Short-range structural order in *Zr*-based multi - *component* glasses, using XAFS

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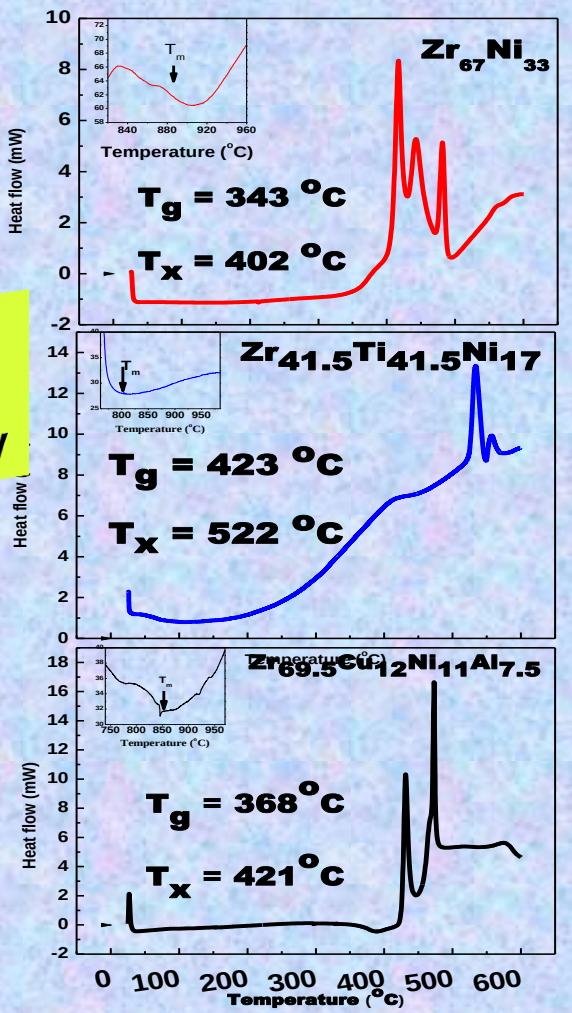
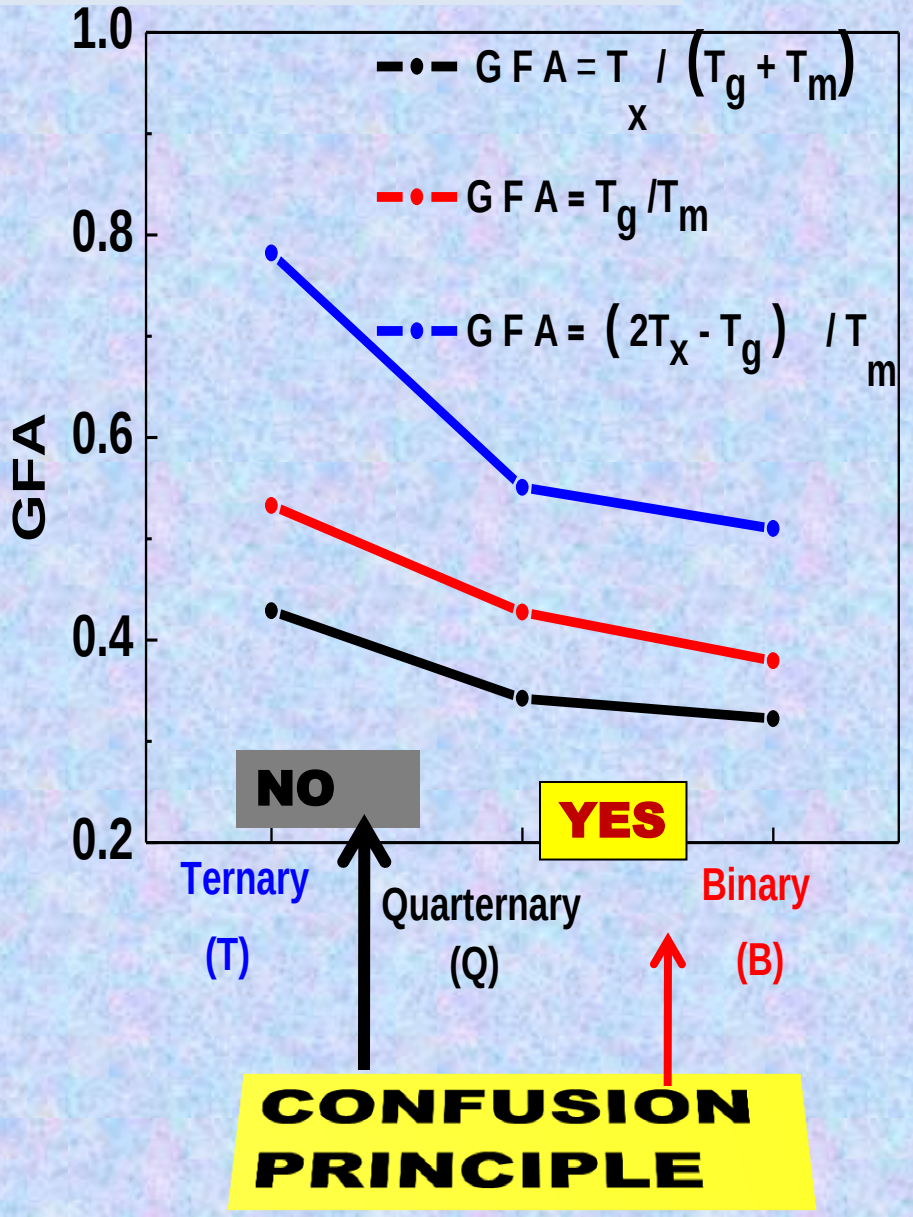
GLASS FORMING ABILITY

$Zr_{41.5}Ti_{41.5}Ni_{17}$ (T)> $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ (Q) > $Zr_{67}Ni_{33}$ (B)

Differential scanning calorimetry





Synthesis of metallic glass ribbons

Alloys: $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$
$Zr_{41.5}Ti_{41.5}Ni_{17}$
$Zr_{67}Ni_{33}$

