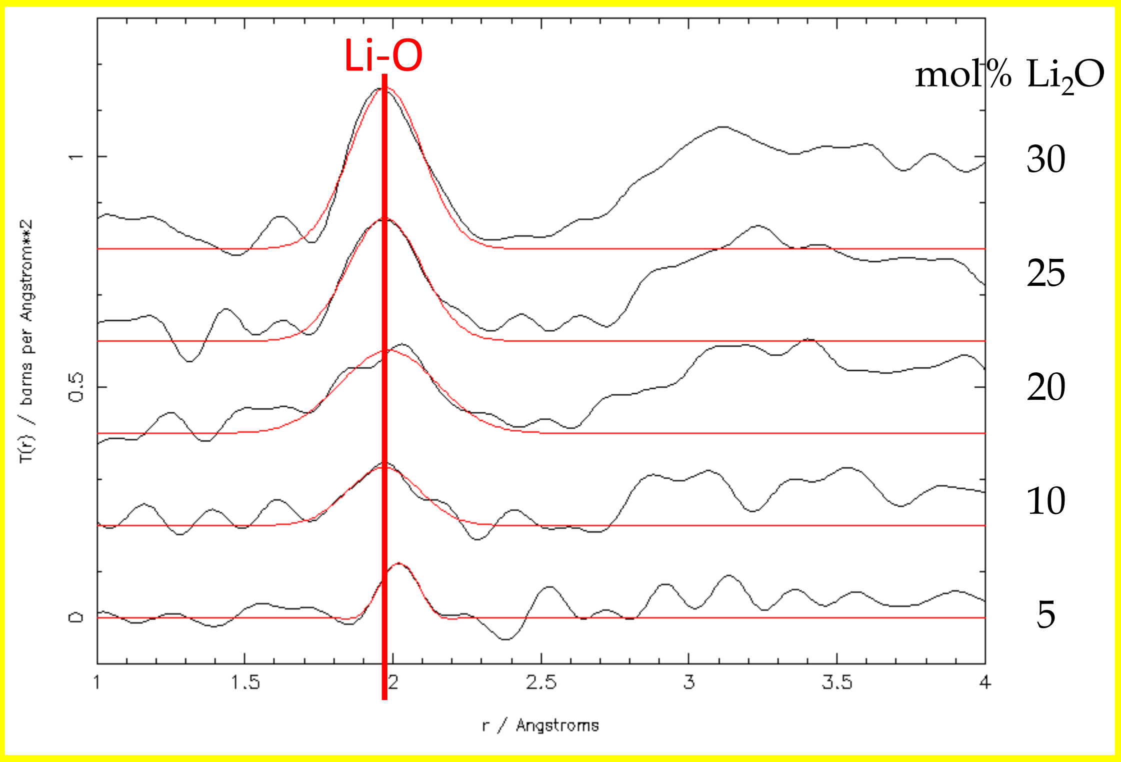


O-Ge
coord num

frac NBO

Ge4-Ge6
coord num

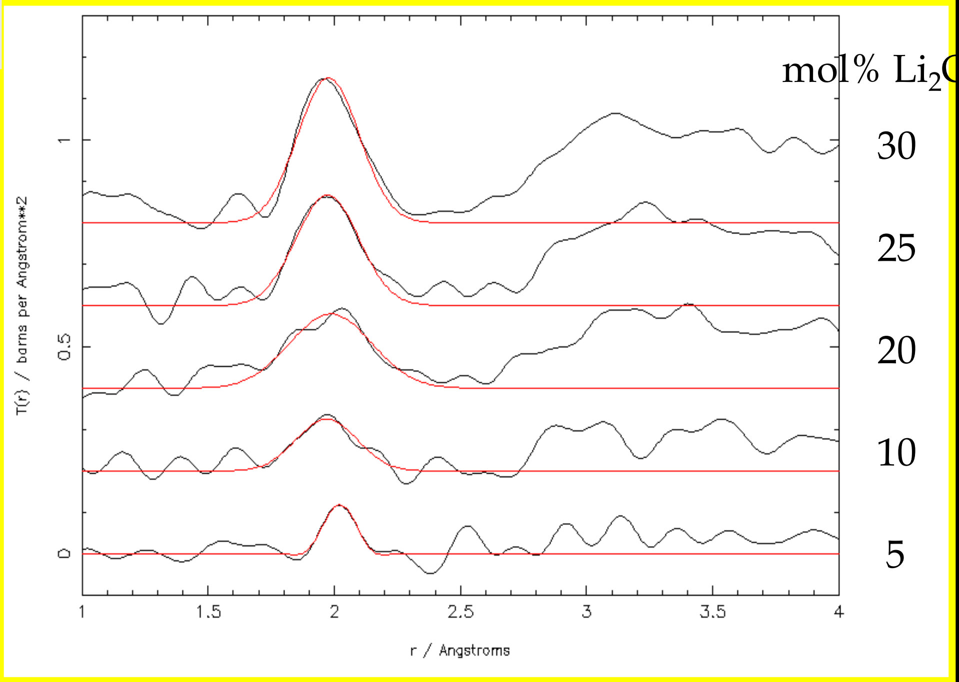
Li-X correlations

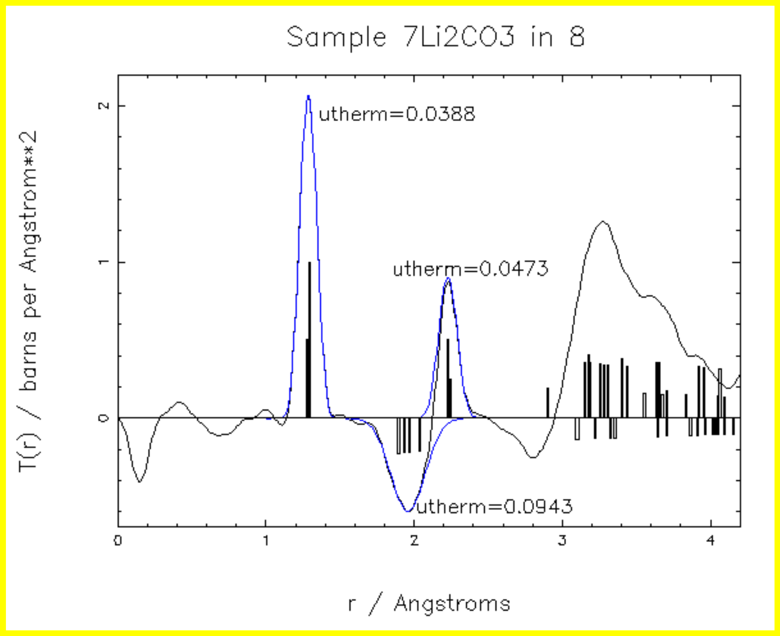


- ^{null}Li – ^{7}Li difference reveals Li-O peak at ~1.98 Å
- Li-Ge distances start at ~2.7 Å
- Second Li-O distances at ~3.5 Å

Li-O thermal motion/static disorder

Li-X





Li_2CO_3

- Li-O peak is unusually broad, σ_{LiO}~0.11 Å

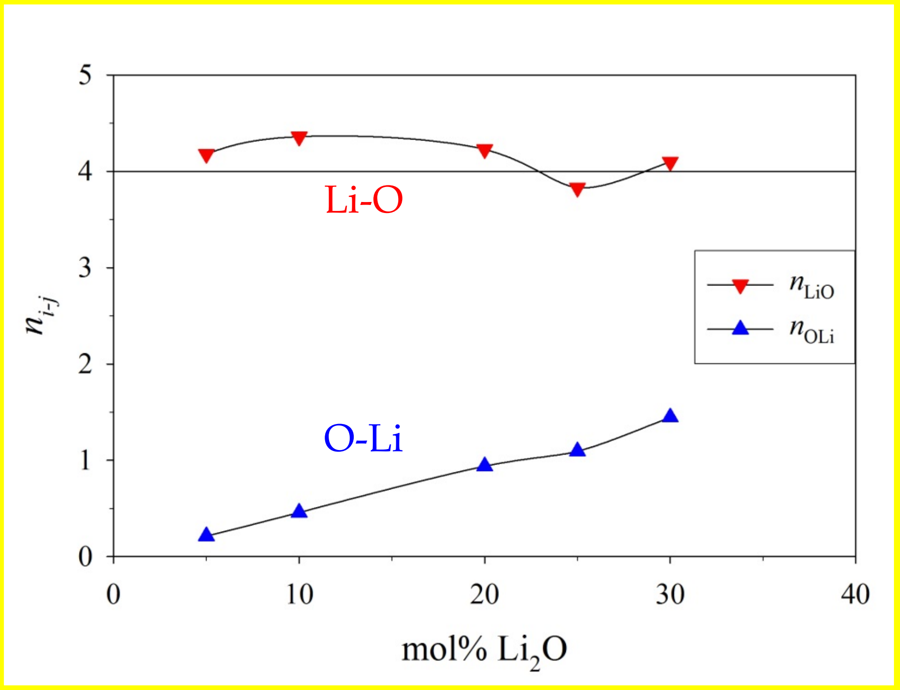
  (compare σ_{GeO}=0.04 Å in pure GeO_2)
- $T(r)$ for crystalline Li_2CO_3 shows thermal broadening of Li-O peak is σ_{LiO}=0.094 Å
- → Li is light and has large thermal motion
- Li-O peak is broad but distribution of distances is actually narrow

