Examining the Link Between Anomalous Mechanical & Thermal Properties in Crystals

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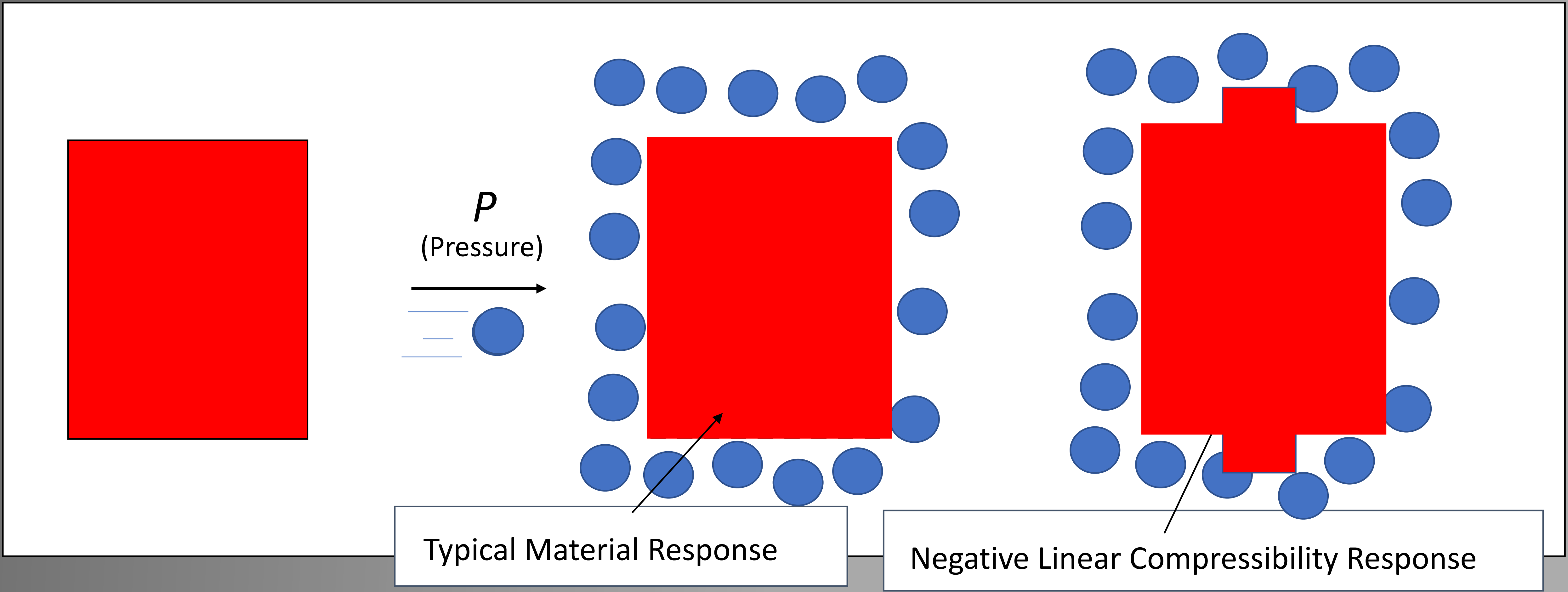