Vacuum arc melting → Melt spinning

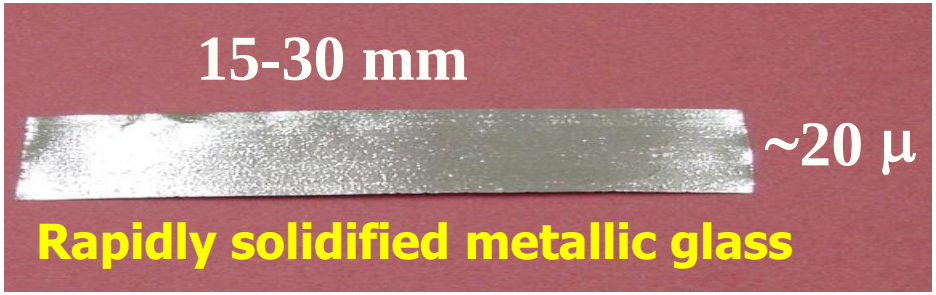
Parameters

Wheel Speed – 55 m/s

Wheel to crucible gap ~ 1 mm

Ar gas pressure – 1 kg/mm²

Melt spinning

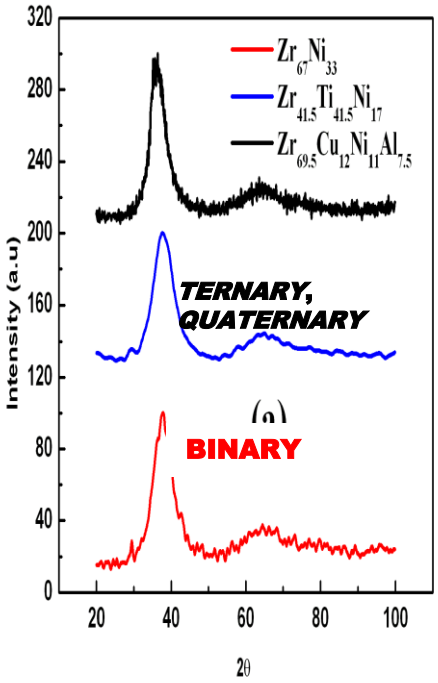


GLASS FORMING ABILITY STRUCTURE

$Zr_{41.5}Ti_{41.5}Ni_{17}$ (T)> $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ (Q) > $Zr_{67}Ni_{33}$ (B)

