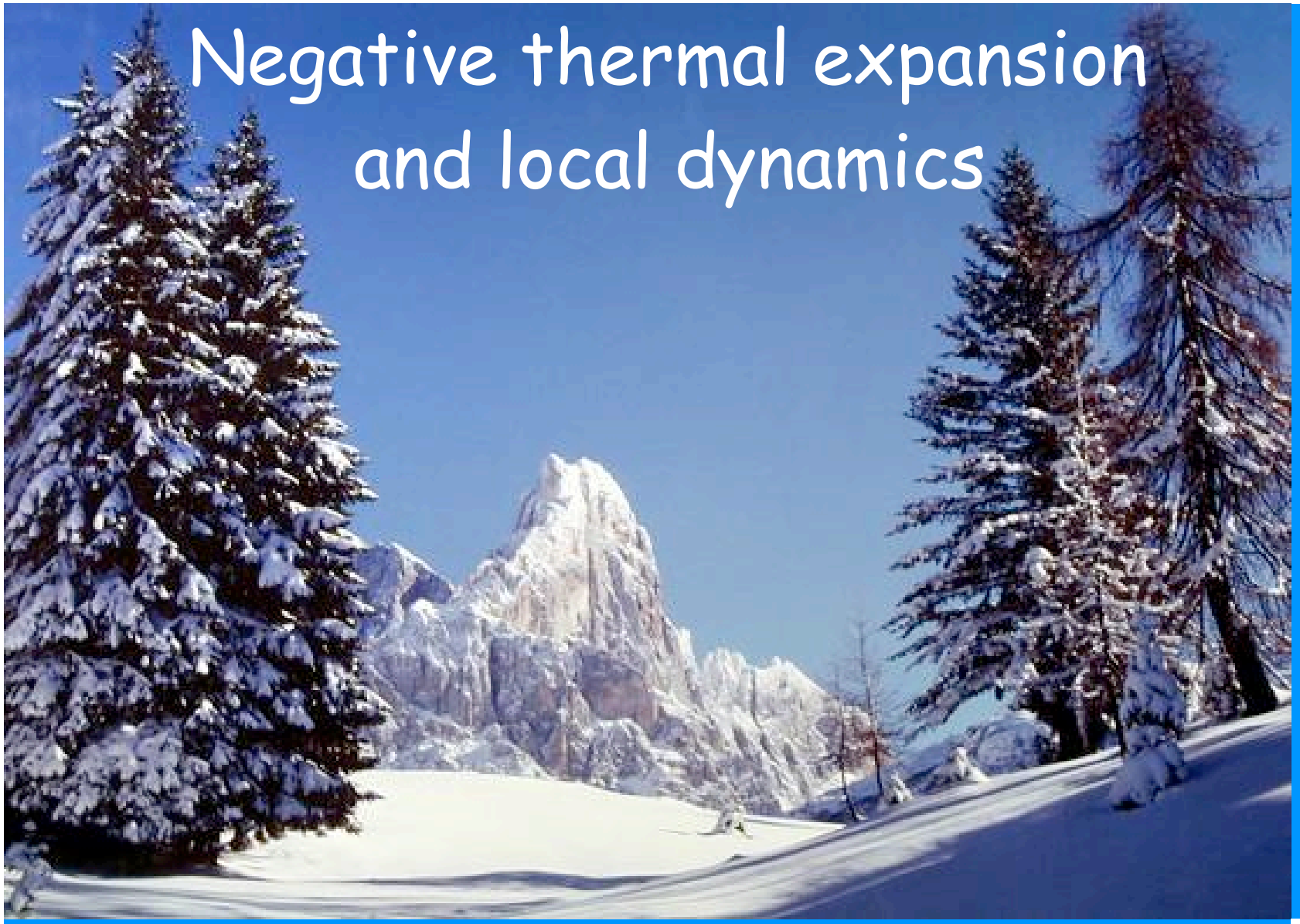
Negative thermal expansion and local dynamics



P. Fornasini,

N. Abd el All, S. I. Ahmed, A. Sanson, M. Vaccari

XAFS XIV

Overview

- Negative thermal expansion (NTE)
- EXAFS and local dynamics
- EXAFS studies of NTE materials

Thermal expansion in 2-atomic systems

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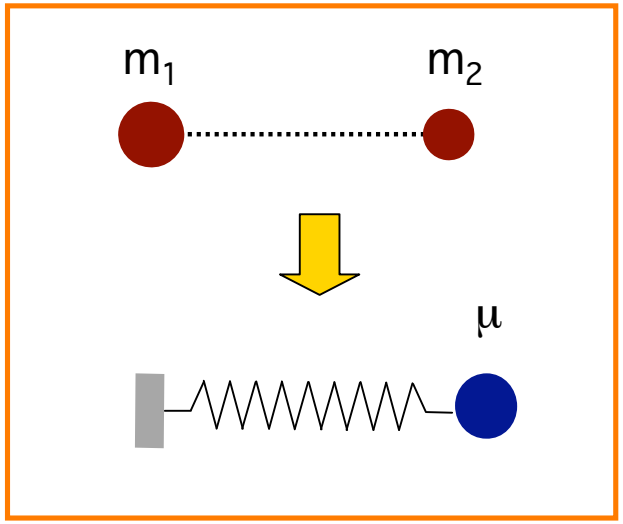
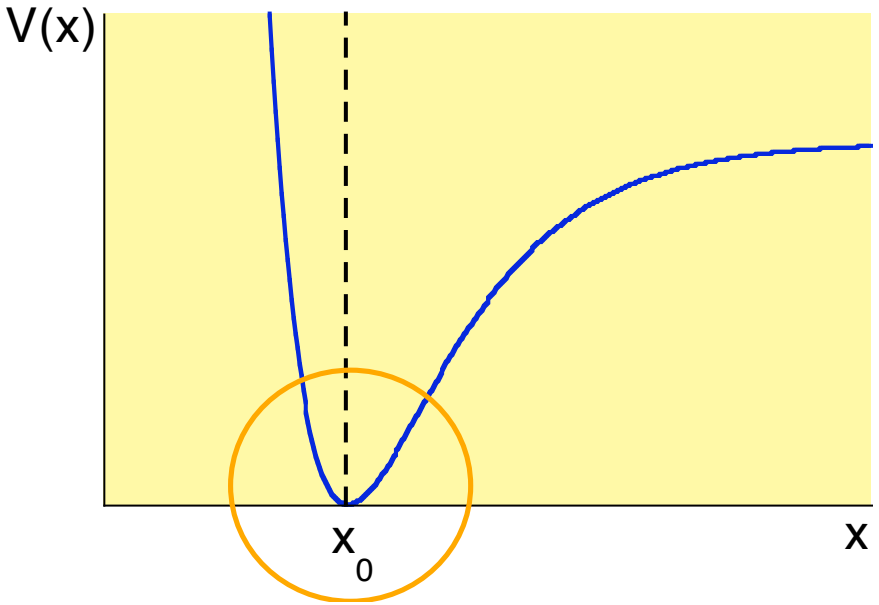
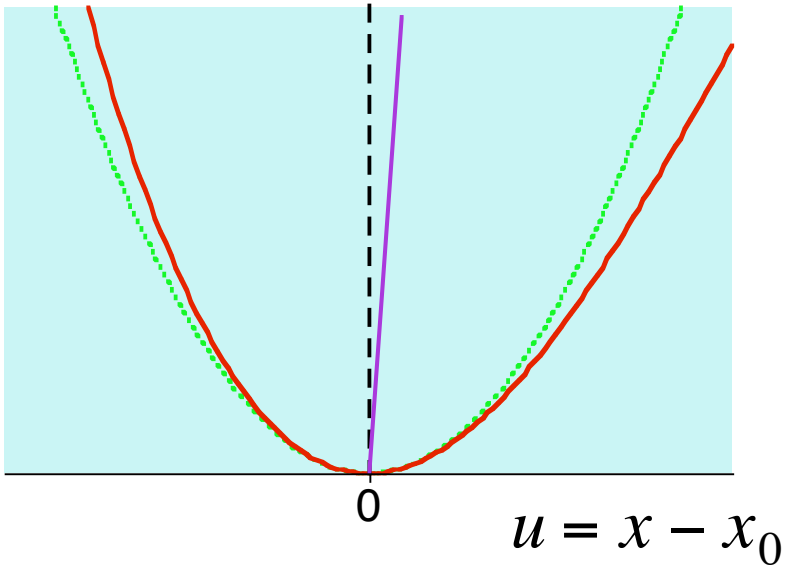