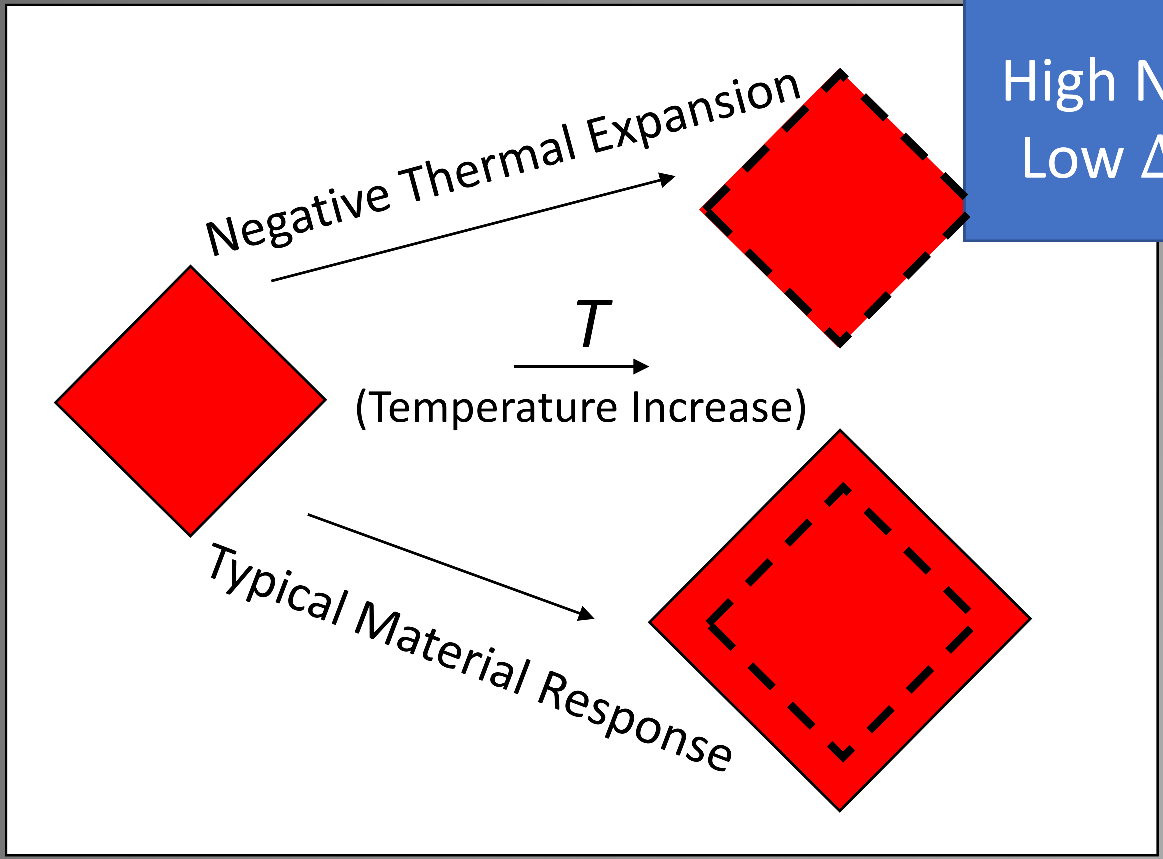
Negative Linear Compressibility: Hydrostatically Compress Material → Reduce Volume *but Expand* an Axis