XRD

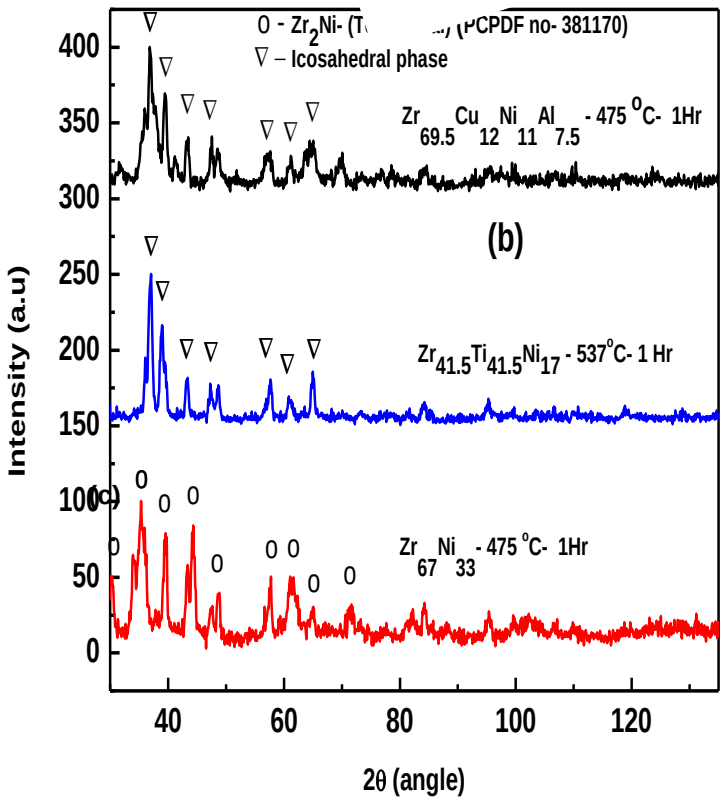
GLASS



QUASI - CRYSTAL

$NiZr_2$

ANNEALED

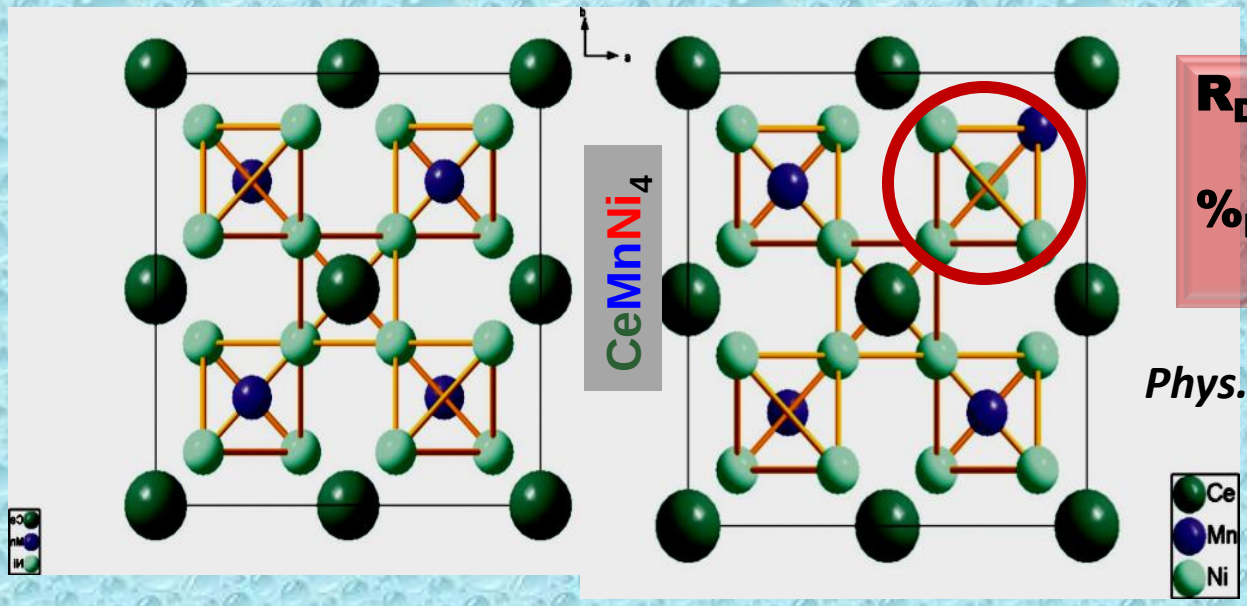


NO *explanation* of GFA from LRO

SHORT - RANGE - ORDER

(SRO)

Local structure ≠ ***Long*-Range order (LRO)**



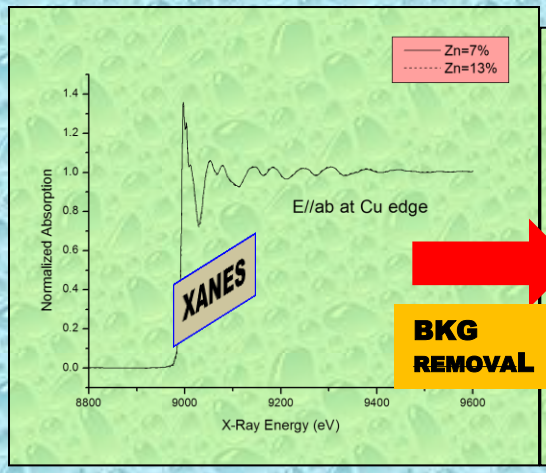
R_{DEFECT} < 8 Å (SRO)

$\%_{DEFECT}$ ≥ 1-5%

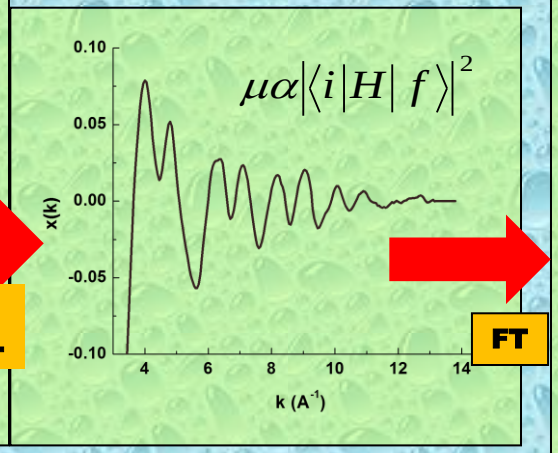
Phys. Rev. B 82, 134424 (2010)

XAFS …

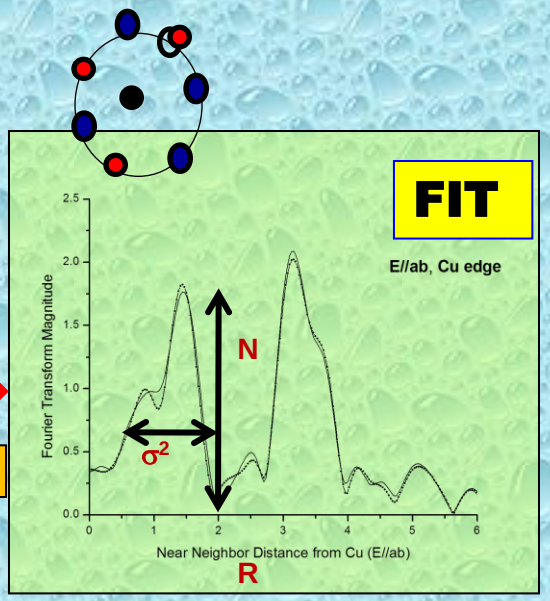
XAFS (X-Ray Absorption Fine Structure)

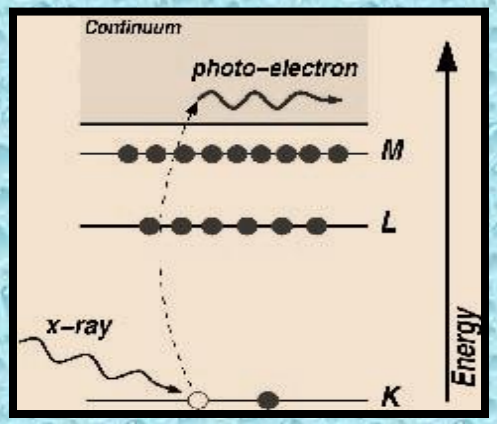


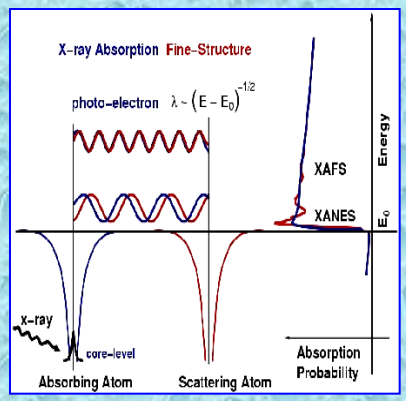
BKG REMOVAL



FT







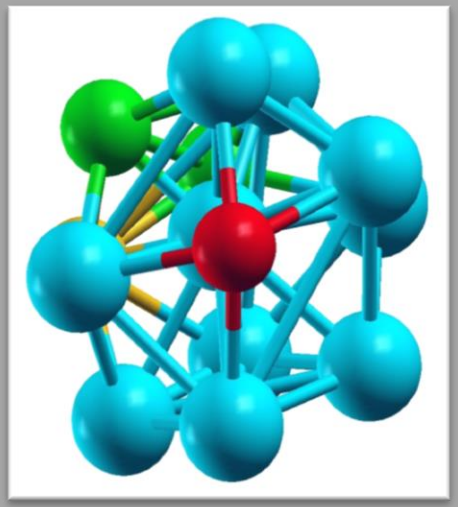
MODEL NOT MUST
FIT AS-IT-IS (error <5%)