Li-O coordination numbers

- Li-O coordination number ~ 4

- O-Li coordination number grows to ~1.5
  for 30 mol% Li_2O…

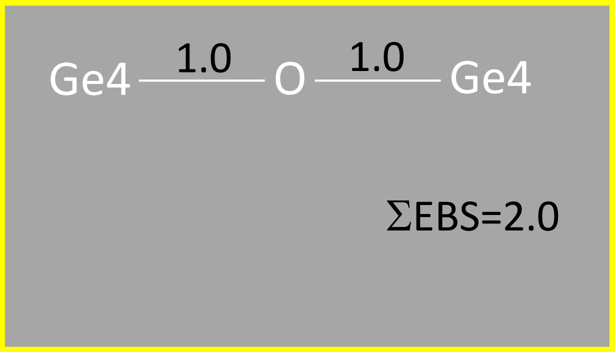
  …then ~half the BO are bonded to 2 Li



Li-BO coordination

- Pauling's electrostatic bond strength (EBS) shows the likely oxygen environments…
- A Ge4-O-Ge4 bridge can accommodate 0 or 1 Li
- A Ge4-O-Ge6 bridge can accommodate 1 or 2 Li
- For 30 mol% Li_2O half the bridges are Ge4-Ge6, and n_{OLi}~1.5

→ both types of bridge have their maximum number of Li


Ge4 —1.0— O —1.0— Ge4

ΣEBS=2.0

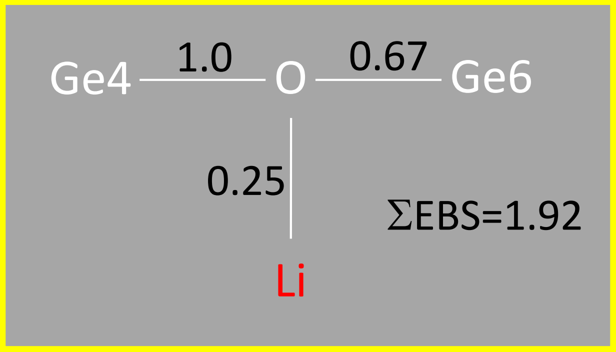

Ge4 —1.0— O —1.0— Ge4

0.25

Li

ΣEBS=2.25

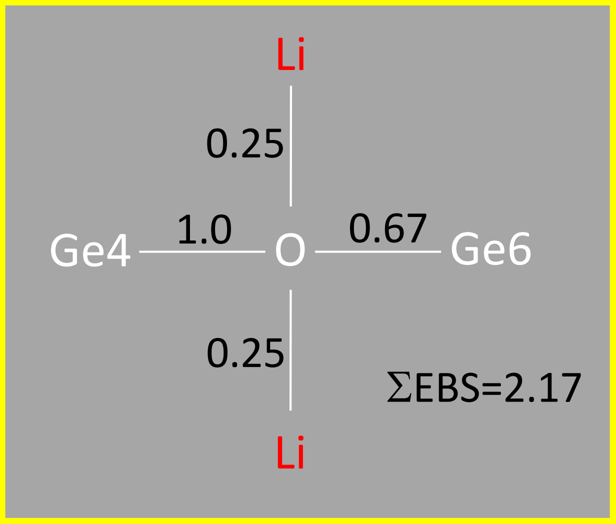
(Pauling, J Am Chem Soc, 1929)
(Hannon, J Non-Cryst Sol, 2016)


Ge4 —1.0— O —0.67— Ge6

0.25

Li

ΣEBS=1.92


Li

0.25

Ge4 —1.0— O —0.67— Ge6

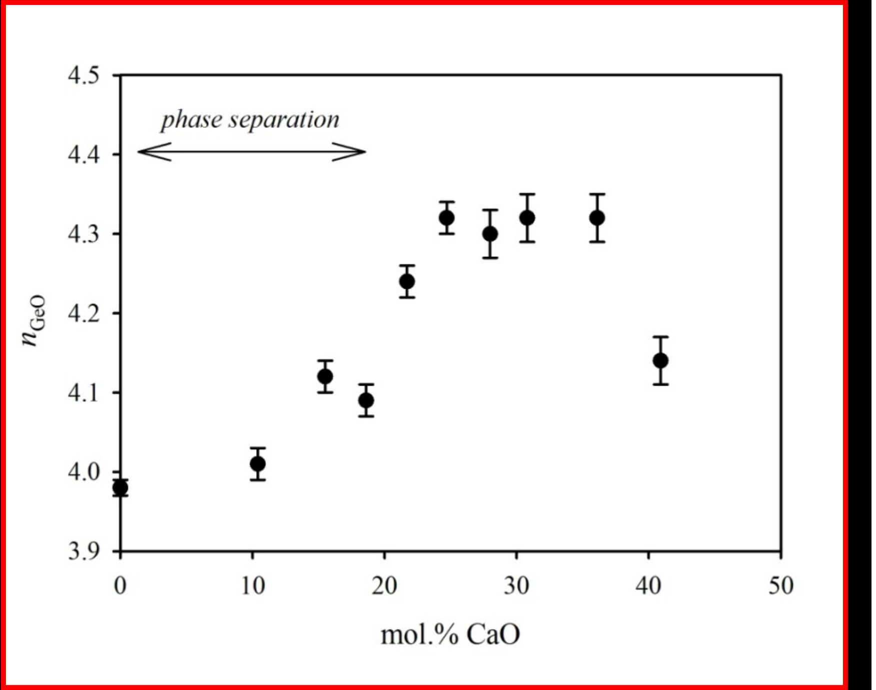
0.25

Li

ΣEBS=2.17

CaO-GeO$_2$ Neutron Diffraction

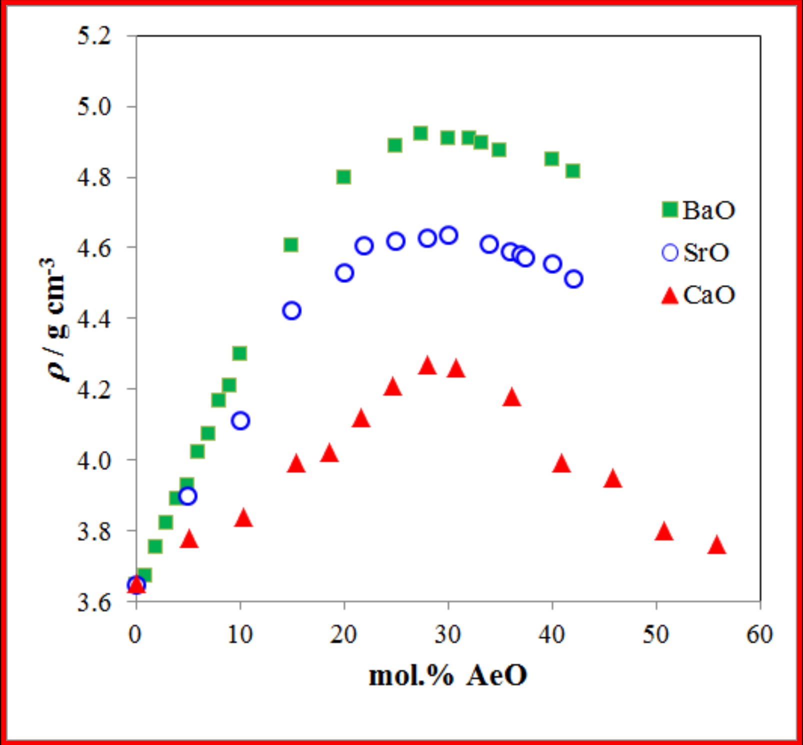
- Again Ge–O coordination numbers greater than 4 are observed
- What factors are involved in the *germanate anomaly*?



(Alderman, J Phys Chem C 2017)

Density

- A maximum in the density is a key signature of the *germanate anomaly*
- Calcium germanate density maximum is at 29.4 mol% CaO
- Other alkaline earth germanates have similar density maxima, at similar positions



(Alderman, J Phys Chem C 2017)

Atom number density

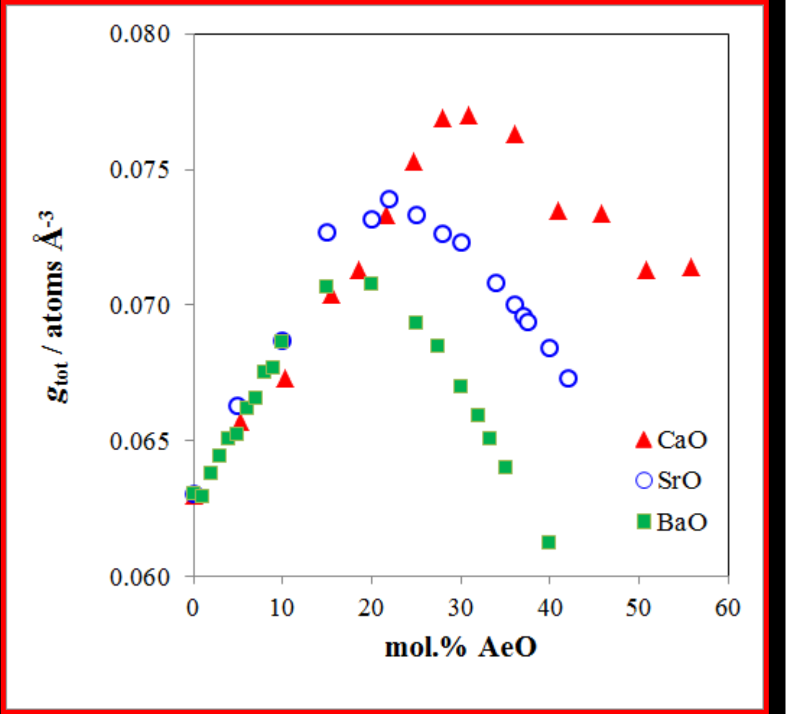
- Density (in g cm^{-3}) is strongly influenced by atomic mass
- To investigate structure, remove the influence of mass

  (Hoppe, J Non-Cryst Solids, 1999)
- Instead of mass density,
  plot atom number density g_{tot}
  i.e. number of atoms per unit volume

$$g_{\text{tot}} = \frac{\rho}{\text{amu}\sum_{l} c_l A_l}$$

Units for g_{tot}: atoms per cubic Ångstrom

A_l=atomic number c_l=atomic fraction



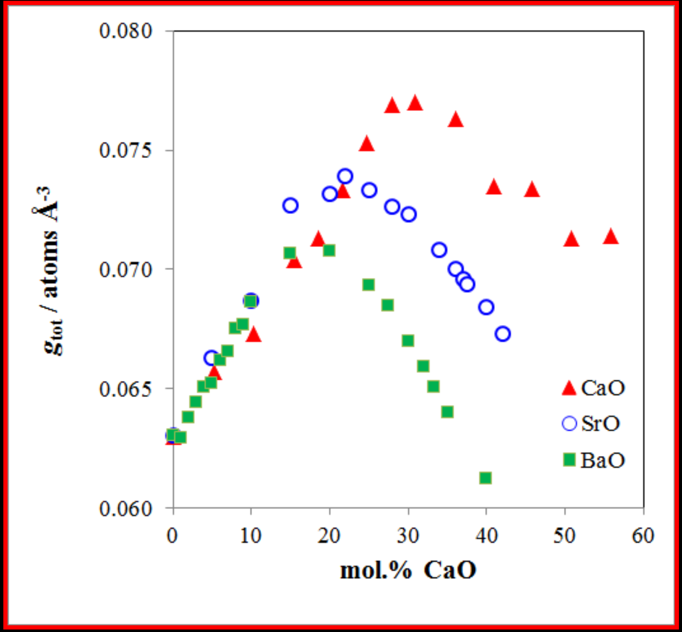
(Alderman, J Phys Chem C 2017)

Packing?