$$V(u) = \frac{1}{2} k_0 u^2 + k_3 u^3 + k_4 u^4 + \ldots.$$

Positive expansion





Thermal expansion in many-atomic systems

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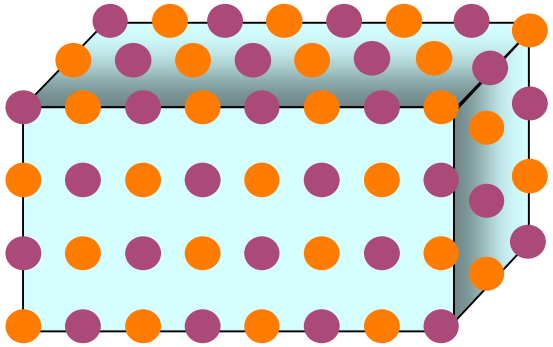

$$V(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_n)$$

Crystal potential
defined in
3n-dim. configurational space

Positive
or
negative

thermal expansion

Isotropic
or
anisotropic

NTE in tetrahedral semiconductors

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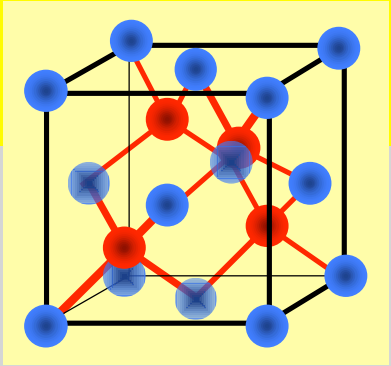

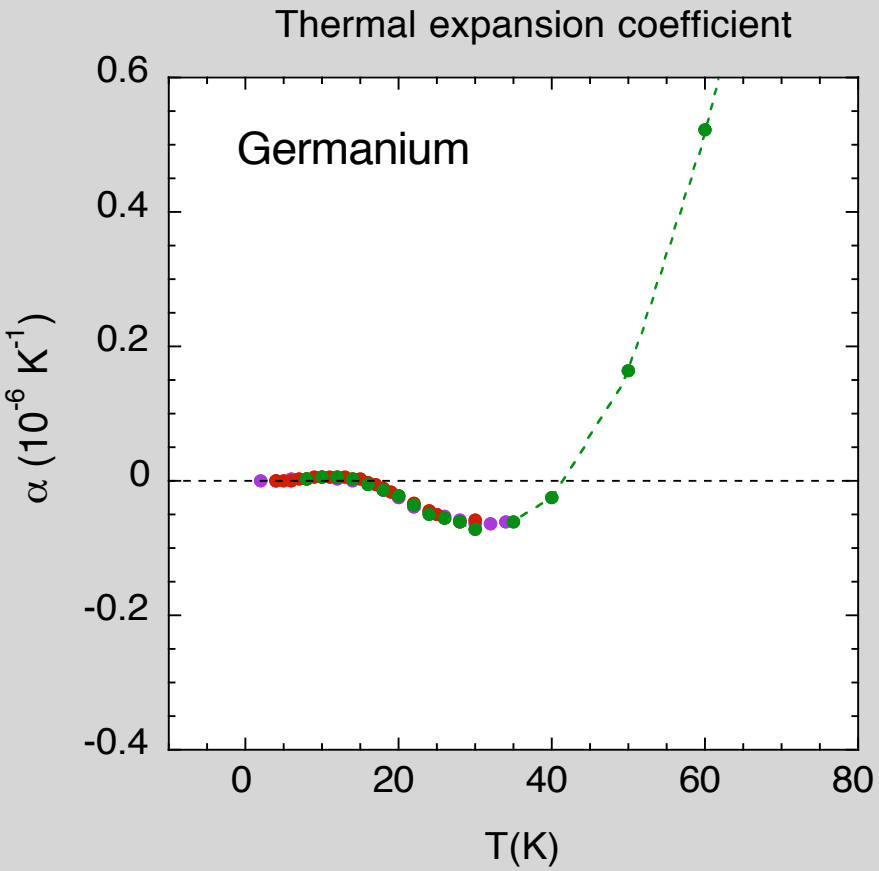

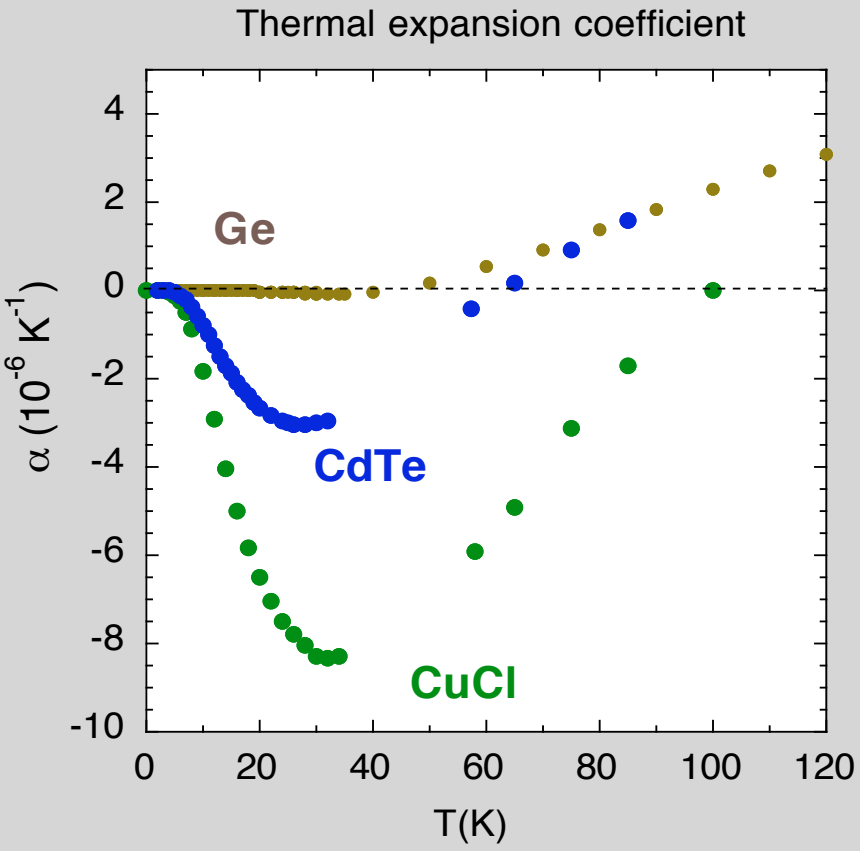

Barron, Birch, White - J. Phys. C 10, 1617 (1977)

NTE in framework structures

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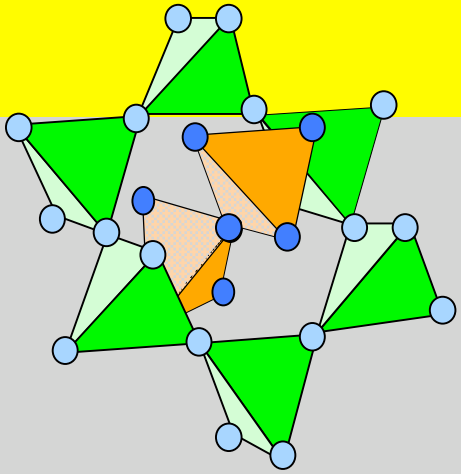