COMPLICATED SYSTEMS

-COMPETETIVE MODELS
- SUPPORTING THEORY / TECHNIQUES

SYNCHROTRON - BESSY (GERMANY), APS (USA)

SRO= CLUSTER

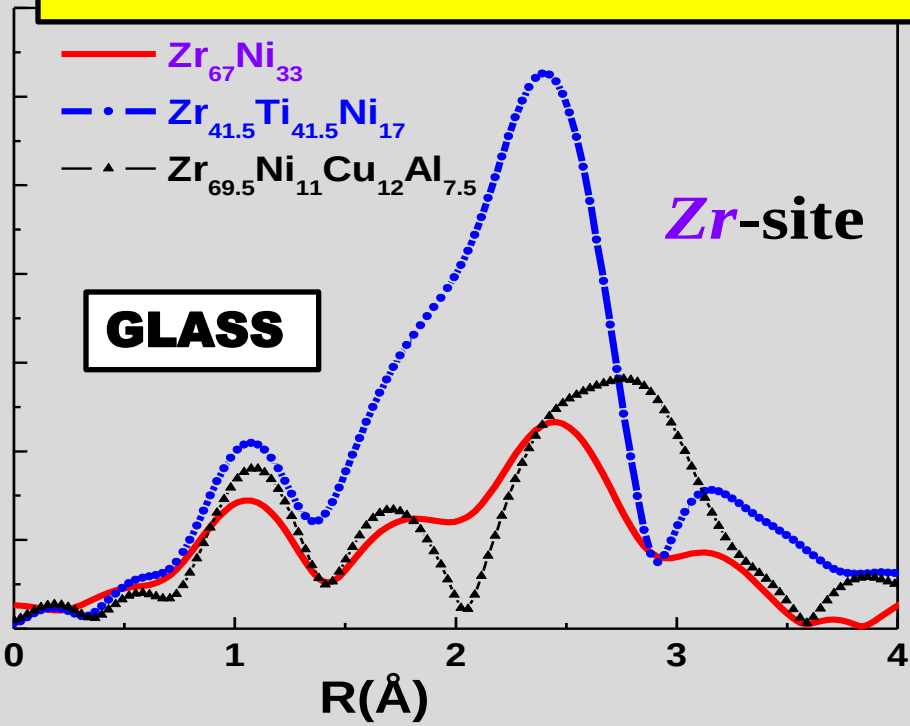


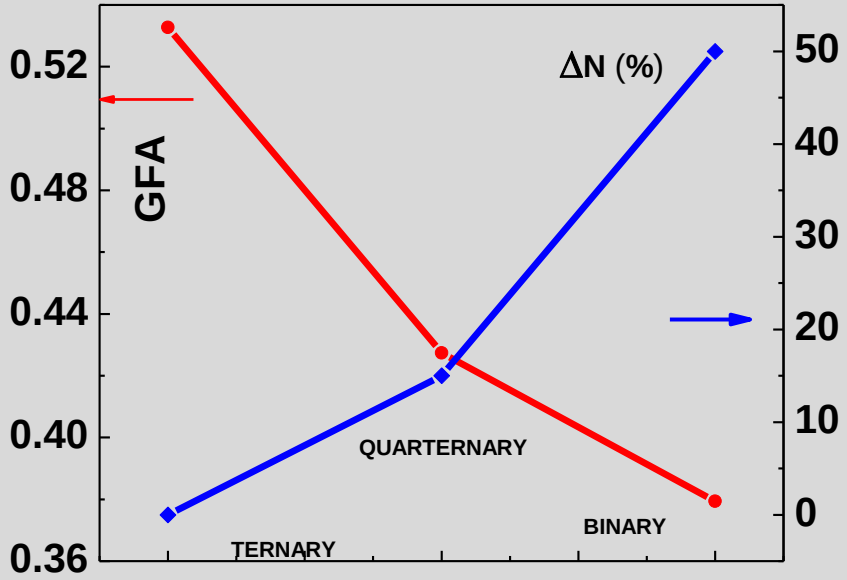
- **CONFIGURATION**
  - ***ICOSAHEDRAL*** **(ISRO : f_{ISRO})**
- ***HETEROGENEITY*** **(Δf)**
- **DEGREE OF DISORDER** σ^2
- **CHEMICAL ORDER**
  - **CHARGE TRANSFER**
  - ***BOND-LENGTH***