- All alkaline earth germanates follow the same g_{tot} line at low AeO content, then…
  - composition for deviation from the line depends on Ae ion size (Ca<Sr<Ba)
  - position of the maximum depends on Ae ion size

    Ionic radius for 8-fold coordination:
    $R_{ca} = 1.12\text{Å}$
    $R_{Sr} = 1.26\text{Å}$
    $R_{ba} = 1.42\text{Å}$

- The dependence on Ae ion size suggests that packing is an important factor in the behaviour



(Alderman, J Phys Chem C 2017)

Ae=Alkaline earth

Partial Atom Number Density

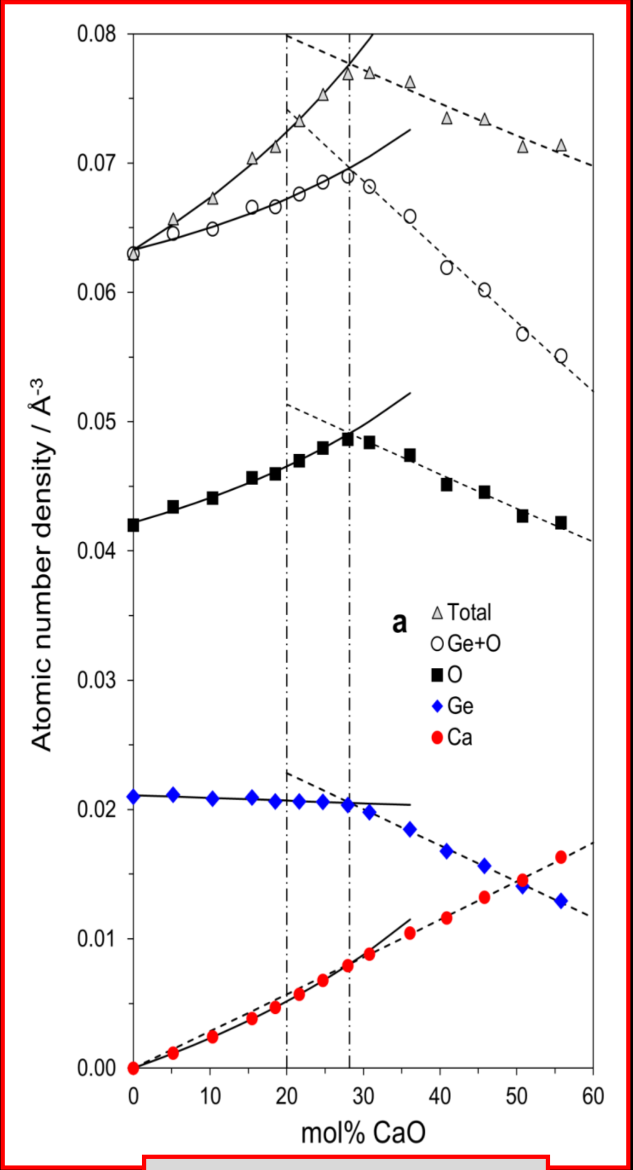
- We can also define a partial atomic number density for each element, g_l

$$\boxed{g_l = c_l g_{\text{tot}}}$$

(c_l = atomic fraction for the element l)

- g_l is simply the number of atoms of element l per unit volume

- From one density measurement (plus known composition) we can determine three partial number densities!



Calcium germanates

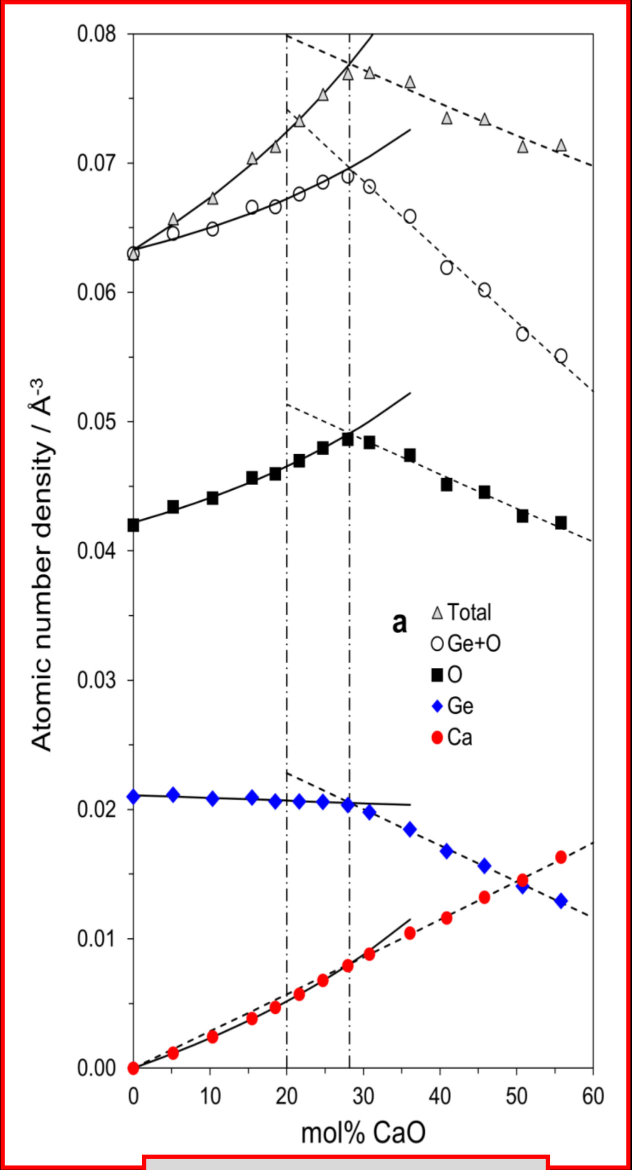
Packing in Ca Germanates

- Ca number density is ~linear
  – the behaviour of ions going into holes in an inert matrix
- Ge number density has two linear regions:

  Low CaO region – g_{Ge} is almost constant, the packing of the germanate network is unchanging

  High CaO region – g_{Ge} declines more rapidly, the insertion of more Ca^{2+} is forcing apart the germanate network

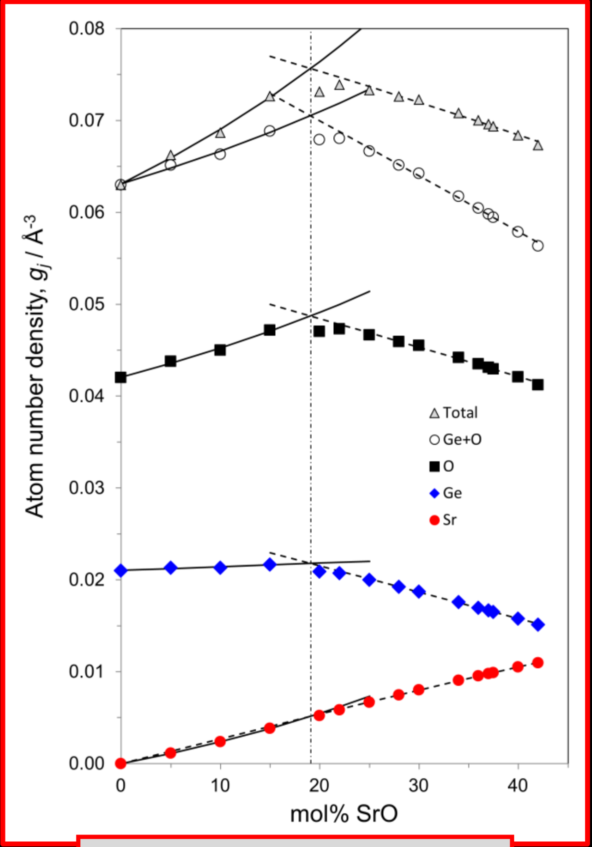
  Intersection is at 28.2 mol% CaO – the position of the number density maximum



Calcium germanates

Sr and Ba Germanates

- Other alkaline earth germanates show the same partial number density behaviour as Ca germanates