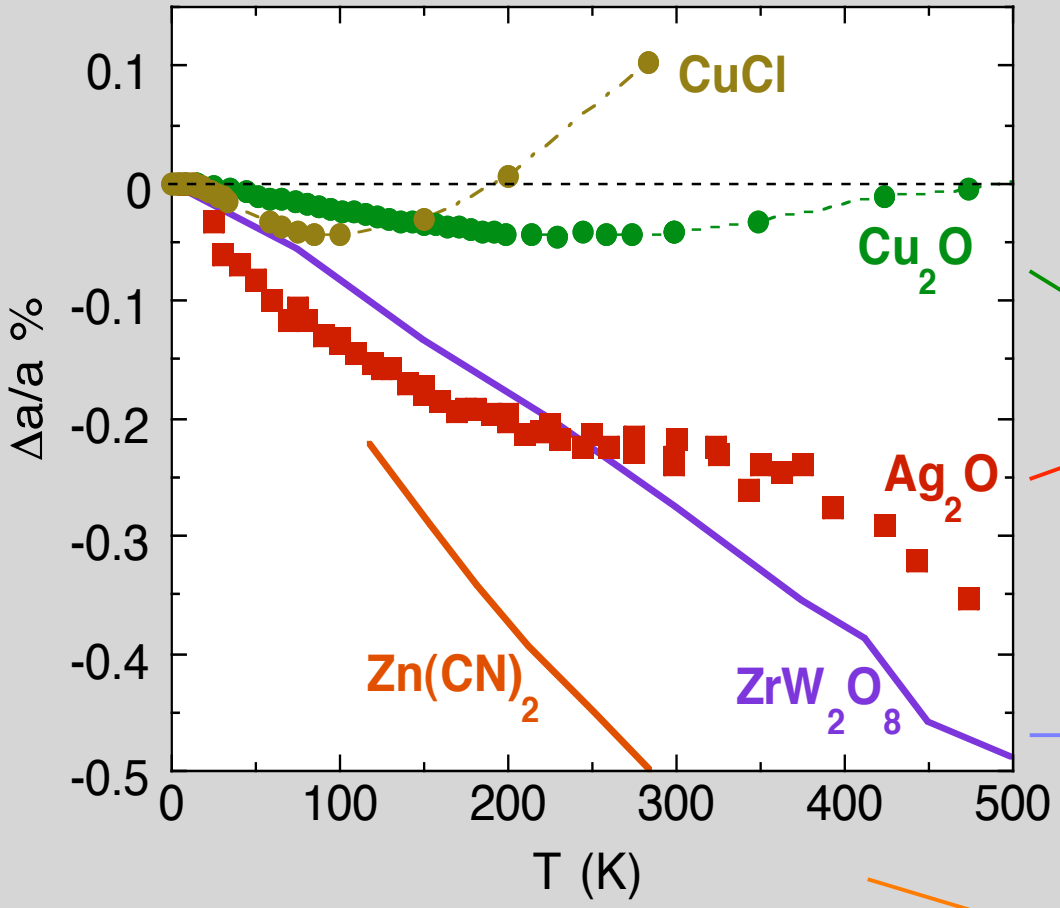

Cuprite structure

Tiano, Dapiaggi, Artioli,
J. Appl. Cryst. 36, 1461 (2003)

Mary, Evans, Vogt, Sleight
Science, 272 (1996)

Chapman, Chupas, Kepert
J. Am. Chem. Soc. 127, 15630 (2005)

“Global” approach to NTE

$$V(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_n)$$

Crystal potential
defined in
3n-dim. configurational space

Born - von Karman power expansion
with respect to atomic displacements

anharmonic terms ⇔ thermal expansion

Quasi-harmonic approximation:

Mode Grüneisen parameters

- positive → Positive contribution
- negative → Negative contribution

“Local” approach to NTE

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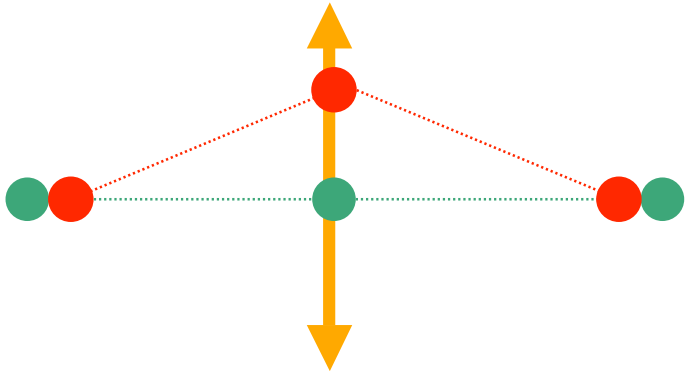
Anharmonicity of effective pair potential V(r)

Bond-stretching effect

Positive contribution

Perpendicular vibrations



Tension effect

Negative contribution

Barrera, Bruno, Barron, Allan - J. Phys. Cond. Matter, 17 (2005)

Bond distances

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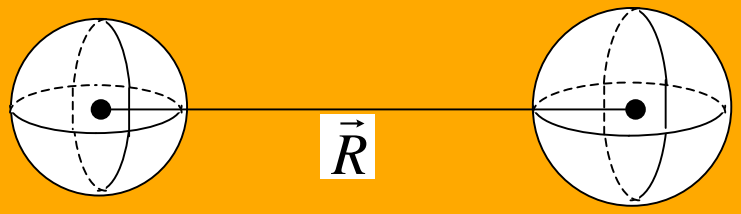
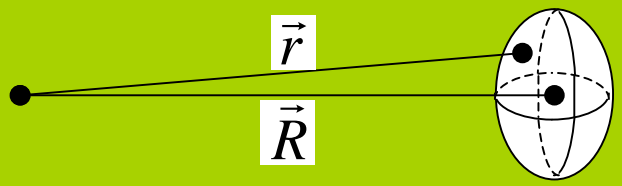
Bragg diffraction, dilatometry $R = \left| \langle \vec{r}_b \rangle - \langle \vec{r}_a \rangle \right|$

Distance between average atomic positions





Average distance

EXAFS, diffuse scattering $\langle r \rangle = \langle |\vec{r}_b - \vec{r}_a| \rangle$

$$\langle r \rangle \approx R + \frac{\langle \Delta u_\perp^2 \rangle}{2R}$$

Perpendicular MSRD

Fornasini et al., Phys. Rev. B 70, 174301 (2004)

Thermal factors

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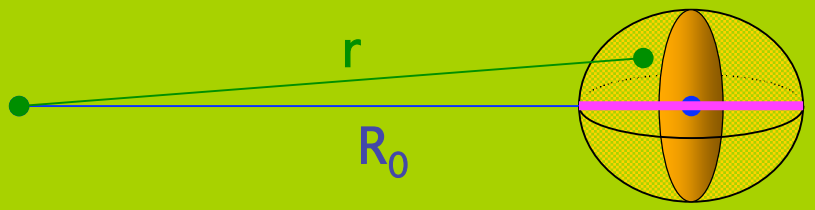
Bragg diffraction: MSDs of single atoms

Absolute vibrations

Relative vibrations



Perpendicular

Parallel

EXAFS & diffraction: MSRDs

Fornasini et al., Phys. Rev. B 70, 174301 (2004)

EXAFS and NTE

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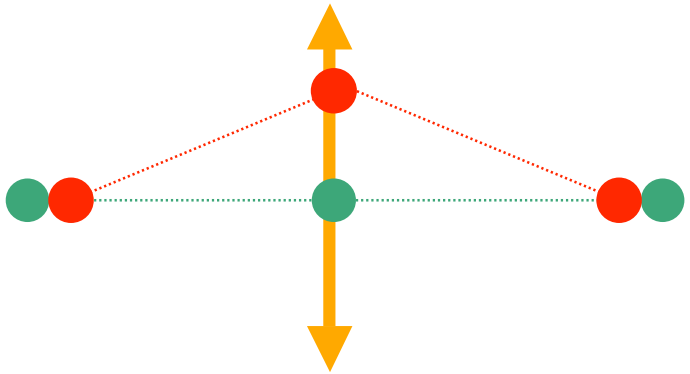
- Expansion of selected bond distances

Bond-stretching effect

- MSRD
  - parallel
  - perpendicular

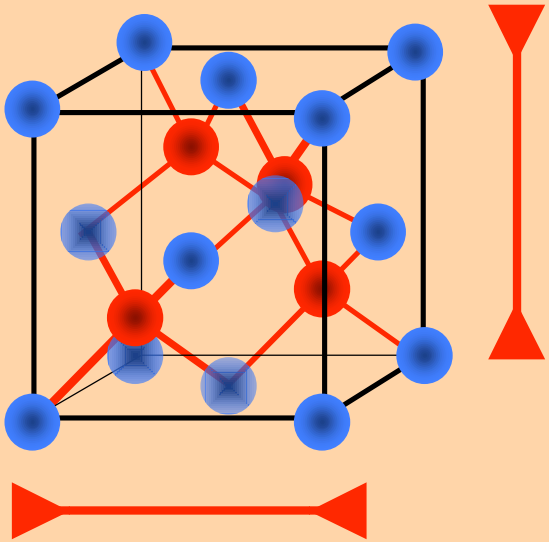


Tension effect

NTE structures studied by EXAFS (a)