XAFS **MOLECULAR DYNAMICS + DOS**

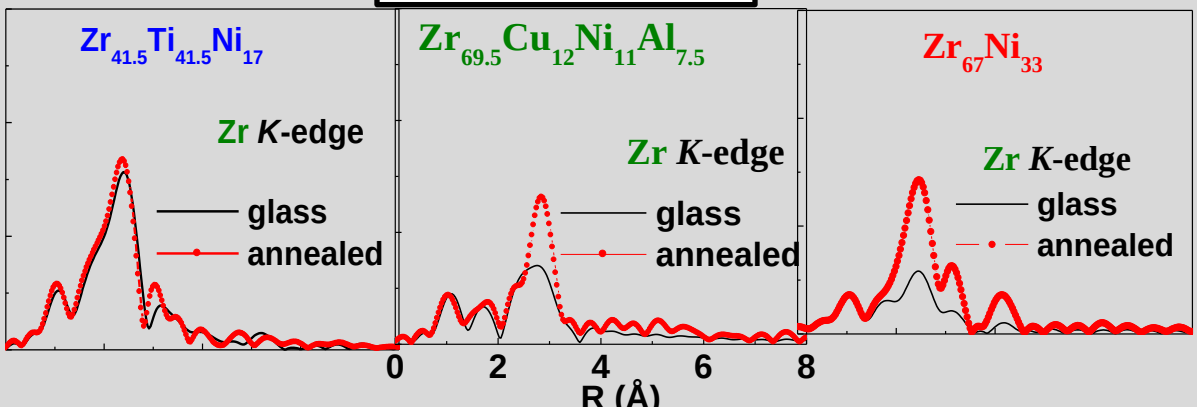
GLASSY + ANNEALED PHASES

XAFS RESULTS





ANNEALING



MULTI-COMPONENT

DISORDER
TOO MANY ELEMENTS

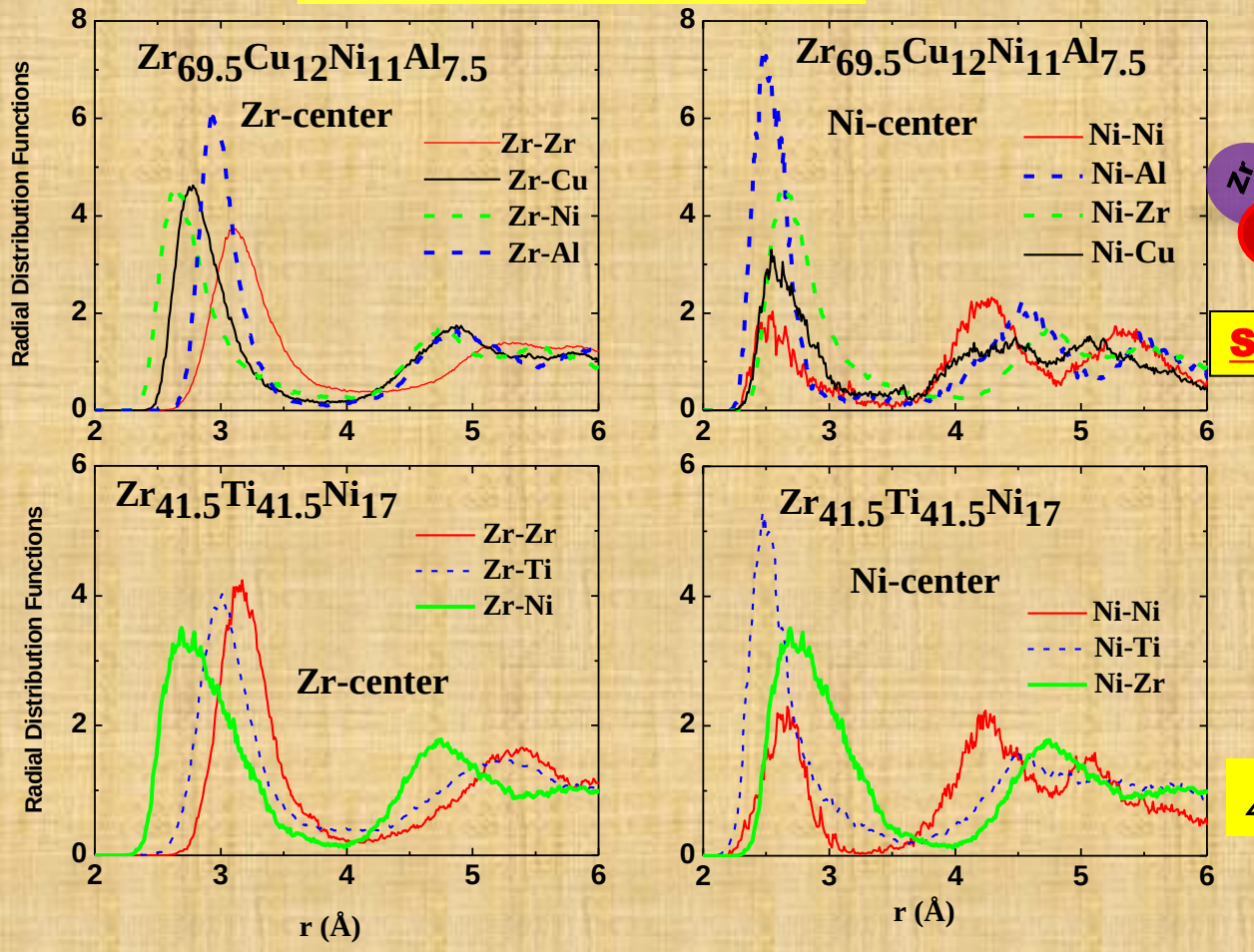
BOND - LENGTHS

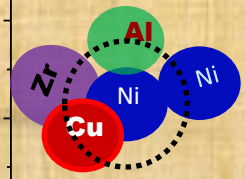
XAFS

$R_{Ni\text{-}Zr}$ = 2.61 Å
$R_{Ni\text{-}Ni}$ = 2.61 Å
$R_{Cu\text{-}Zr}$ = 2.72 Å
$R_{Zr\text{-}Zr}$ = 3.07 Å

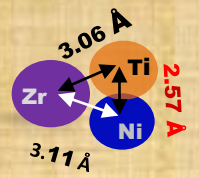
$R_{Ni\text{-}Zr}$ = 3.11 Å
$R_{Ni\text{-}Ti}$ = 2.56 Å
$R_{Ti\text{-}Zr}$ = 3.06 Å
$R_{Zr\text{-}Zr}$ = 3.24 Å