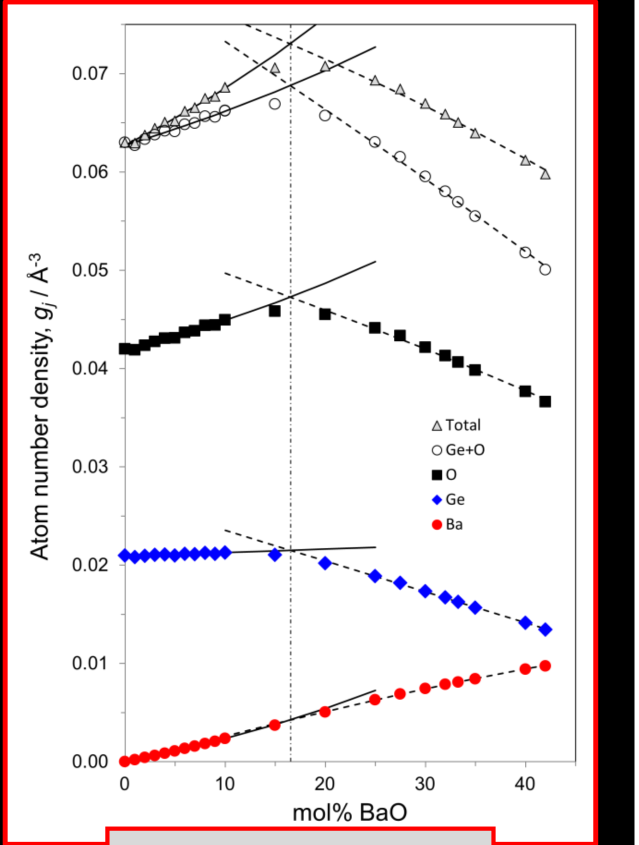
Strontium germanates

- Ge number density change is at:

19.1 mol%SrO

16.5 mol% BaO

- Packing behaviour

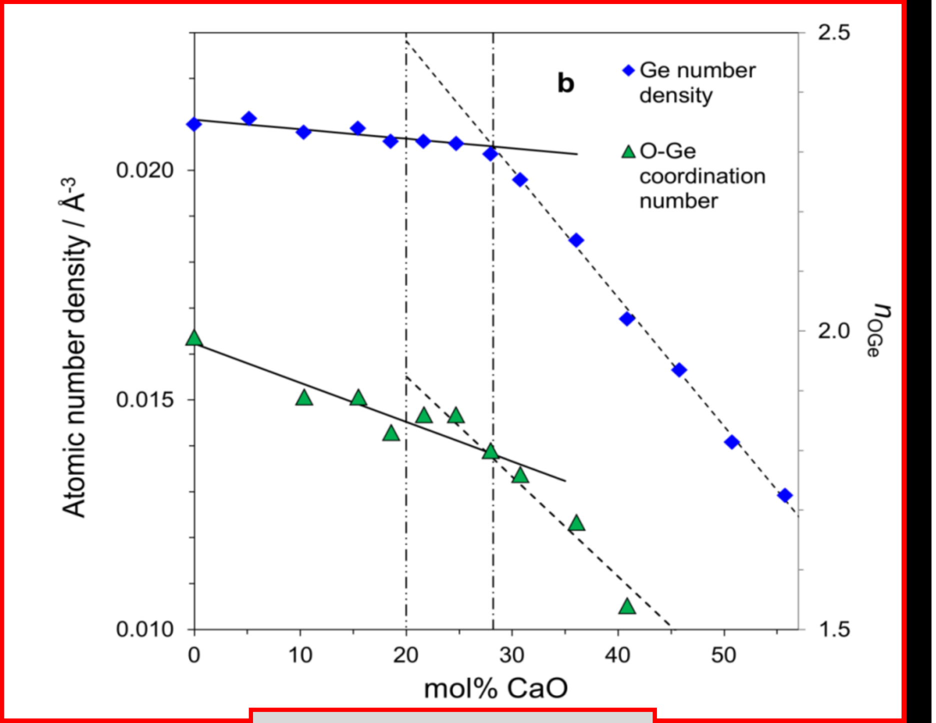


Barium germanates

Coordination number / Number density Comparison

- The O-Ge coordination number, n_{OGe}, is a measure of the depolymerisation of the germanate network (appearance of NBOs)
- n_{OGe} and Ge number density change behaviour at the same composition as the maximum of g_{tot}

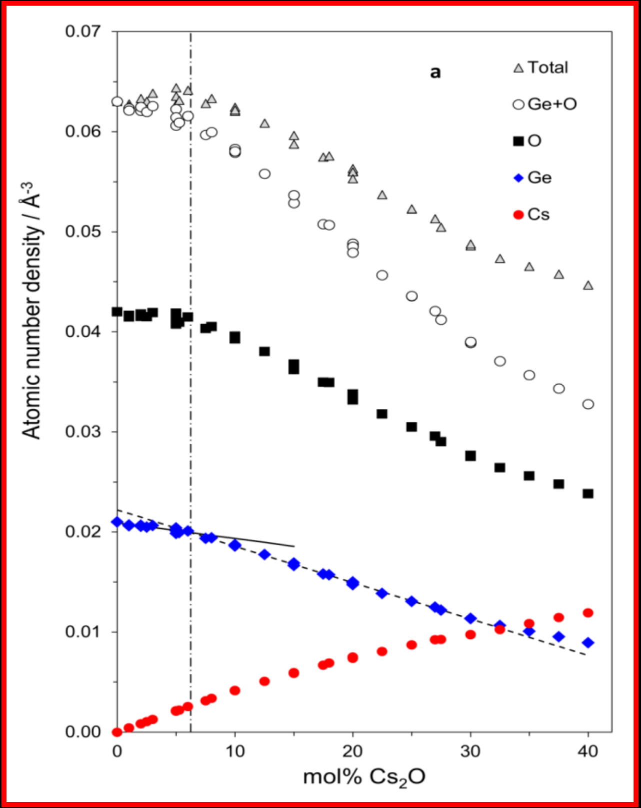
→ This means that the O-Ge coordination number decreases strongly at the same composition that Ca^{2+} ions start pushing the germanate network apart



Calcium germanates

Caesium Germanates Number Density

- Partial number densities have similar behaviour to alkaline earth germanates, and…
- Maximum of g_{tot} and change in g_{Ge} behaviour occur at similar composition:
  - g_{tot} maximum is at 4.7 mol% Cs_2O
  - g_{Ge} changes at 6.2 mol% Cs_2O

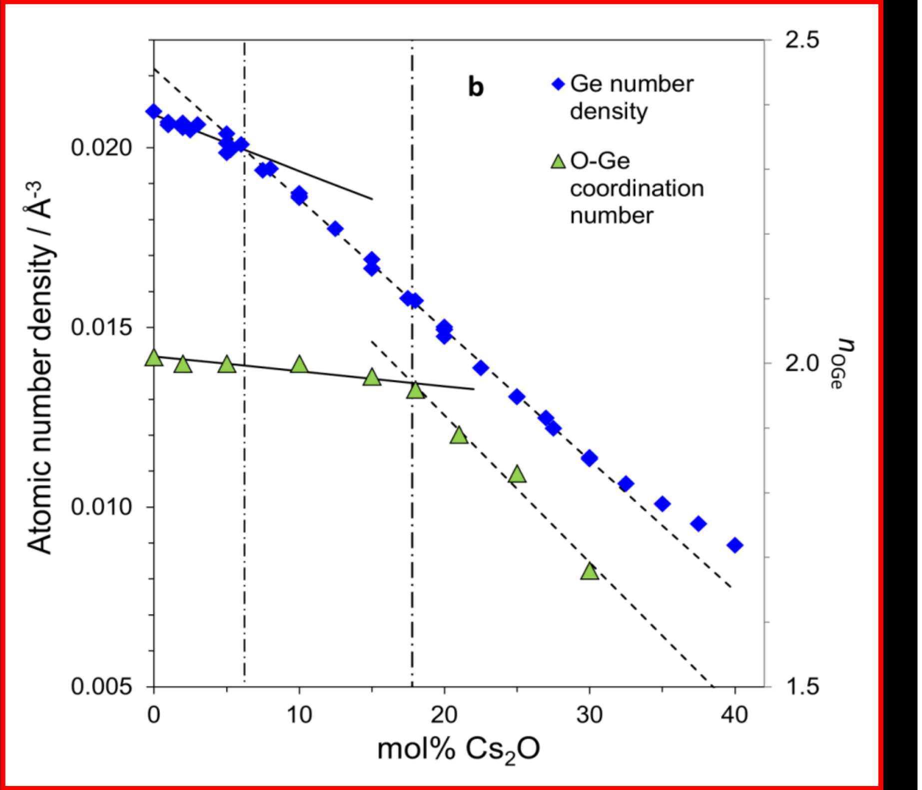


Caesium Germanates Coordination Number

- Maximum of g_{tot} and change in g_{Ge} behaviour occur at similar composition:
  - g_{tot} maximum is at 4.7 mol% Cs_2O
  - g_{Ge} changes at 6.2 mol% Cs_2O

- But the O–Ge coordination number decline does not start until 17.8 mol% Cs_2O

→ This means that the addition of Cs^+ ions starts to push apart the germanate network, without causing it to depolymerise.
But the coordination number behaviour seems not to be associated with other structural factors of the anomaly.