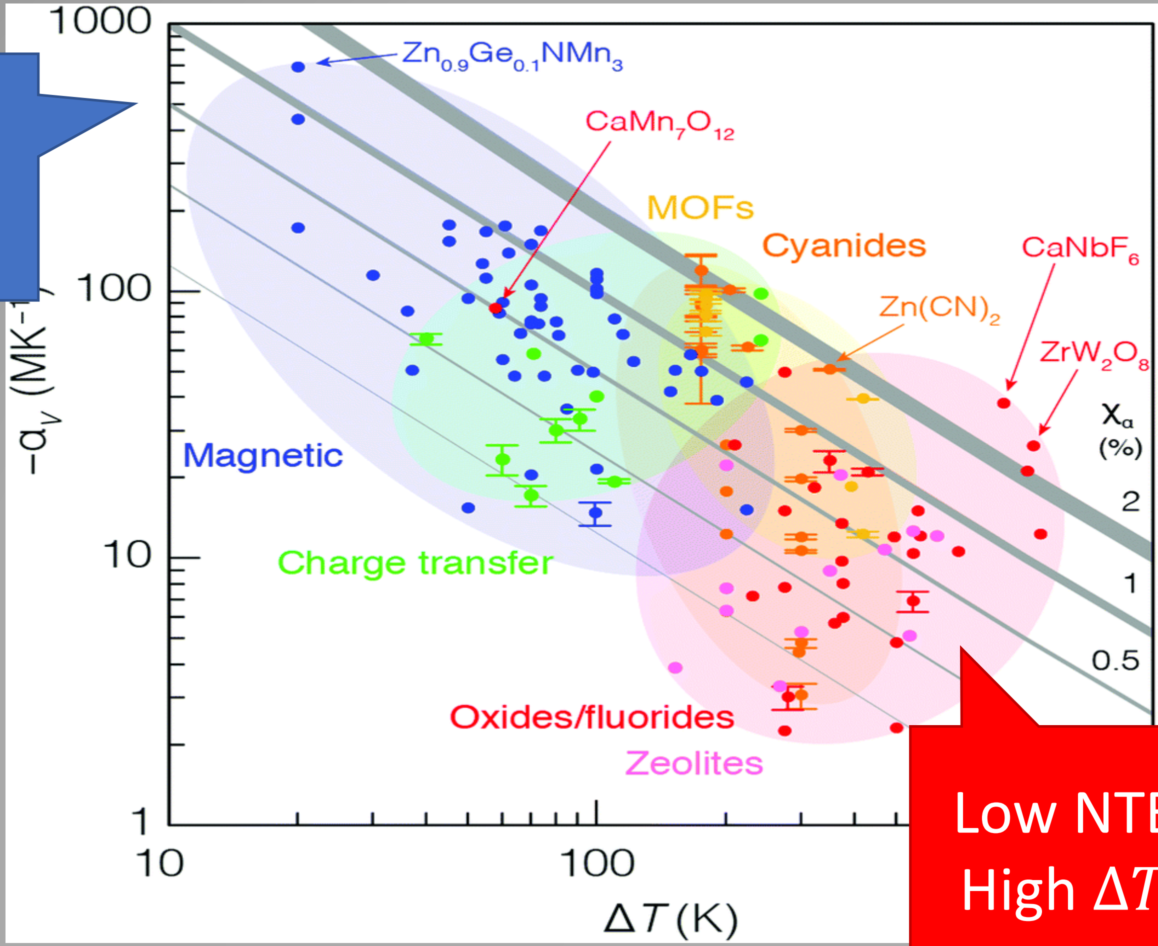


Cairns and Goodwin. *Physical Chemistry Chemical Physics*, The Royal Society of Chemistry, 14 May 2015

Negative Thermal Expansion:
Heat Material → *Decrease* Volume or *Shrink* an Axis.