Zincblende

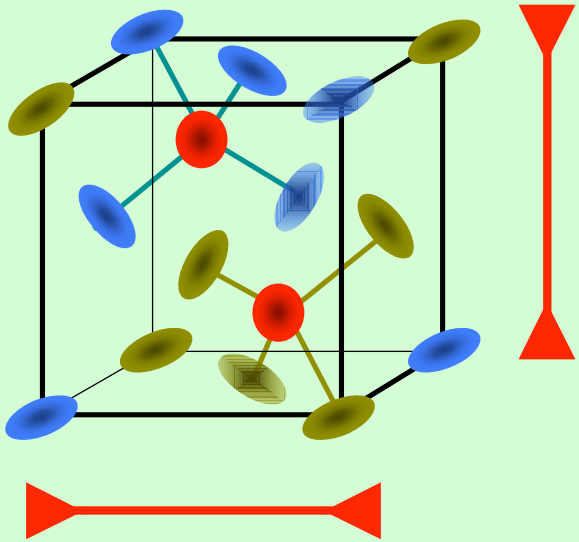
Ge, CdTe, CuCl



Isotropic NTE

Cuprite

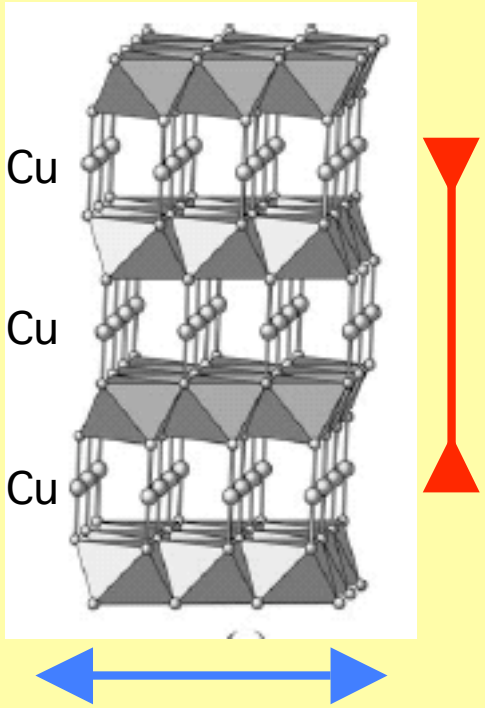
Cu_2O, Ag_2O



Isotropic NTE

Delafossite

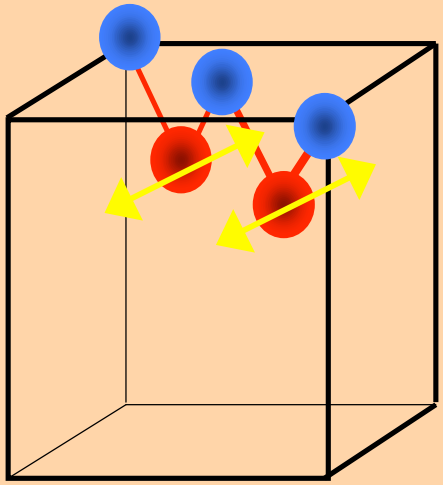
$CuScO_2$, $CuLaO_2$



Anisotropic NTE

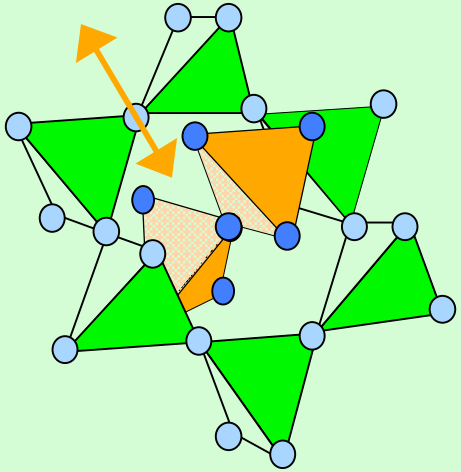
NTE structures studied by EXAFS (b)

Zincblende

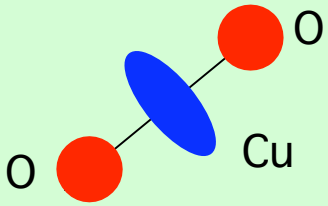


TA acoustic modes
at BZ boundary
with negative
Grueneisen parameters

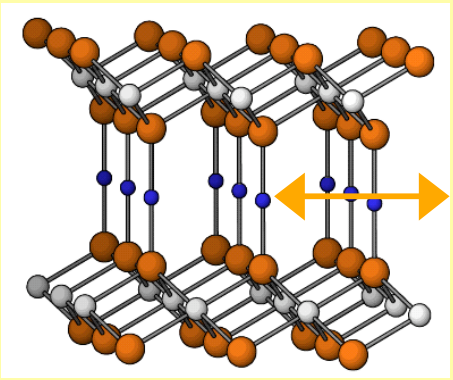
Cuprite



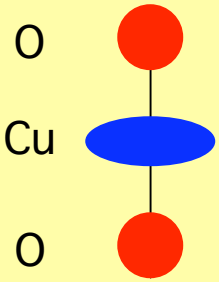
Framerwork structure:
2 networks of
M_4O tetrahedra