Neutron diffraction:
(Hannon et al, J Phys Chem B, 2007)

Germanates Summary

- Ge-O coordination number always grows above tetrahedral $n_{\mathrm{GeO}}=4$ and then declines, consistent with charge avoidance model

- For Cs_2O-GeO_2 the higher n_{GeO} value is 5

- For Li_2O-GeO_2 the higher n_{GeO} value is mostly 6

- Alkaline earth germanates (CaO-GeO_2) are different, and the behaviour is consistent with a packing mechanism

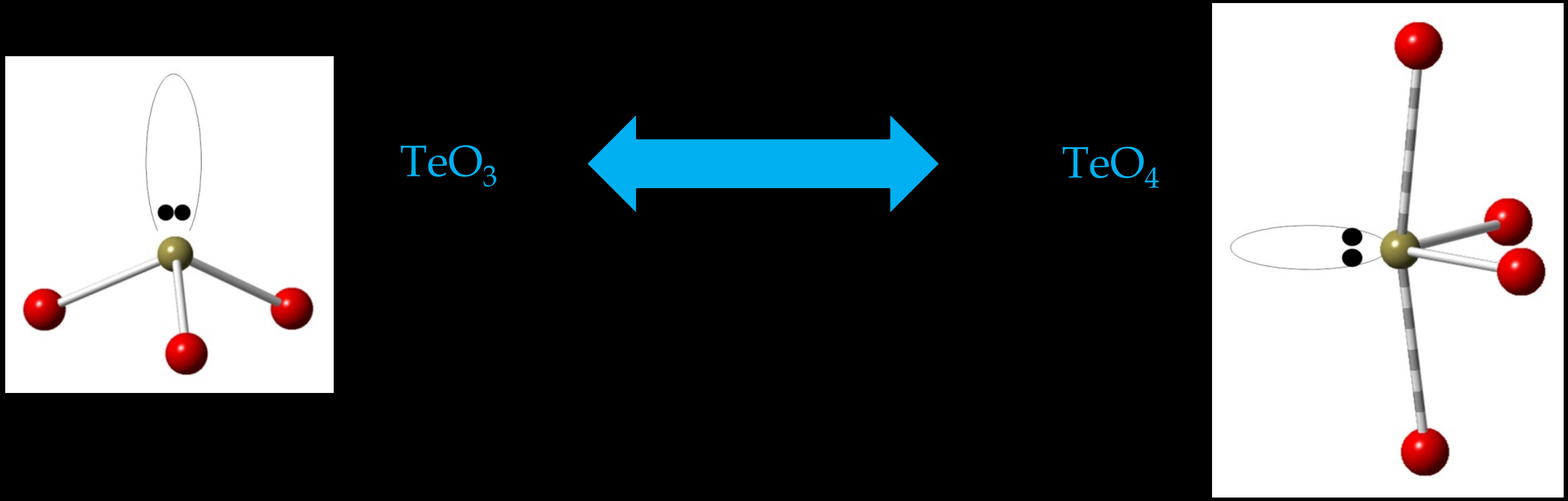
Tellurite glasses

e.g. K_2O-TeO_2

- Applications interest, *e.g.* optical devices
- Fundamental structural interest…

Many structural studies, but slow progress to a clear, quantitative structural understanding – *Why*?...

1. Difficulty of making the end-member: pure amorphous TeO_2
2. Structure is complex and subtle, involving interconversion of TeO_4 and TeO_3 units

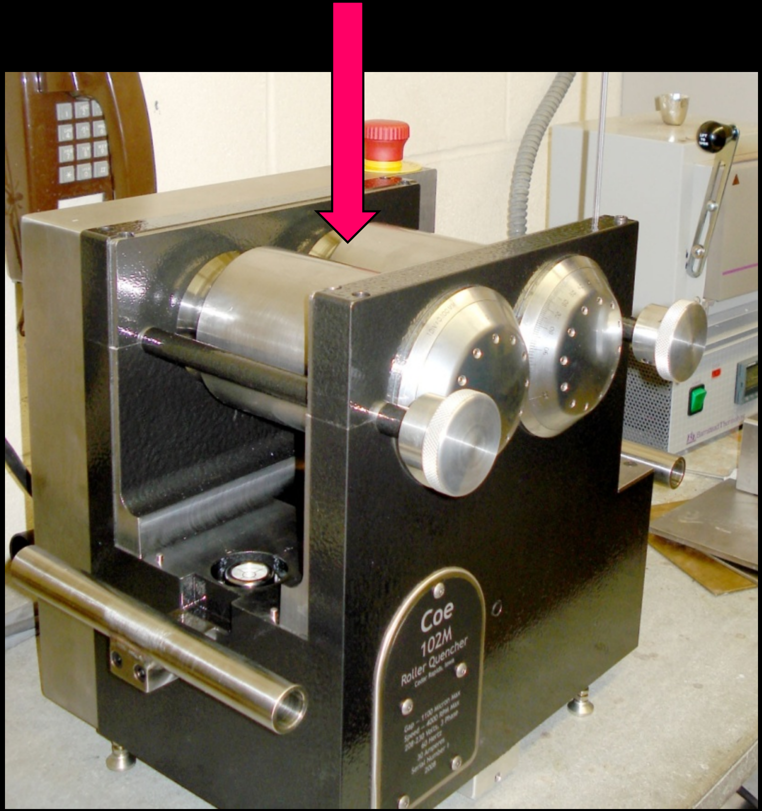


Pure amorphous TeO_2 - rapid quenching

- Pure amorphous TeO_2 is difficult to make, except in milli-gramme quantities
- Usually addition of modifier is required to stabilise the glass

  (Lambson et al, JNCS 1984)
- We made few gramme sample of pure amorphous TeO_2 by twin-roller rapid quenching at Coe College

  (Havel, Feller et al, Glass Technology 2009)

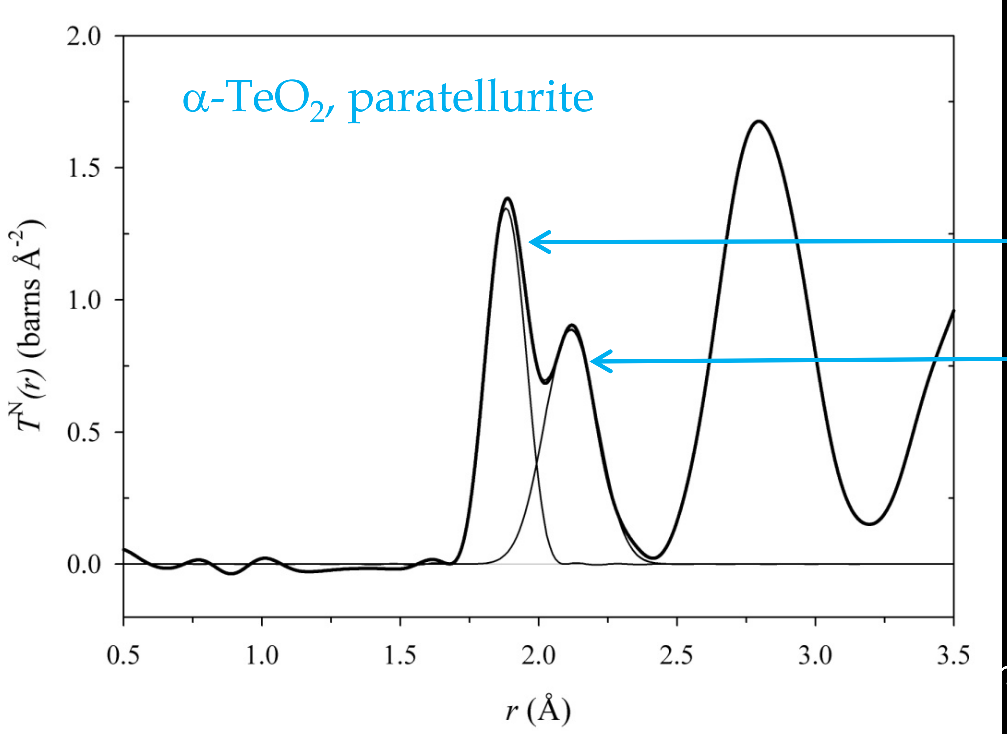

Melt goes in here!

(A crucible-quenching method has recently been perfected by Tagiara et al, J Non-Cryst Solids, 2017)

Neutron diffraction (ND)

- ND can provide the most accurate coordination numbers
- Error can be ~1%

- e.g. for GeO_2 glass we measured n_{GeO}=4.03
- e.g. for crystalline α-TeO_2 we measured n_{TeO}=3.95



Short Te-O 1.882Å 1.95 atoms

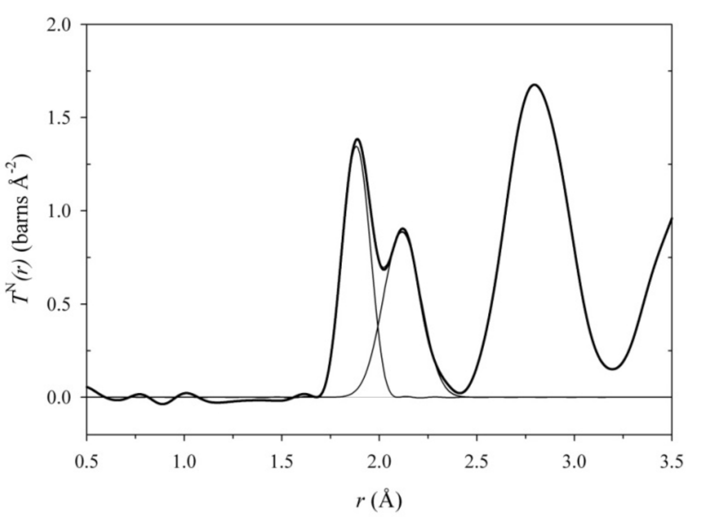
Long Te-O 2.117Å 2.00 atoms

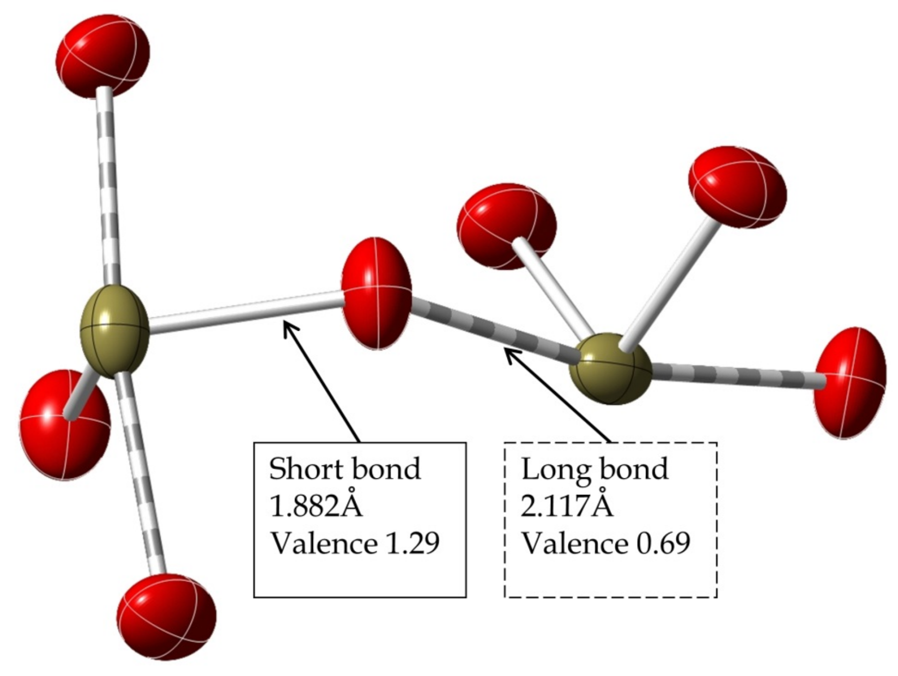
Barney, Hannon, Holland,
J Phys Chem C 2012

nnon, J Phys Chem B 2007)