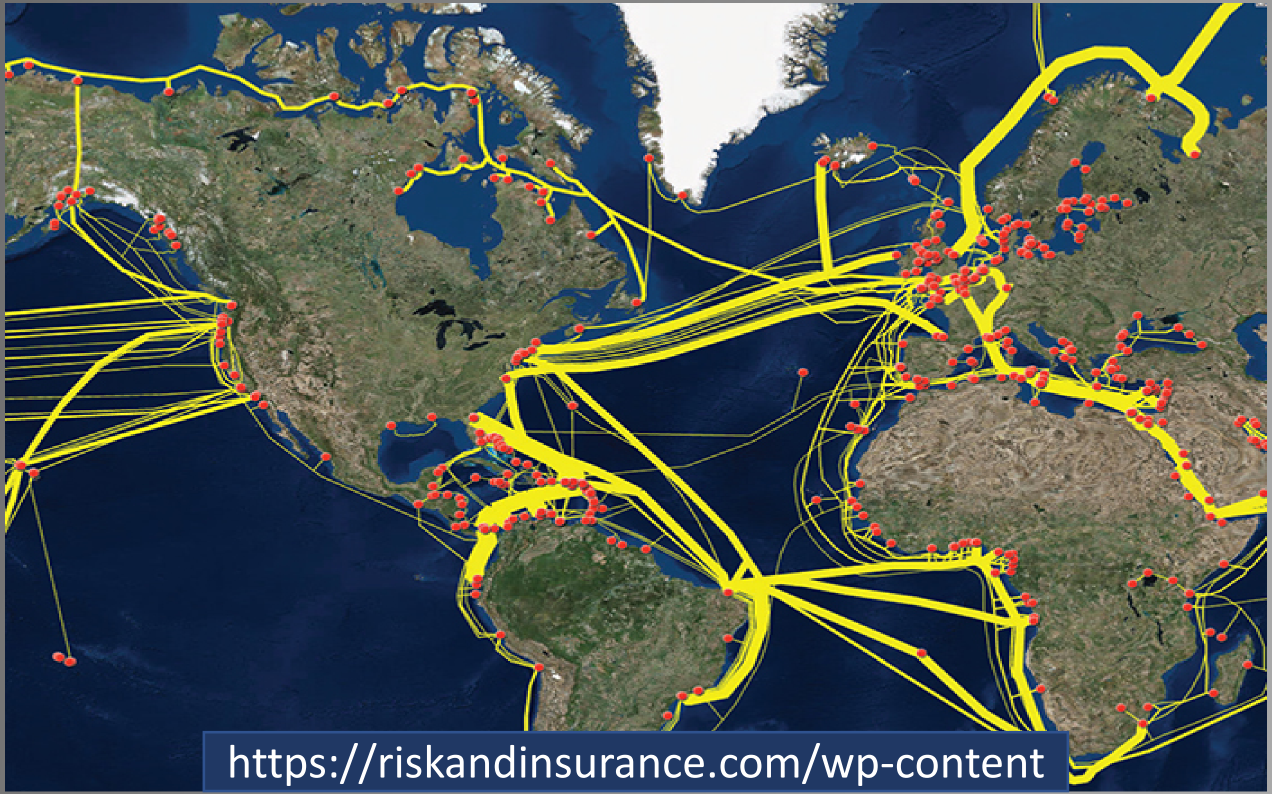
High NTE
Low ΔT



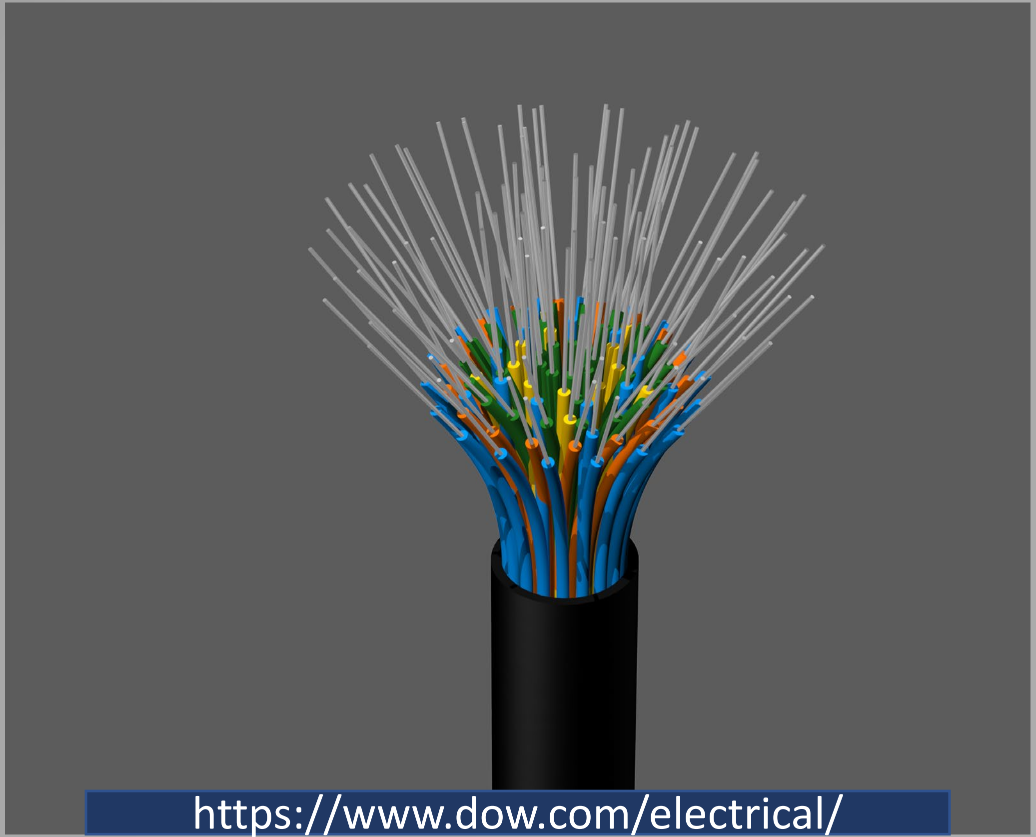
Low NTE
High ΔT

Coates and Goodwin. *Materials Horizons*, The Royal Society of Chemistry, 4 Oct. 2018