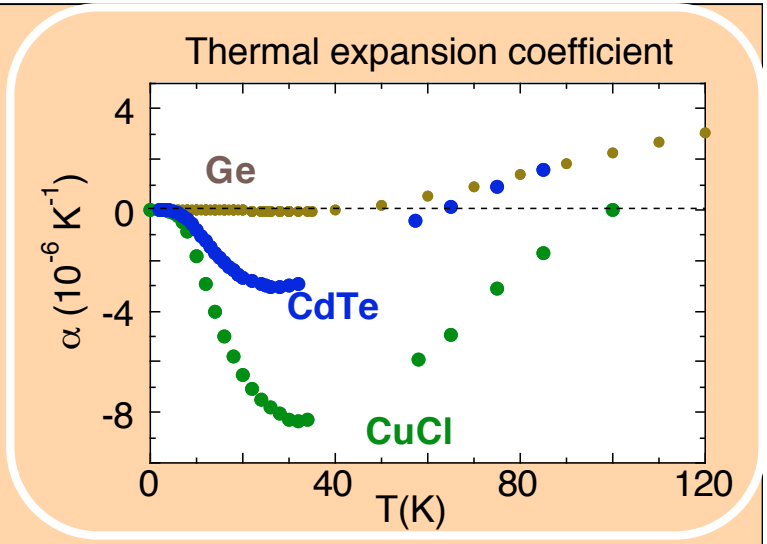
Delafossite

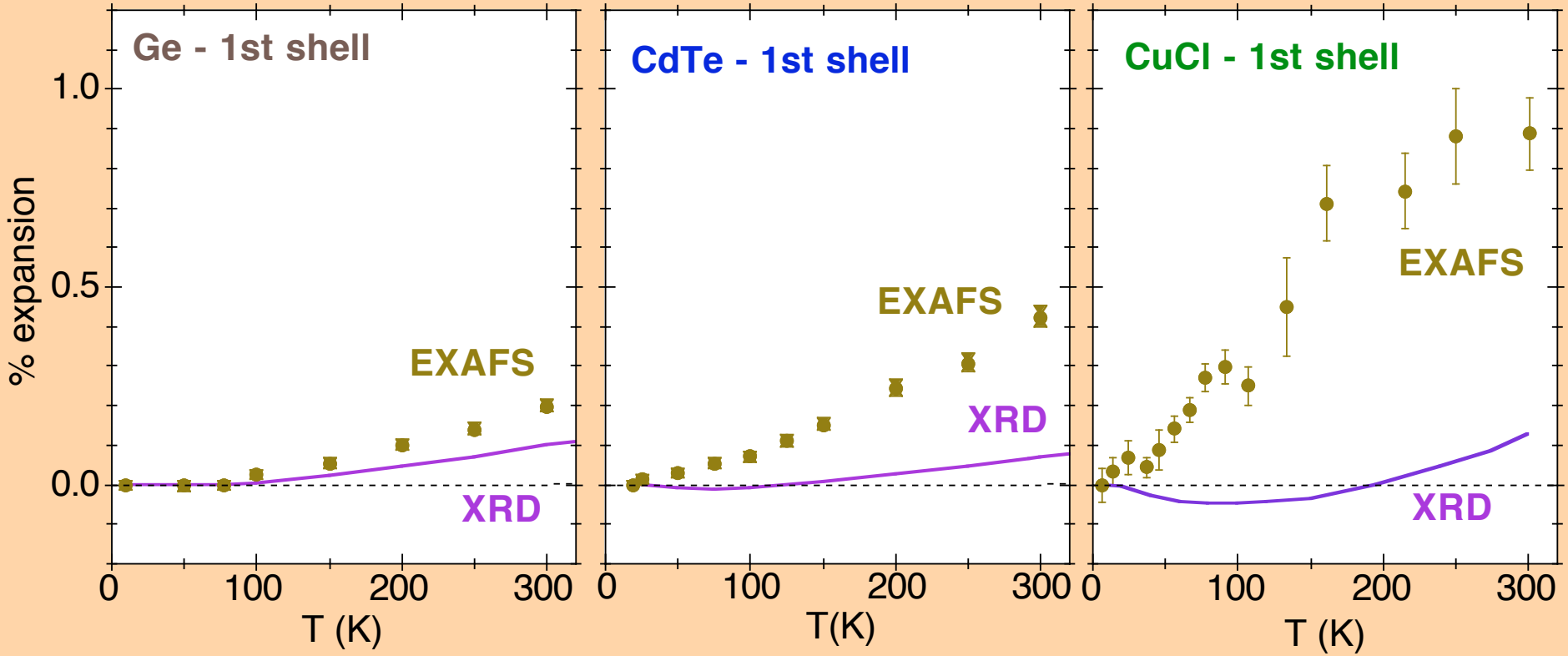


Neutron diffraction:
Cu-O NTE
Anisotropic Cu motion



Bond expansion in zincblende structures



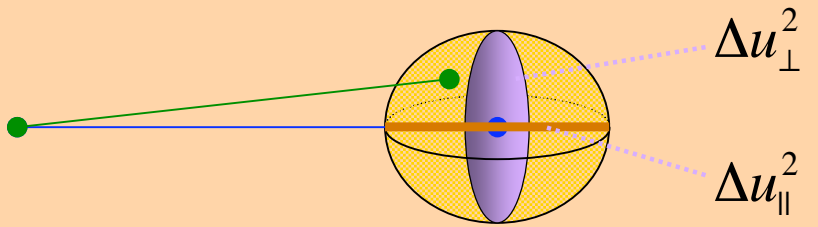


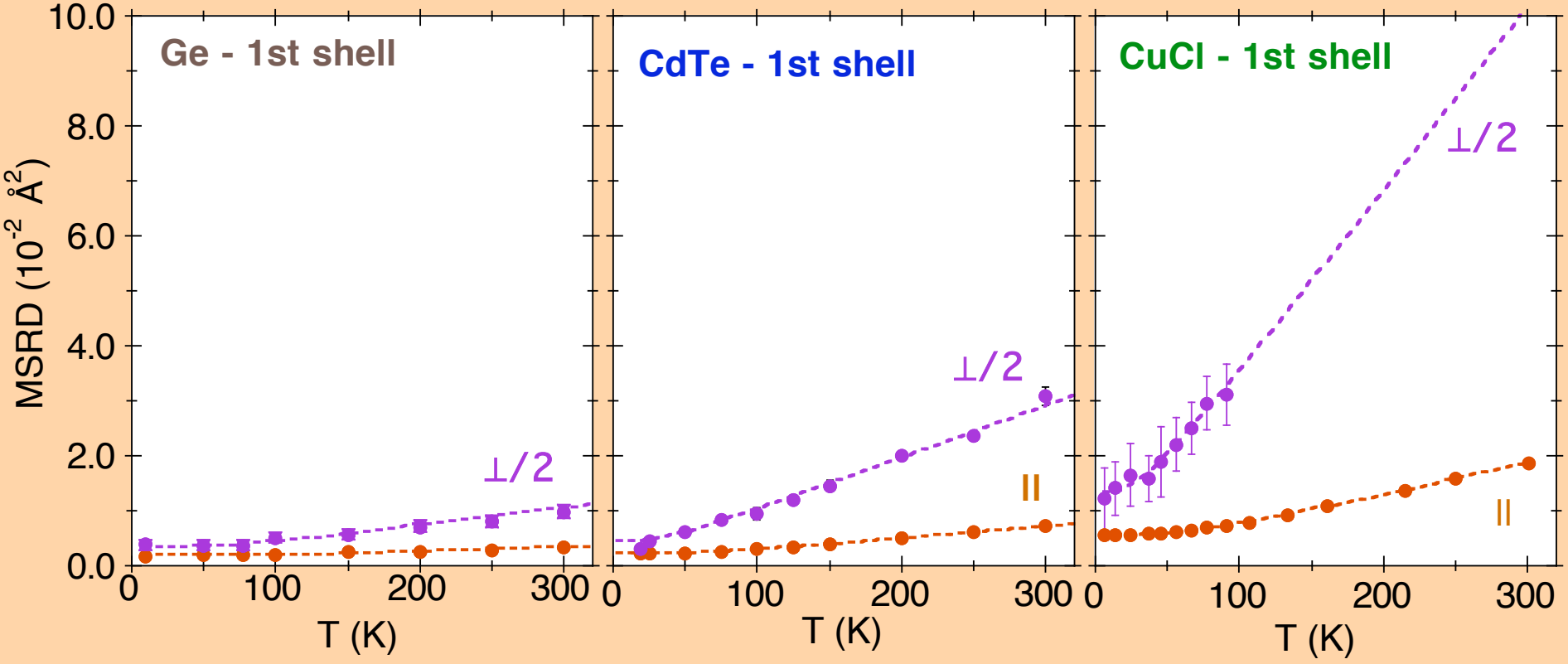
PRL 82, 4240 (1999)

Poster PS1-62, XAFS14

PRB 75, 184307 (2007)

MSRD: zincblende structure

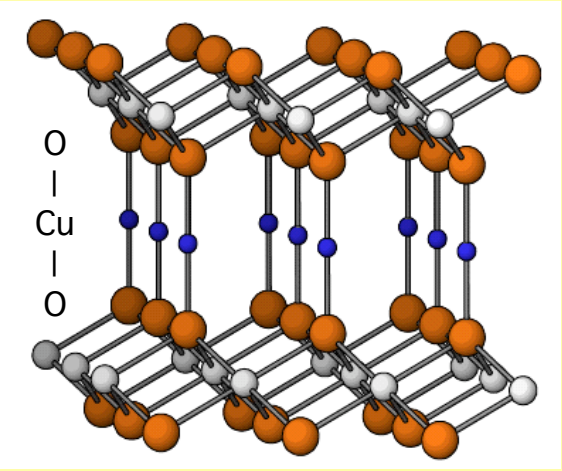


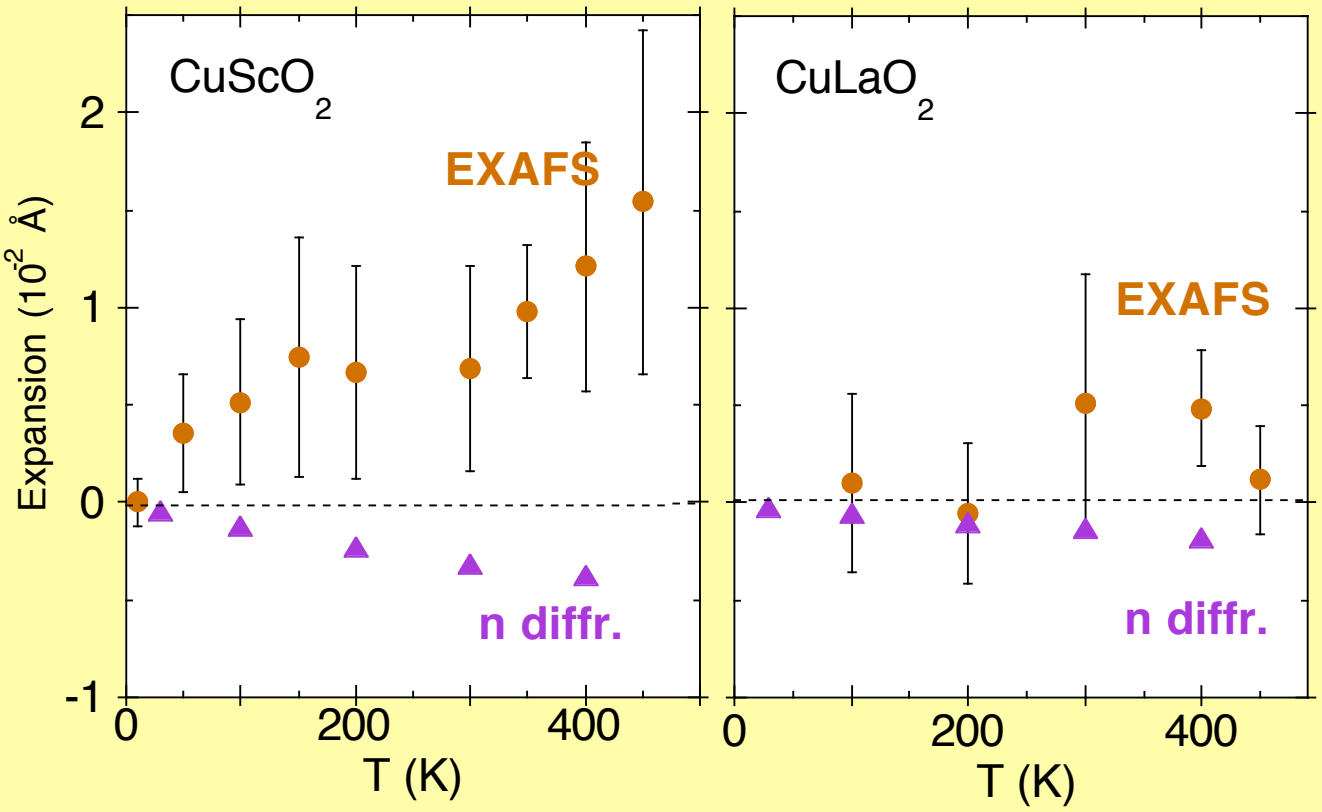


NTE strength increases

Force constants $k_{\parallel}$ and $k_{\perp}$ decrease
Anisotropy $k_{\parallel}/k_{\perp}$ increases