MOLECULAR DYNAMICS





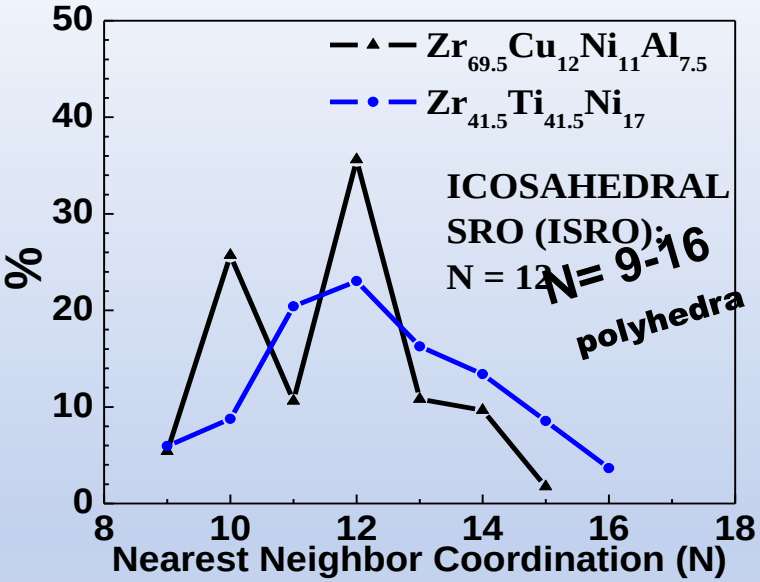
SAME ***bond-length***



ΔR = 0.5 Å

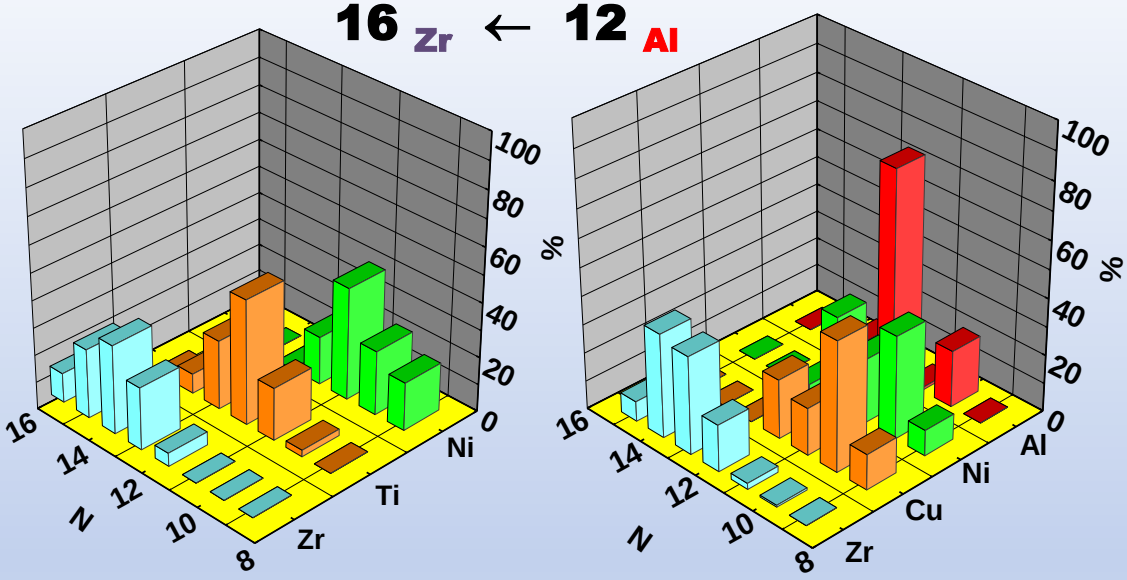
NEAREST NEIGHBOR CONFIGURATION

AIMD SIMULATIONS

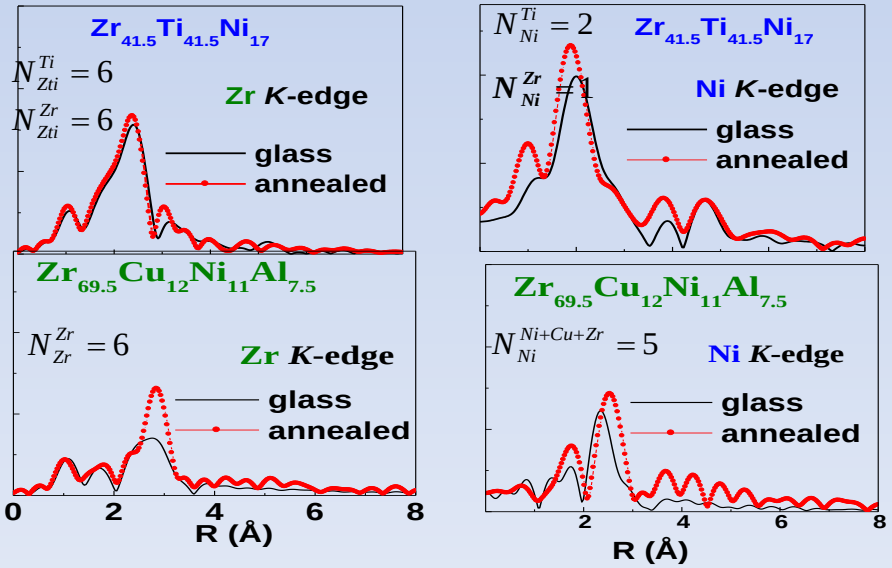


HETEROGENEOUS

16 Zr ← 12 Al

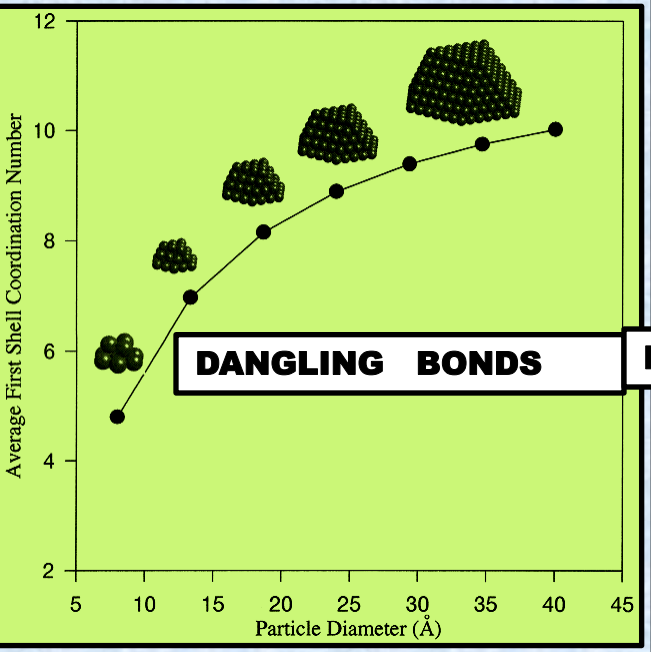


XAFS

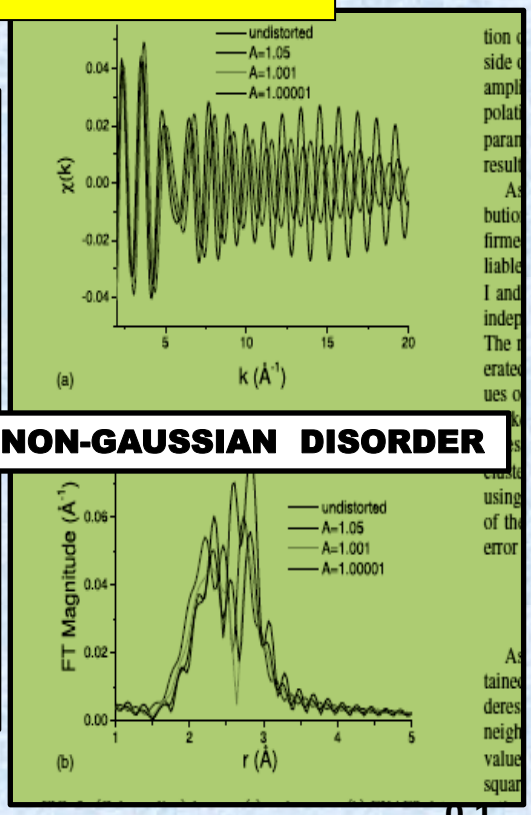


EFFECTIVE *COORDINATION NUMBER* (SITE-AVERAGE)