α-TeO_2 Crystal Structure (paratellurite)

- Each bridge between two TeO_4 units has one short and one long Te-O bond
- It is often assumed that amorphous TeO_2 has a similar structure, based on TeO_4 units



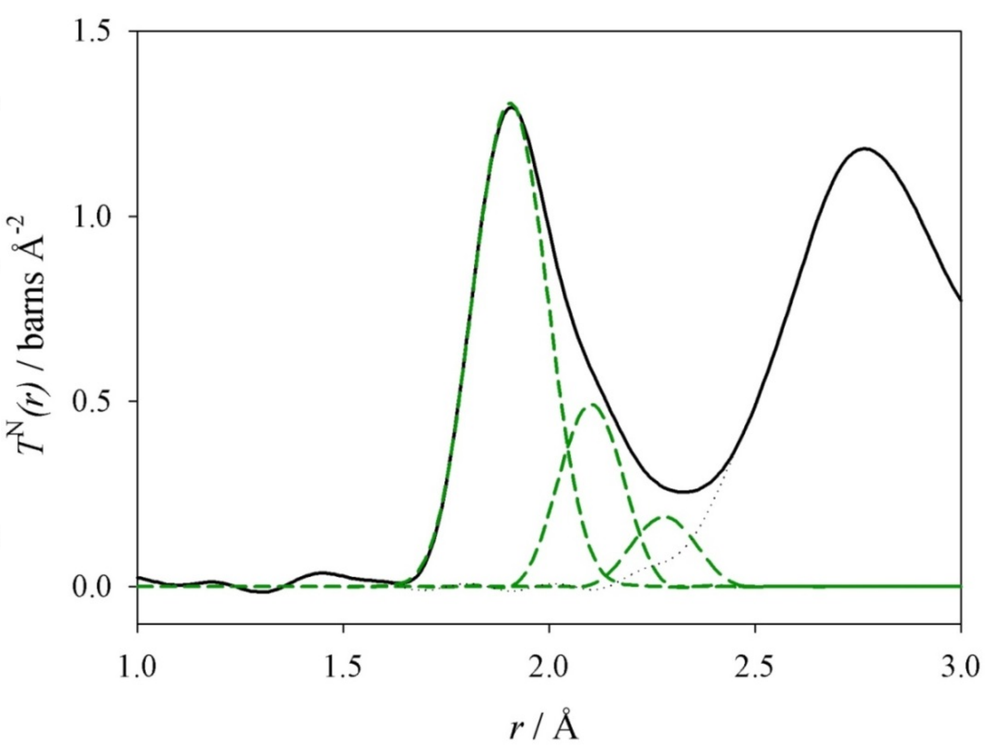


Short bond
1.882Å
Valence 1.29

Long bond
2.117Å
Valence 0.69

Barney, Hannon, Holland, J Phys Chem C 2012

Amorphous TeO_2 – Neutron Diffraction



If $n_{TeO}<4 \Rightarrow n_{OTe}<2$
i.e. if there are 3-coordinated Te, there must be terminal oxygens

- Neutron diffraction at ISIS Facility neutron source
- Fitting gives Te-O coordination number n_{TeO}=3.68(4)
  and then…
- 32% of Te are 3-coordinated
- n_{OTe}=1.84(1)
  i.e. 16% of oxygens are terminal

Barney, Hannon et al,
J Phys Chem Lett, 2013

Terminal Oxygens

Barney, Hannon et al,
J Phys Chem Lett, 2013

A terminal oxygen is bonded to only one cation.
A non-bridging oxygen is bonded to one glass-former cation
PLUS some modifier cations

- A TeO_2 molecule is known – it has two terminal Te=O bonds of length 1.83Å

  (Zasorin et al, J Struct Chem 1974)
- Some workers consider α-TeO_2 to be a molecular crystal of TeO_2 molecules

  (Gabuda, J Phys Chem B 2006)
- Molecular Dynamics for amorphous TeO_2 gives $n_{TeO}=3.69$ & $n_{TeO}=1.85$

  (Piettrucci et al, Phys Rev B 2008)
- Raman spectrum of amorphous TeO_2 recently interpreted to give n_{TeO}~3.67

  (Kalampounias, Vib Spec 2012)
- $5V_2O_5{\cdot}95TeO_2$ glass – ND gives $n_{TeO}=3.3\pm0.2$

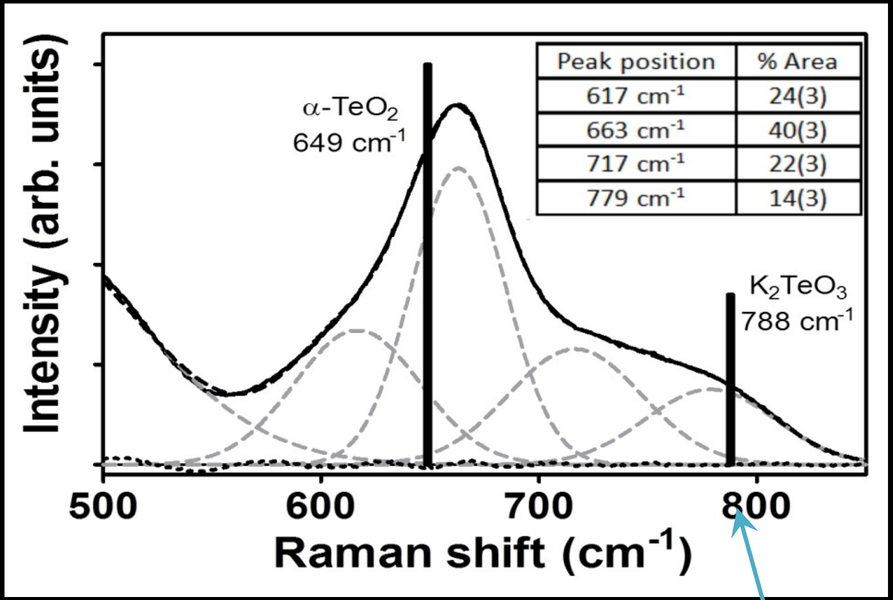
  (Sinclair et al, JNCS 1998)
- P_2O_5 glass is now well known to have terminal P=O bonds

  (Hoppe et al, J Phys Cond Matt 1998)

TeO_2 Raman Spectrum

- α-TeO_2: contains only TeO_4, principal peak 649cm^{-1}
- Crystalline K_2TeO_3: contains only TeO_3, principal peak 788cm^{-1}
- Amorphous TeO_2: Areas of fitted peaks give n_{TeO}=3.64

Following *(Kalampounias, Vib Spec 2012)*



Peak position	% Area
617 cm^{-1}	24(3)
663 cm^{-1}	40(3)
717 cm^{-1}	22(3)
779 cm^{-1}	14(3)