Cu-O bond expansion in delafossite structures

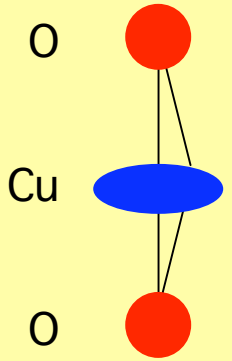


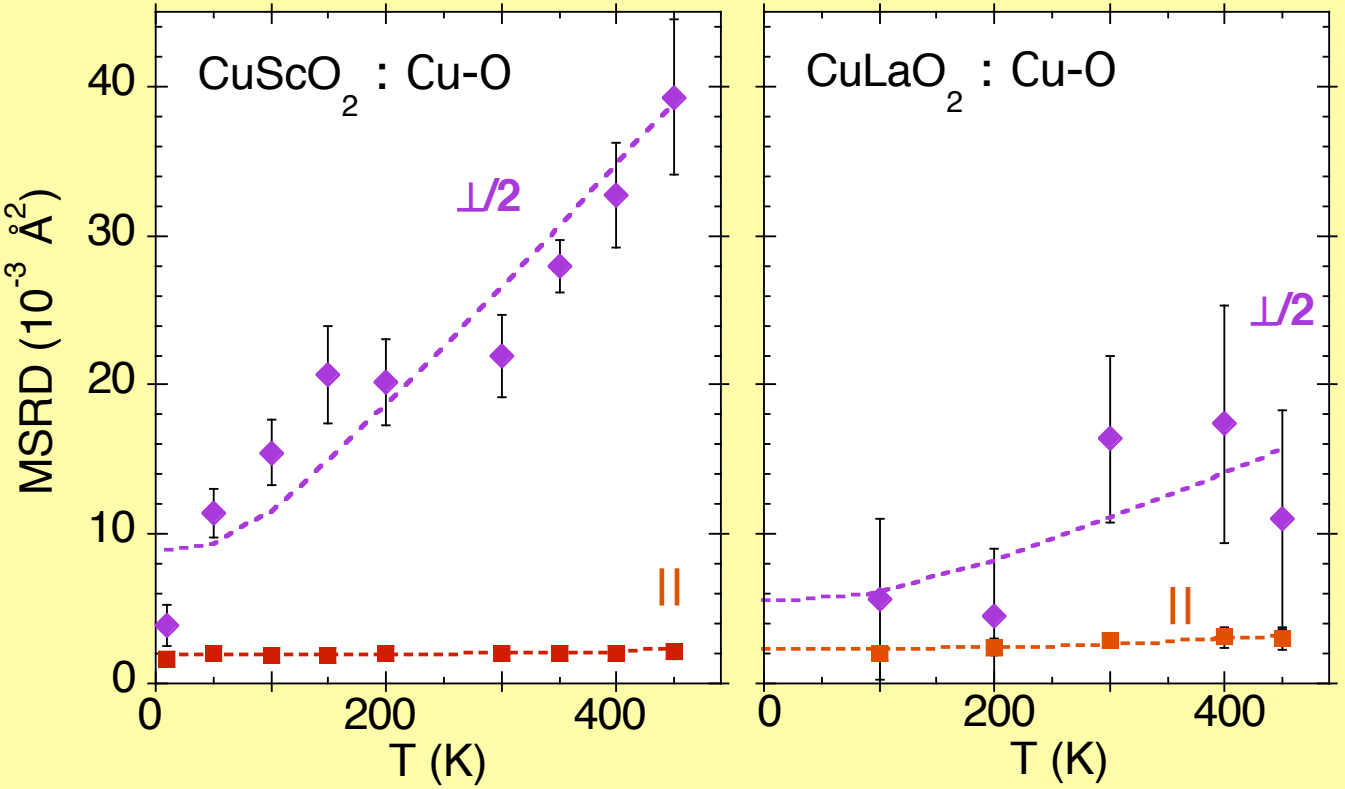


PRB 78, 104302 (2009)

Sleight et al.
J. Solid St. Chemistry
178, 285 (2005)