CLUSTER SIZE / DISORDER



DANGLING BONDS

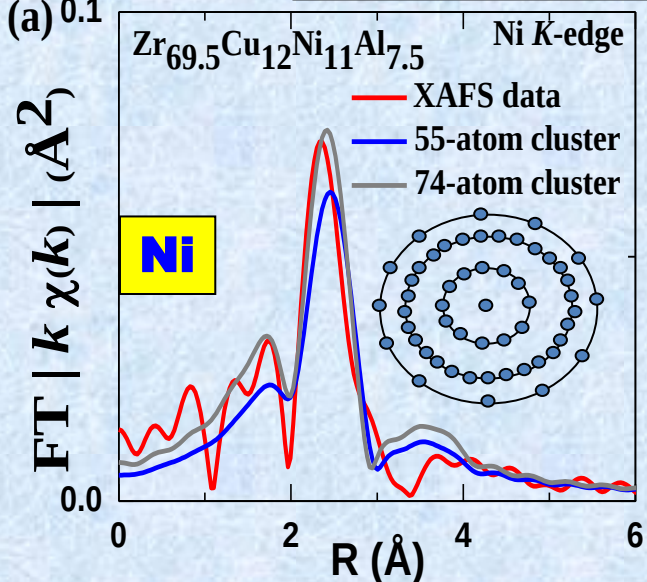


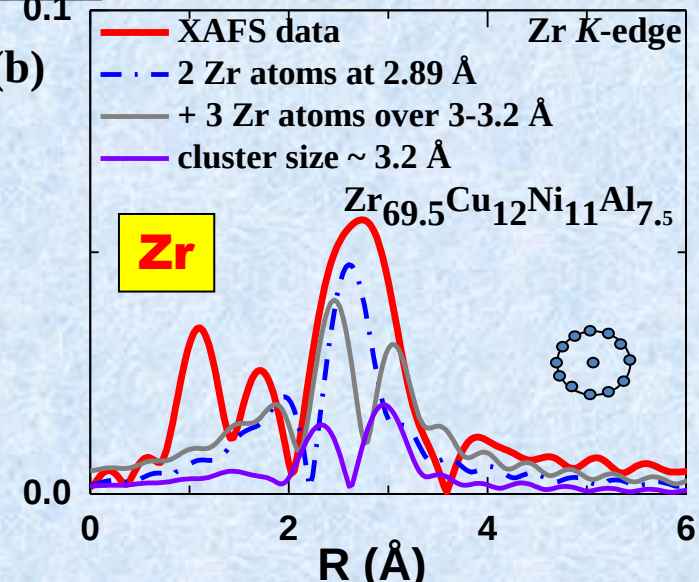
NON-GAUSSIAN DISORDER

J. Phys. Chem. B 105 (51), 12699 (2001);

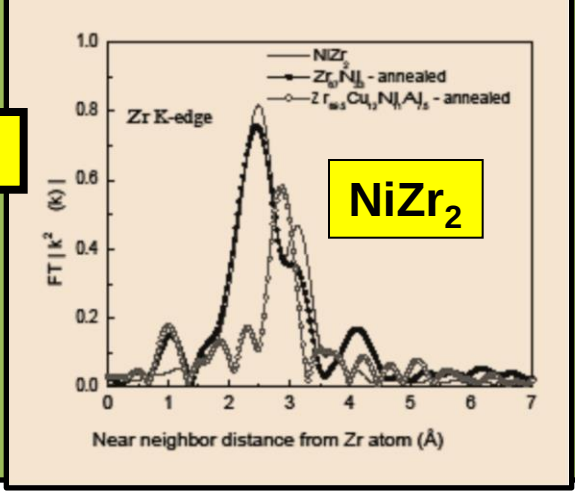
PRB 81, 115451 (2010) ... A.I FRENKEL

XAFS + AIMD

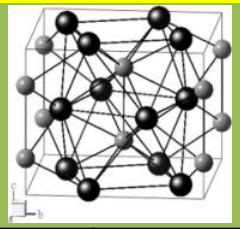




BINARY



> 2ND NEAREST NEIGHBOR



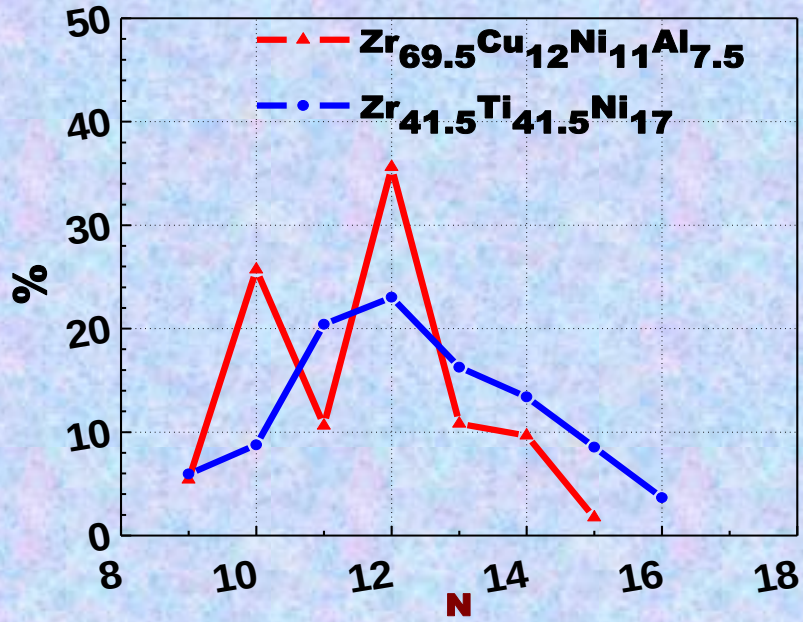
R_{Zr-Ni} = 2.66 Å	R_{Zr-Zr} = 3.05 Å	R_{Zr-Zr} = 3.32 Å
$NiZr_2$: 2.76 Å	2.98-3.07 Å	3.36-3.43 Å

MULTI- *component* VS. *BINARY*

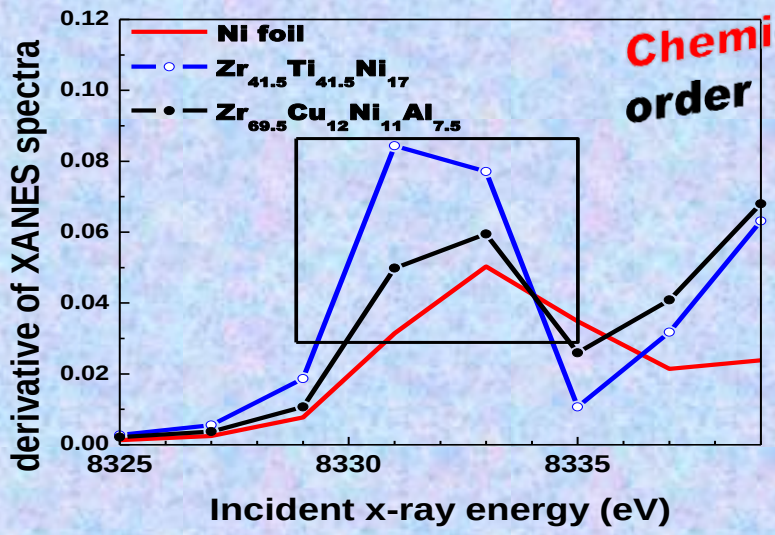
GOOD	POOR

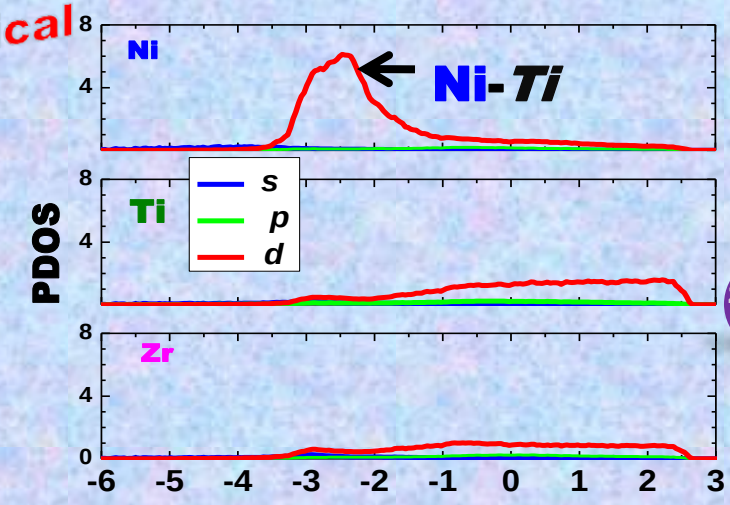
Cluster parameters	Correlation with **GFA**
f_{ISRO}	+
Δf	+
σ^2	-
ΔN ▶ annealing	-

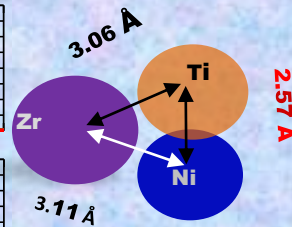
$Zr_{41.5}Ti_{41.5}Ni_{17}$ > $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$



	$Zr_{41.5}Ti_{41.5}Ni_{17}$	$Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$
f_{ico} *Icosahedral fraction*	24%	35%
Δf Configuration Diversity	36%	13%







SUMMARY

MULTI-*COMPONENT*

$Zr_{41\text{-}5}Ti_{41.5}Ni_{17}$,

$Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$

CHEMICAL ORDER

BINARY

$Zr_{67}Ni_{33}$

- **CONFIGURATION**
  - ISRO >25% ↔ XTAL
- ***HETEROGENEITY***
  - > 10% ↔ 0%
- **DEGREE OF ORDER**
  - 1st SHELL
  - > 2nd SHELL

UNDER INVESTIGATION

- **MEDIUM-RANGE-ORDER**
- **STRUCTURAL CHANGES**
  - ***UNDER DEFORMATION***
  - ***COOLING RATES***

ACKNOWLEDGEMENTS

- HIGH PRESSURE & SYNCHROTRON RADIATION PHYSICS DIVISION - BARC
- MATERIALS SCIENCE DIVISION - BARC
- HELMHOLTZ-ZENTRUM - GERMANY
- BESSY - GERMANY
- APS - USA