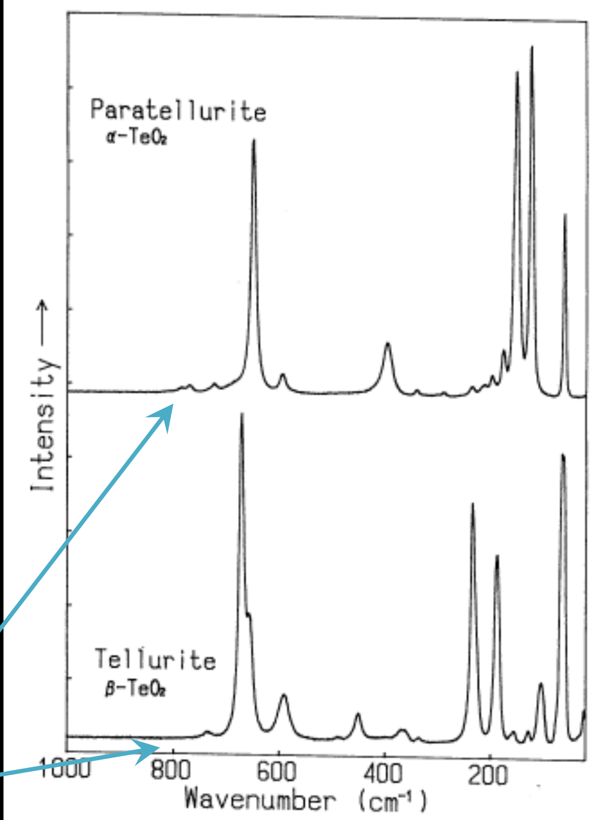


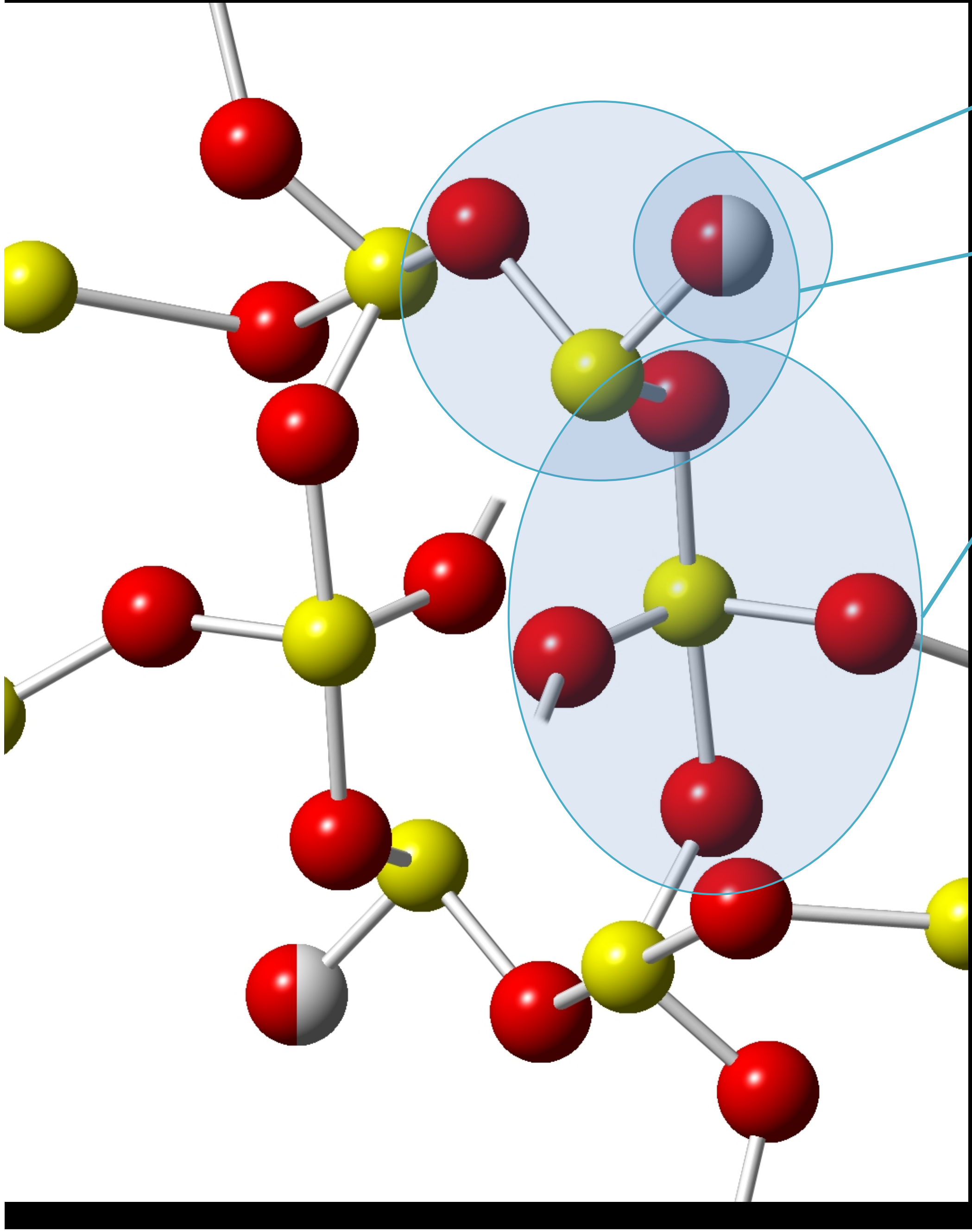
Fig. 1. Raman spectra of two polymorphic forms of TeO_2 crystals, paratellurite and tellurite.

Sekiya et al, J Cer Soc Jpn 1989

Vibration at ~780cm^{-1} is associated with TeO_3 units
Crystals containing only TeO_4 units have little or no intensity at ~780cm^{-1}

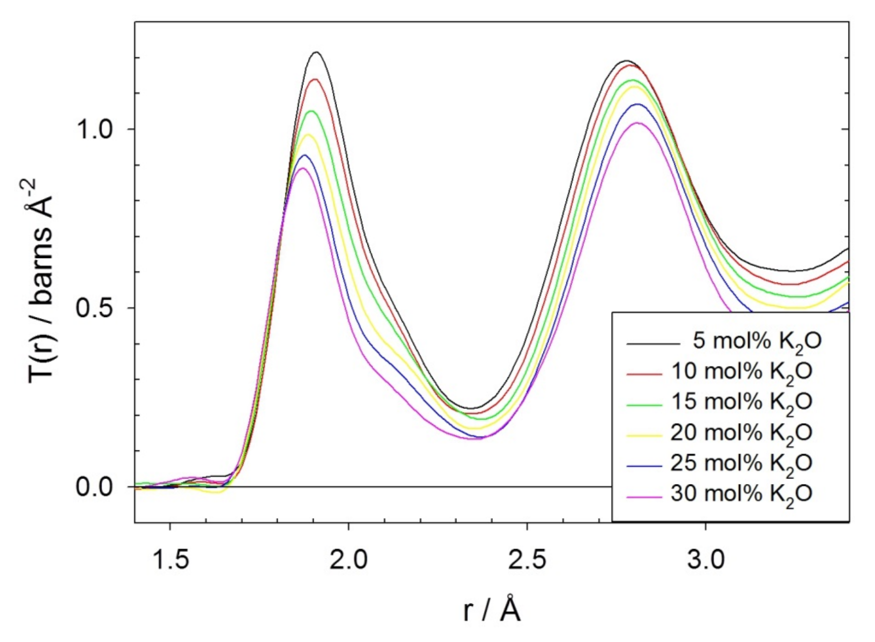
Barney, Hannon et al, J Phys Chem Lett 2013

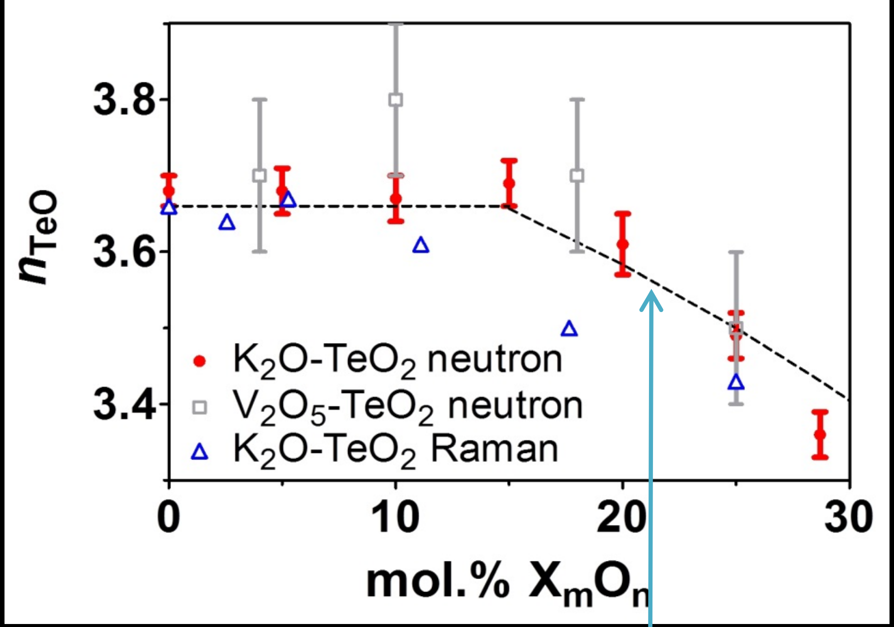
TeO_2 Structure



- Terminal oxygen
- TeO_3
- TeO_4
- Based on crystal structure of $K_2Te_4O_9$ *(Becker et al, Inorg Chem 1997)*

K_2O–TeO_2 glasses – Neutron Diffraction





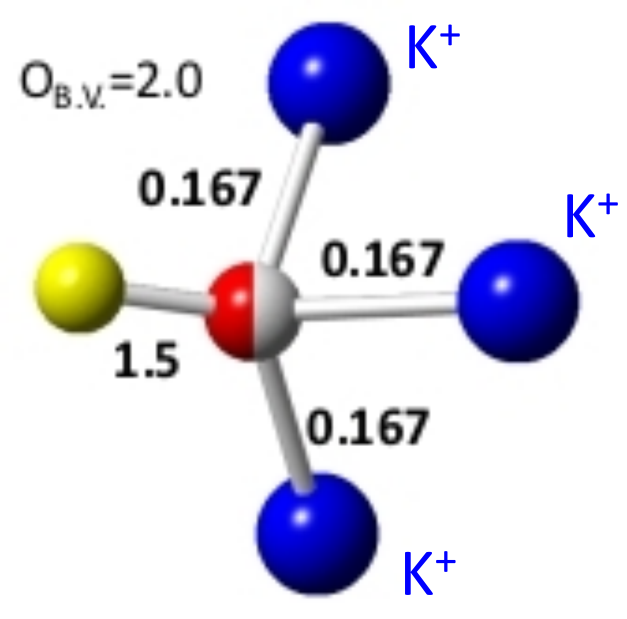
dashed line is model

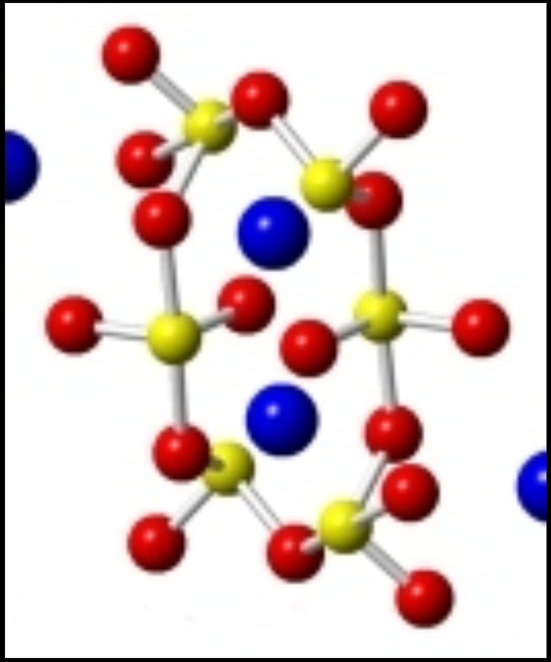
- ND on series of K_2O–TeO_2 glasses
  (roller quenched at Osaka Prefecture University)
- Te–O coordination number ~constant below ~15 mol% K_2O, decreases above ~15 mol% K_2O