Negative Thermal Expansive Materials For Improving Pressure Applications

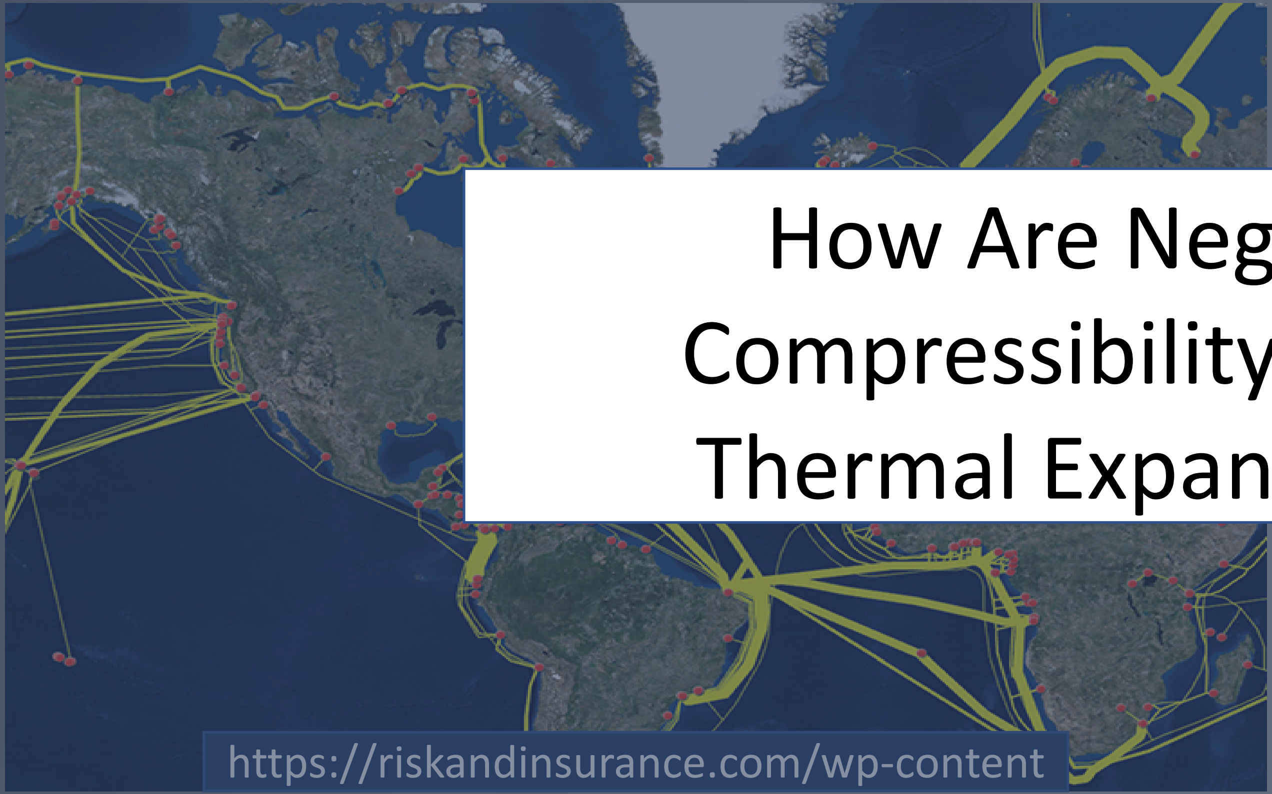


https://riskandinsurance.com/wp-content

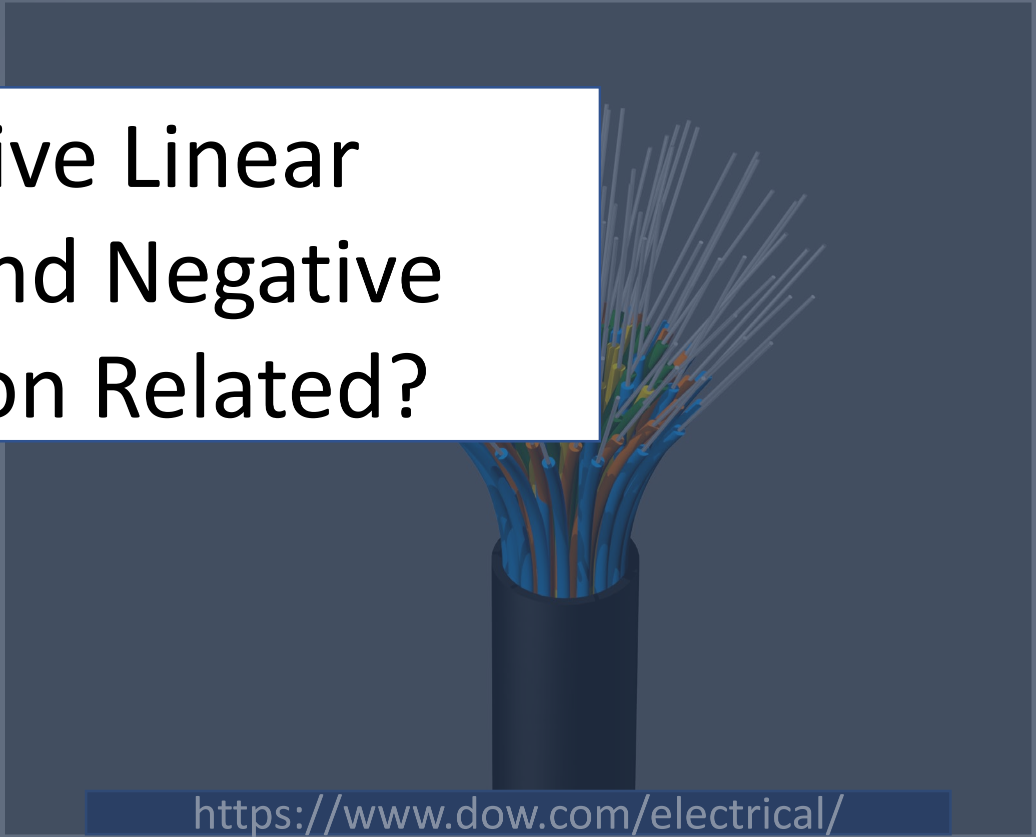


https://www.dow.com/electrical/

Negative Thermal Expansive Materials For Improving Pressure Applications



How Are Negative Linear Compressibility and Negative Thermal Expansion Related?