Cu-O MSRD in delafossite structures

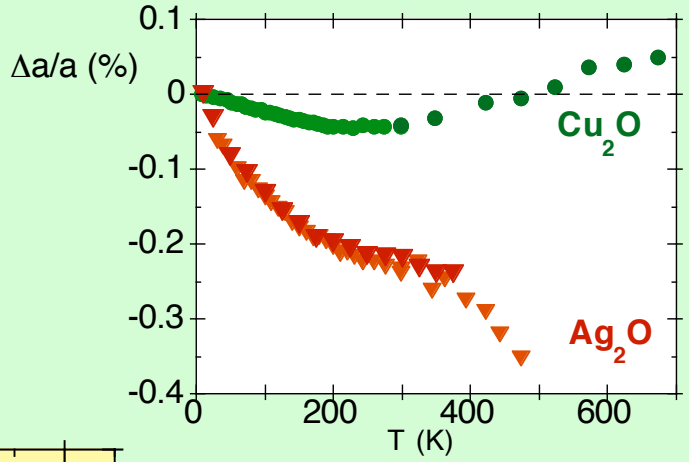


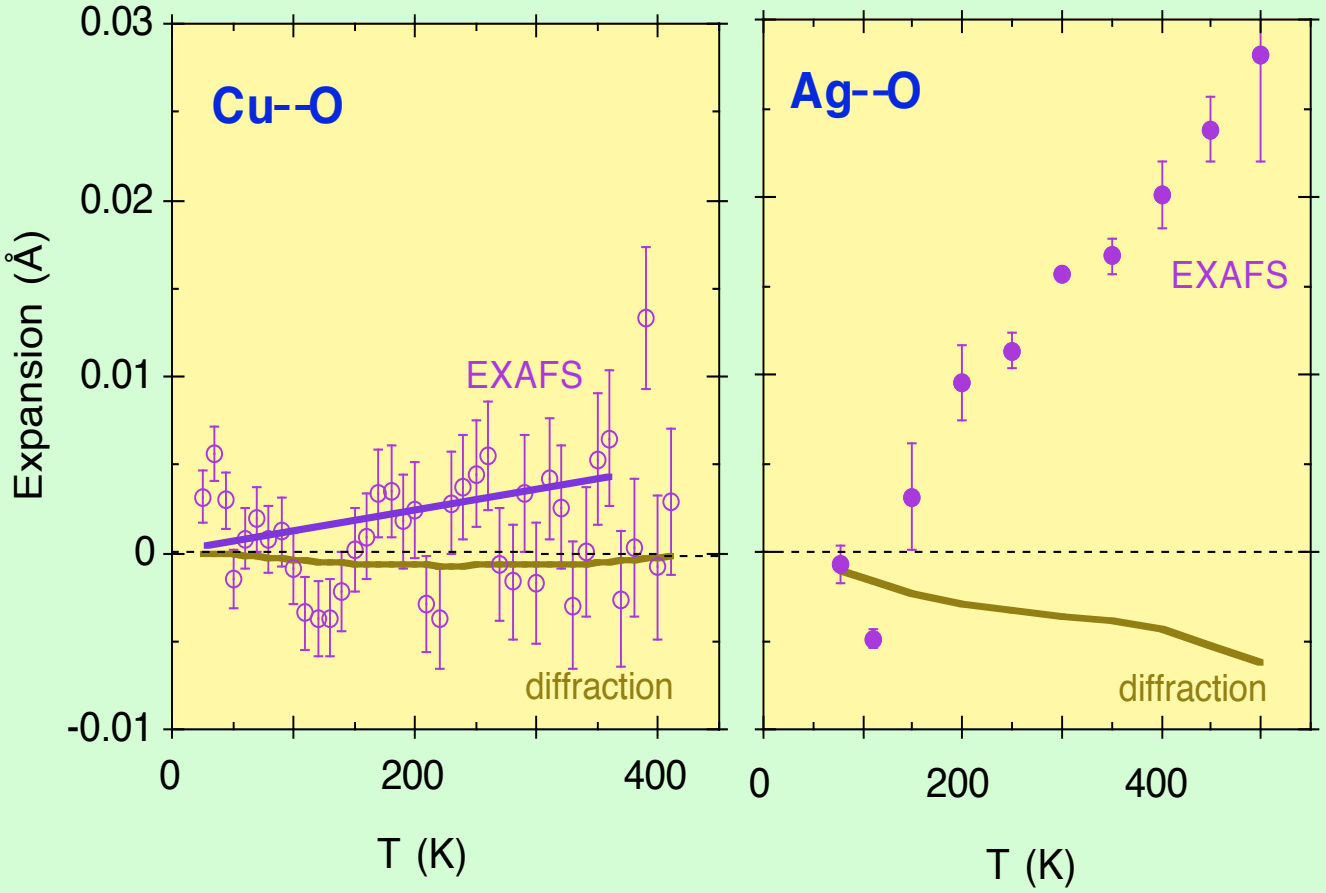


NTE strength increases

Force constants $k_{||}$ and $k_{\perp}$ decrease
Anisotropy $k_{||}/k_{\perp}$ increases

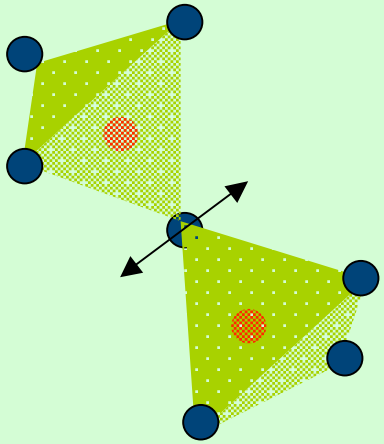
Bond expansion in cuprite structures

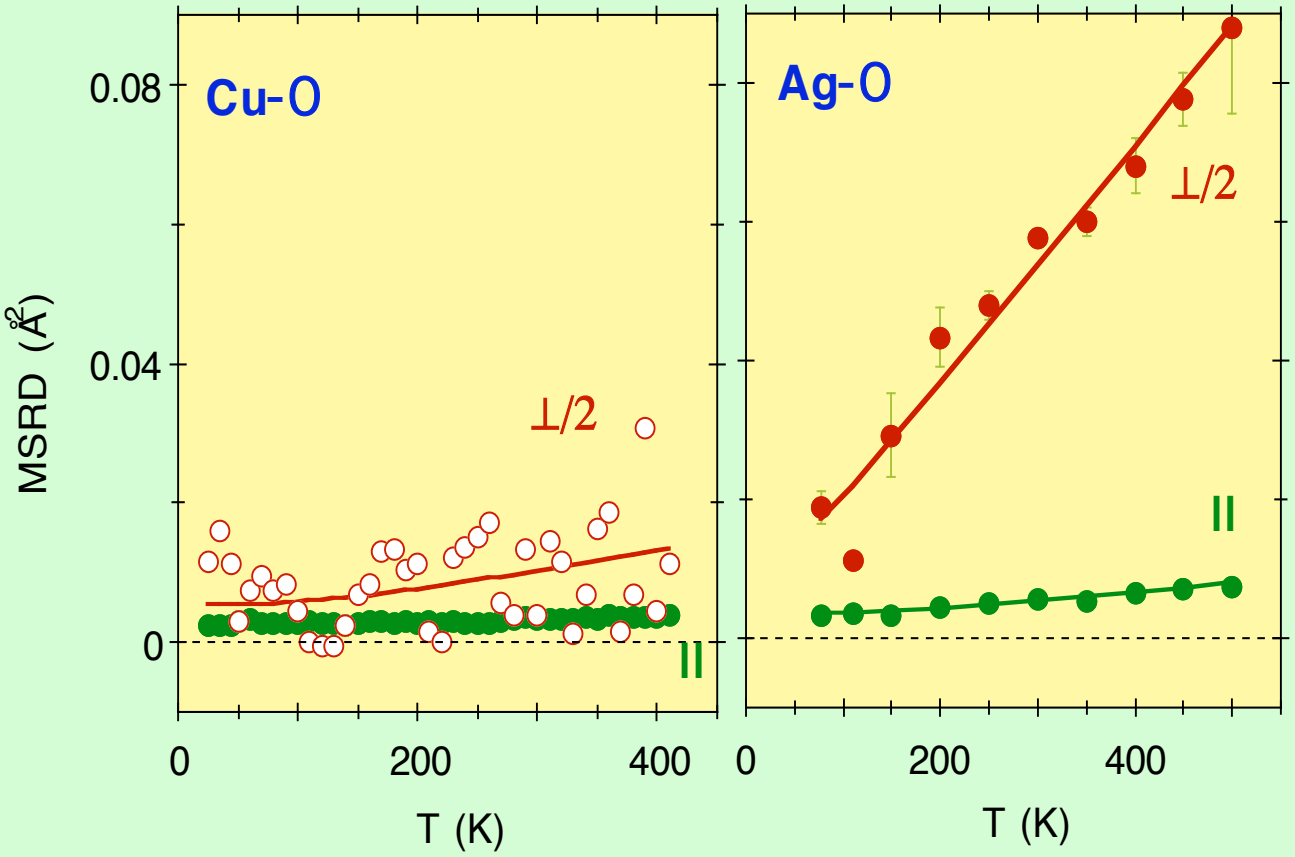




PRL 89, 25503 (2002) - PRB 73, 214305 (2006)

M-O MSRDs in cuprite structures





PRL 89, 25503 (2002) - PRB 73, 214305 (2006)