Barney, Hannon et al,
J Phys Chem Lett 2013

Model for Tellurites

- Model is inspired by $K_2Te_4O_9$ crystal *(Becker et al, Inorg Chem 1997)*
- $K_2Te_4O_9$ has both TeO_3 and TeO_4 units, and non-bridging oxygens
- Each NBO is coordinated by 3 K^+ ions
- Model is based on 6-membered ring in $K_2Te_4O_9$ crystal

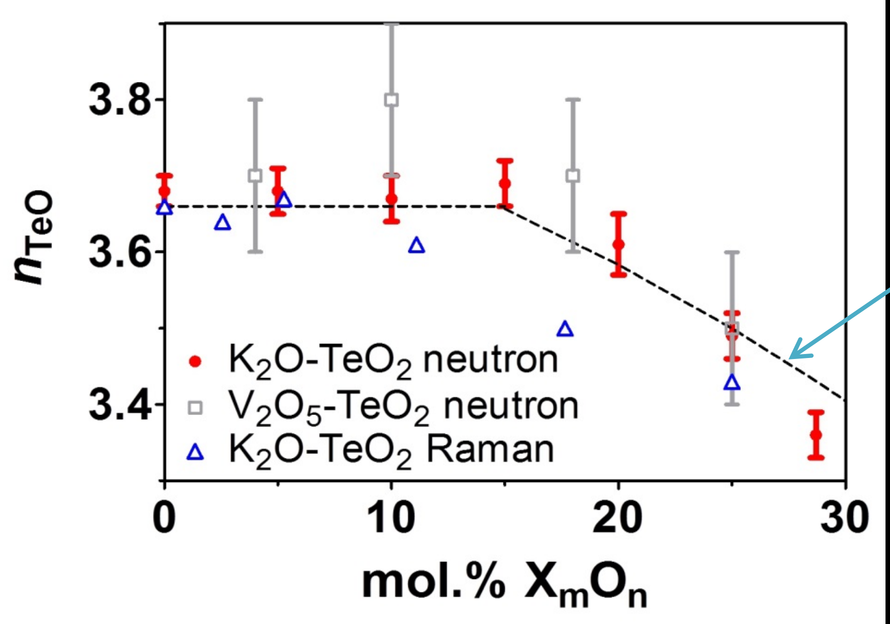




Barney, Hannon et al, J Phys Chem Lett, 2013

Model for Tellurites

- Adding K_2O to pure TeO_2 creates NBOs, n_{TeO} does not change
- Each K^+ ion bonds to 6 oxygens, 3 new NBOs, and 3 previously terminal oxygens
- At composition 14.3 mol% K_2O, all terminal oxygens are used up – then adding more K_2O causes conversion of TeO_4 to TeO_3 …

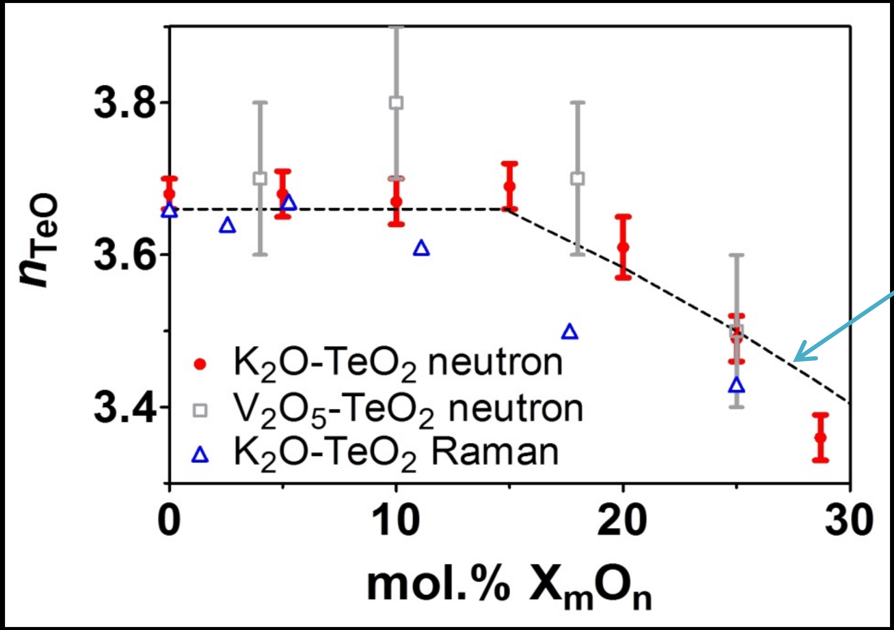


dashed line is model

Barney, Hannon et al, J Phys Chem Lett, 2013

Model for Tellurites

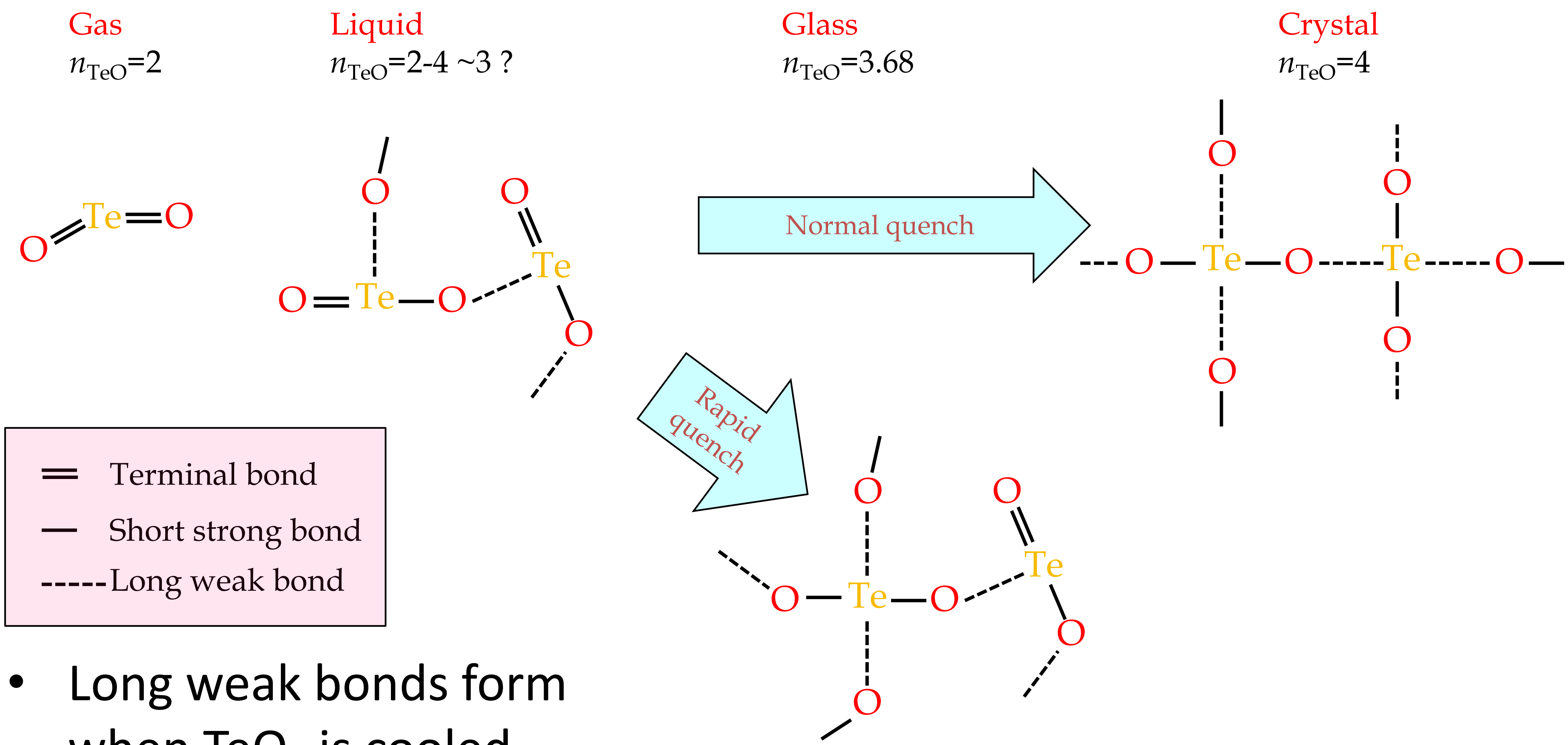
- For more than 14.3 mol% K_2O, the addition of K_2O breaks one additional Te–BO bond, converting TeO_4 to TeO_3
- K^+ ions now bond to some BO as well as NBO
- For this model, limit of glass formation is 31.8 mol% K_2O
  - we made glass up to 28.7 mol% K_2O



dashed line is model

Barney, Hannon et al, J Phys Chem Lett, 2013

Glass Formation



- Long weak bonds form when TeO_2 is cooled

Tellurites Summary

- Grammes of amorphous TeO_2 can be made by roller quenching
- Te–O coordination number is n_{TeO}=3.68(4) ,
  one third of Te are 3-coordinated,
  16% of oxygens are TERMINAL
- In K_2O-TeO_2 glasses, Te–O coordination number is unchanged for low K_2O, then decreases for more than ~15 mol% K_2O
- A model, based on discovery of terminal oxygens in pure TeO_2, accounts for the change in Te–O coordination number in tellurite glasses

Barney, Hannon et al, J Phys Chem Lett, 2013

Thanks for listening!
Any questions?