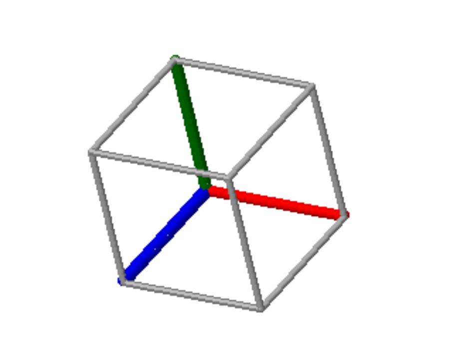
Conventional Way of Solving Negative Thermal Expansion: Cubic Systems

(Thermal Expansion)

(Linear Compressibility)

$$\alpha_i \cong K\,\Upsilon$$

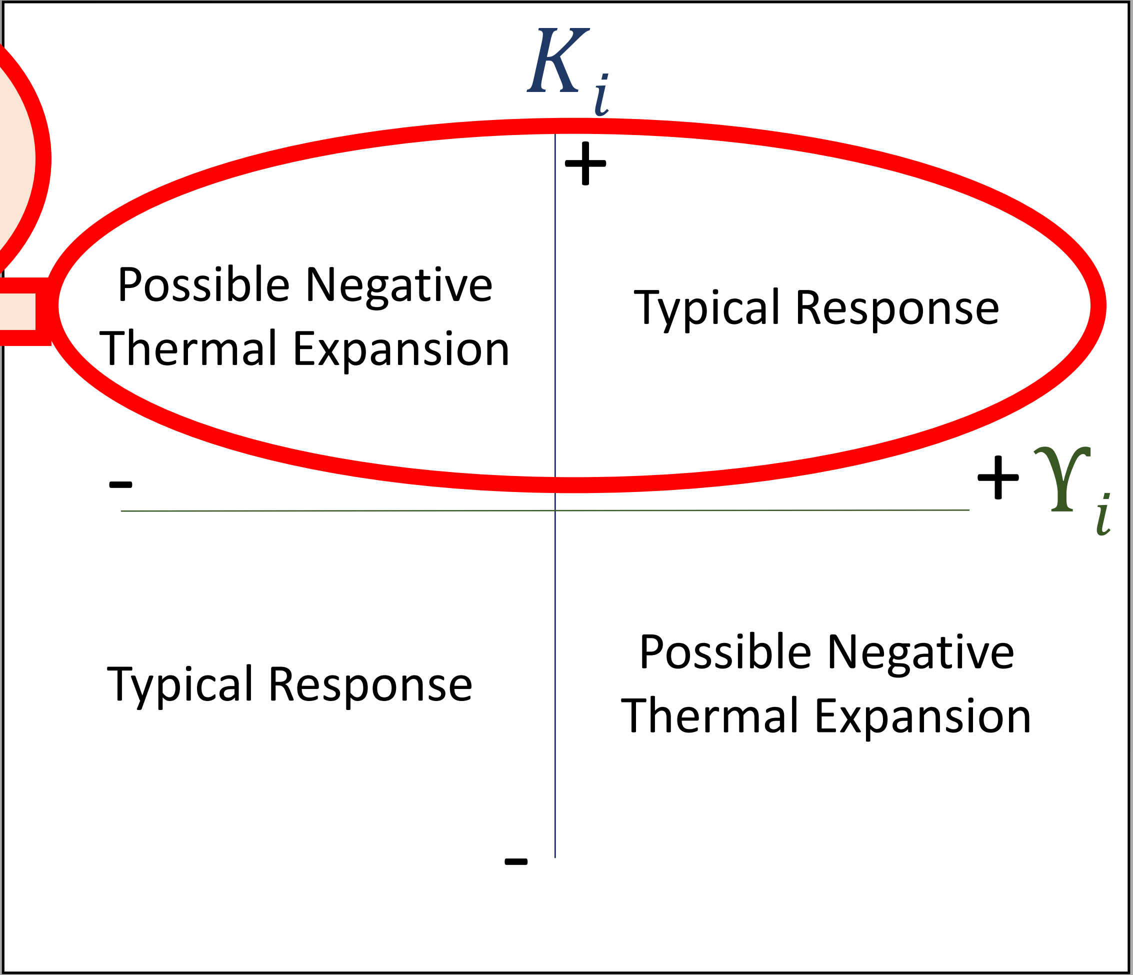
(Grüneisen Parameter)



www.chem.wisc.edu

K is Positive
in Cubic Systems

Most Research Found Here



Munn. *Physics C Solid State Physics*, “Role Of the Elastic Constants”, March 2018

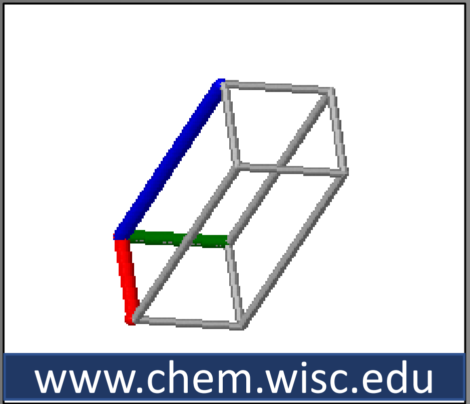
New Way of Solving Negative Thermal Expansion:
Tetragonal Systems