EXAFS and NTE

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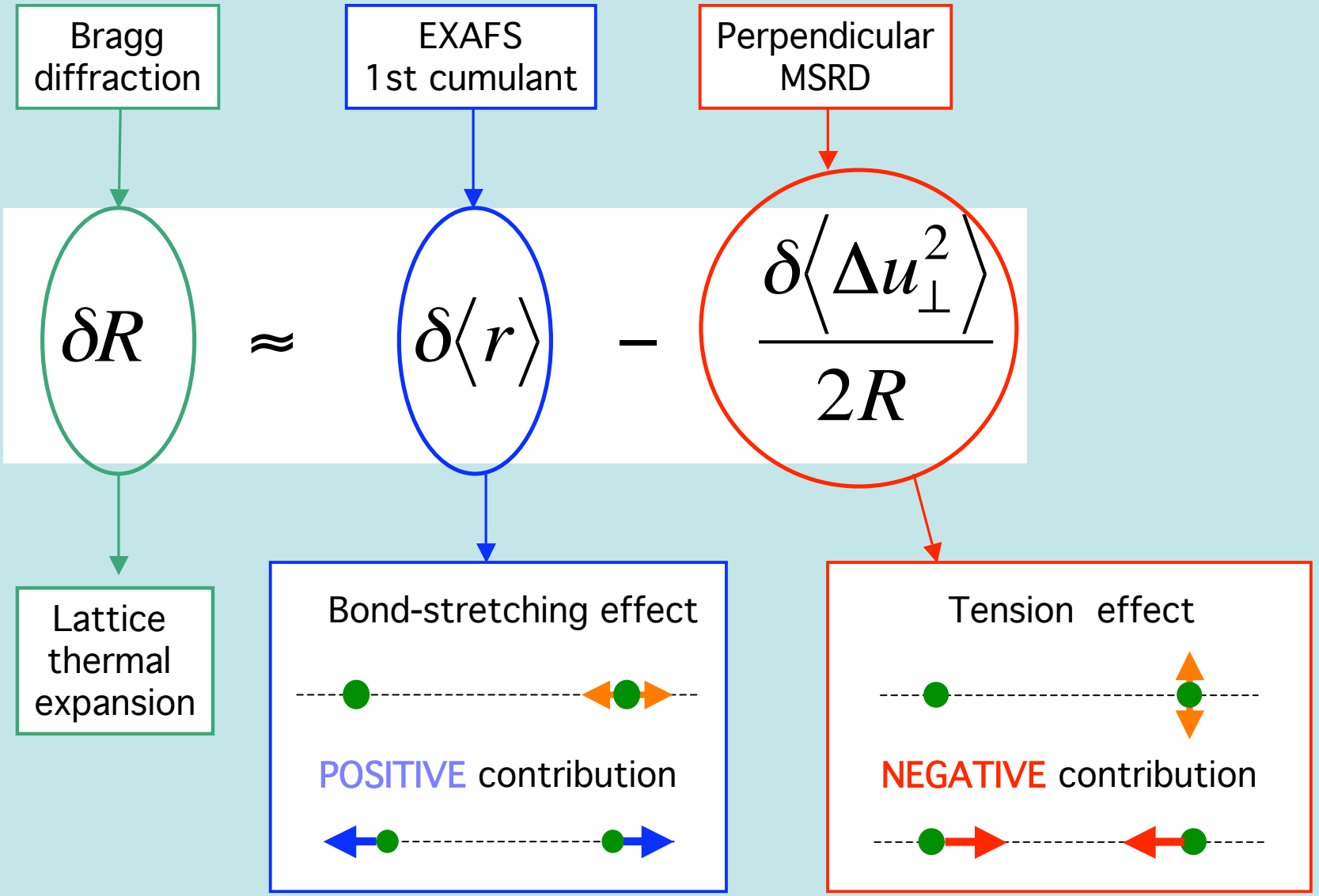
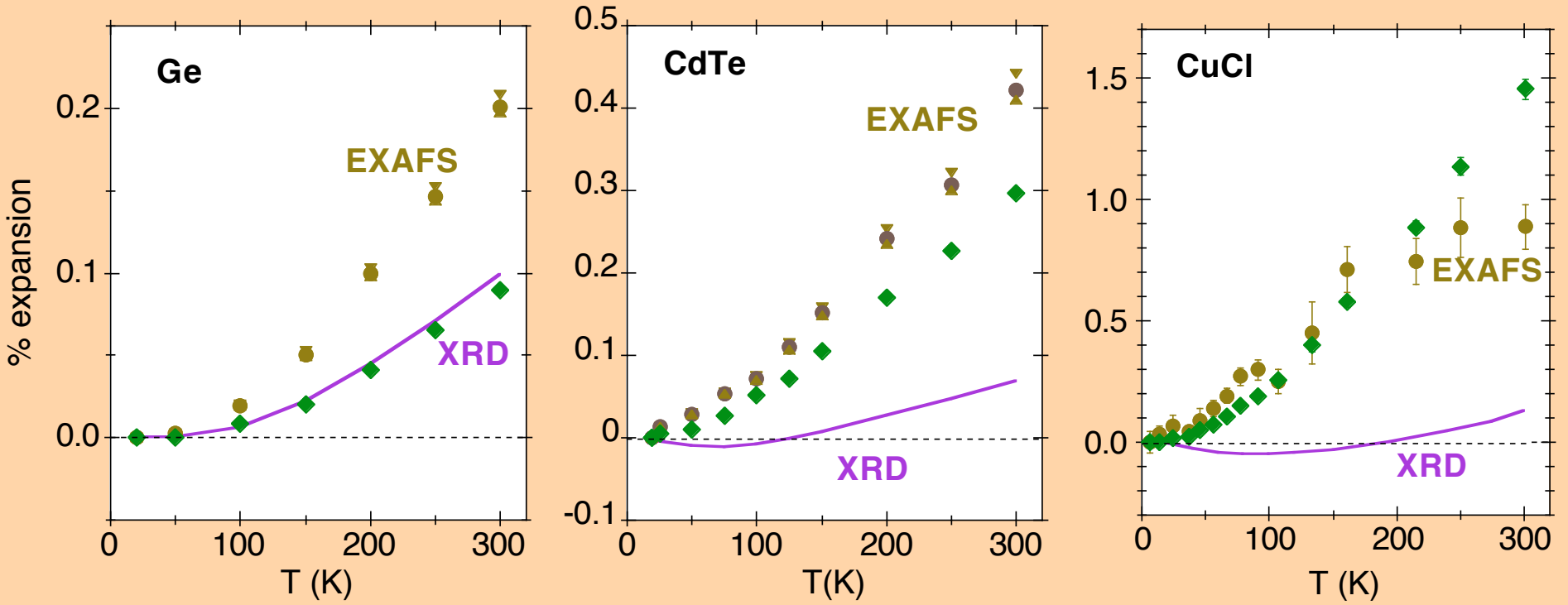


Bond expansion and asymmetry of the effective potential

◆ Thermal expansion due to asymmetry $\delta a = -3k_3\,\delta C_2^*/k_0$



EXAFS thermal expansion

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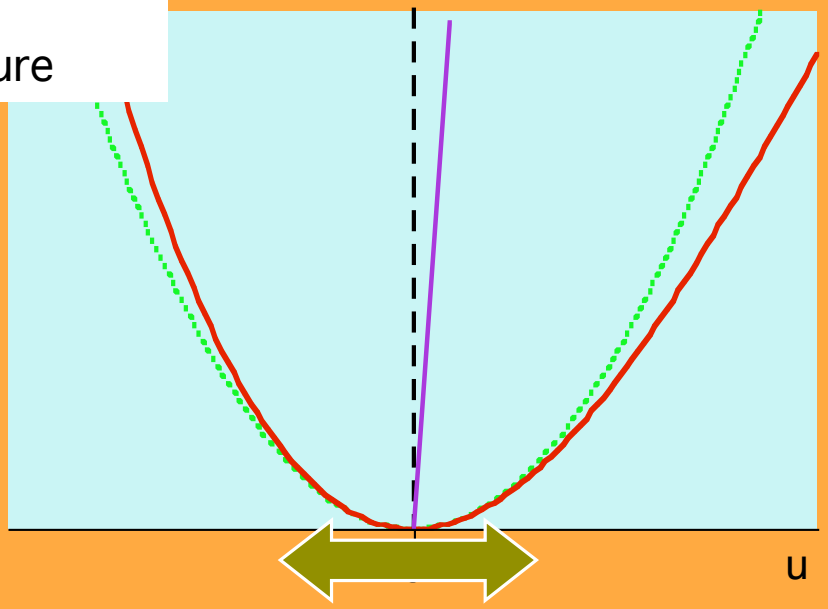
Effective potential
dependent on temperature



EXAFS
thermal expansion

=

Potential asymmetry

+

Potential shift

1st cumulant

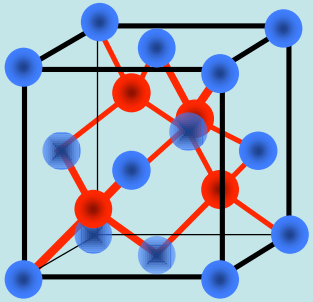
3rd cumulant

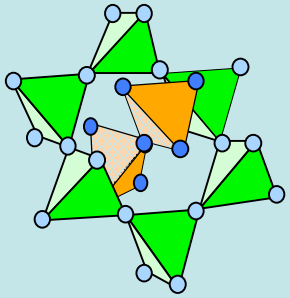
See also:

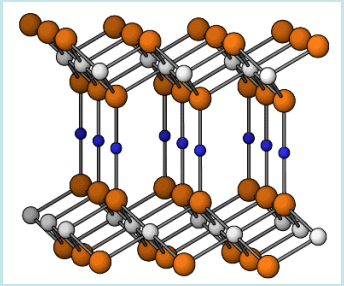
XAFS14, Poster Ps1-24

Phys. Rev. B 70, 174301 (2004)

Local dynamical properties of NTE materials







zincblende | cuprite | delafossite

	Cu	Ge	CdTe	CuCl	Cu_2O	Ag_2O	$CuLaO_2$	$CuScO_2$	
$k_\perp$ (eV/Å^2)	2.72	2.9	0.9	0.3	2.9	0.5	2.5	1.0	Bending
$k_\parallel$ (eV/Å^2)	3.2	8.5	3.8	1.4	11.6	5.9	15.5	24.2	Stretching
$\xi = \frac{k_\parallel}{k_\perp}$	1.17	2.9	4.2	5.4	4.0	11.8	6.0	24.2	Anisotropy

NTE strength

Conclusions

- The NN bond always undergoes positive expansion (PTE).
- For iso-structural crystals, the stronger is the lattice NTE, the stronger are the bond PTE and the perpendicular MSRD.
- A correlation can be established between MSRD anisotropy and NTE strength.
- EXAFS measurements substantiate the local model based on the competition between stretching and tension effects.
- Bond stretching is due to anharmonicity plus shift of the effective pair potential.

Authors

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