(Thermal Expansion)

(Linear Compressibility)

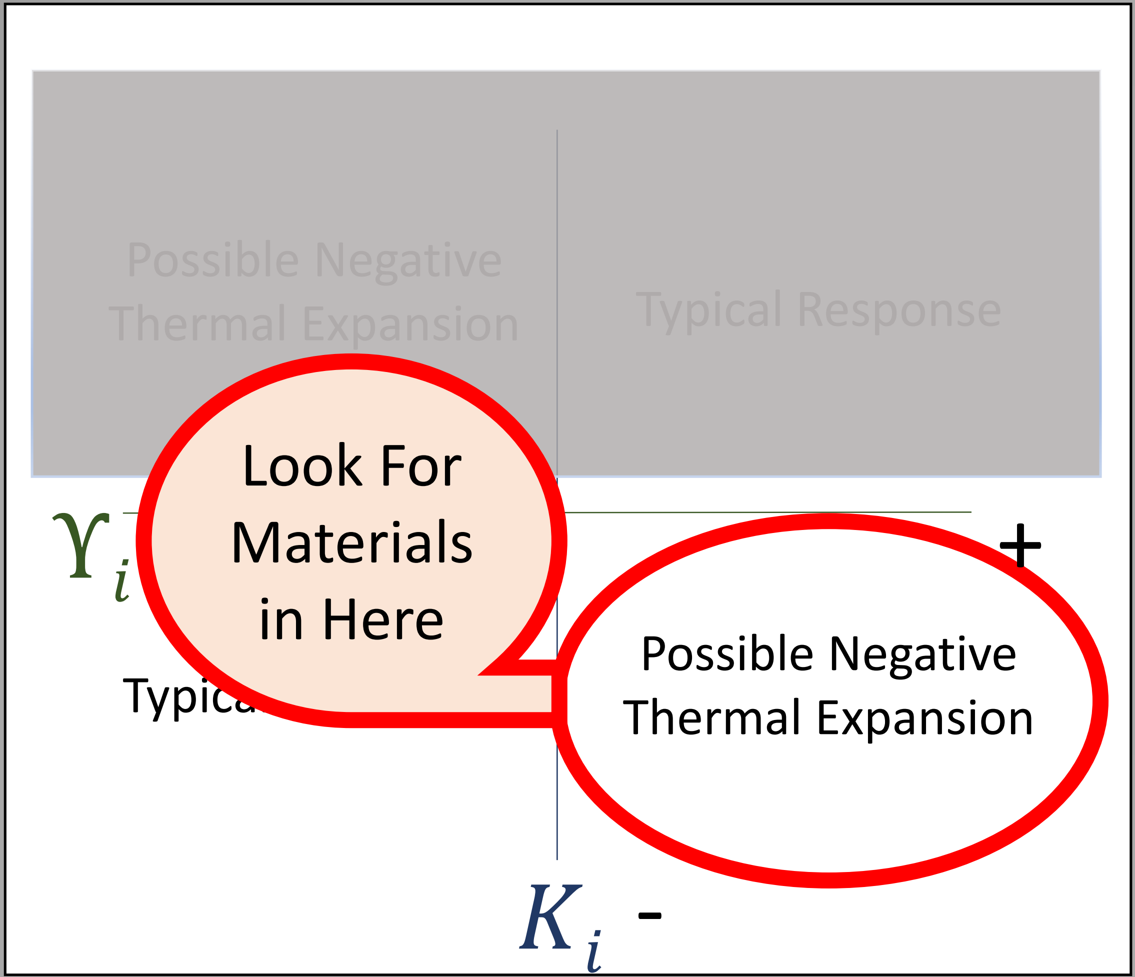
$$\alpha_i \cong (K_0\Upsilon_0 + \overbrace{K_1}\Upsilon_1)$$

(Grüneisen Paramenter)



Let Υ be <u>Positive</u>

In Non-Cubic Systems



Munn. *Physics C Solid State Physics*, "Role Of the Elastic Constants", March 2018

The Strategy:

1st & 2nd Step – Survey Literature and Organize Data

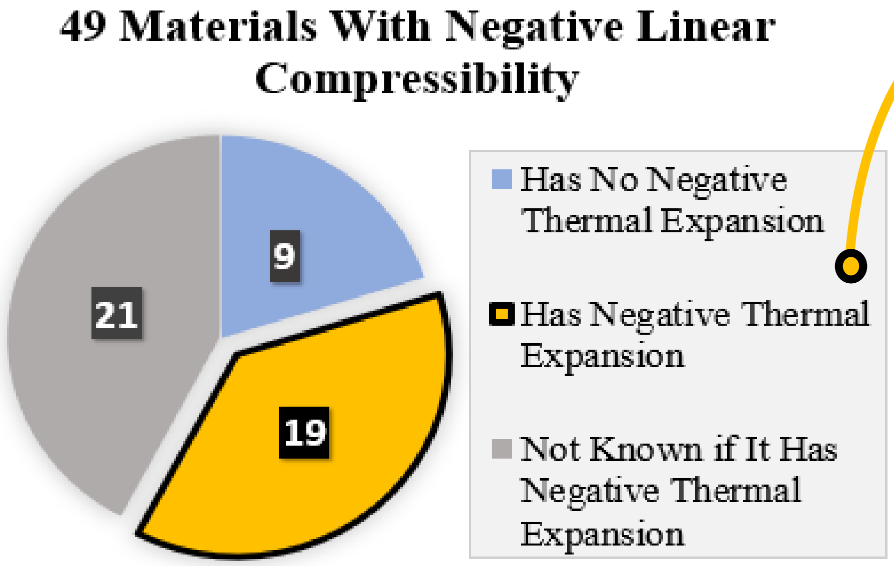
Survey The Literature

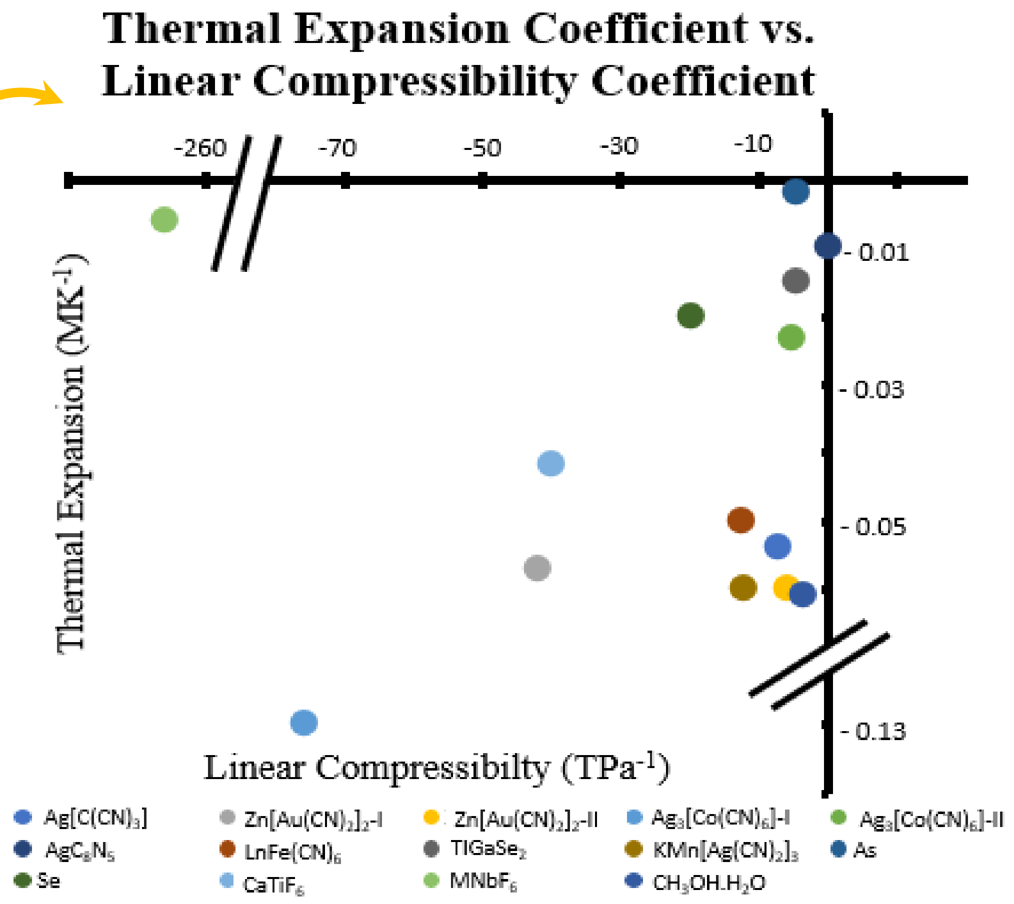
Look for Negative Linear Compressibility

List & Organize Materials

Look for Materials with Existing Structures and Organize

Survey of Literature Results: 19 Materials Exhibit Negative Linear Compressibility & Negative Thermal Expansion





Grosse, R. et al 1978 J. Phys. C: Solid State Phys. 11 45
Chang, D. et al., J. Phys. Chem. C 2018, 122, 12421–12427
Gupta, M. K., et al., Phys. Rev. B, 2017, 96, 214303
Goodwin, A. L., et al., Science., 2008, 319
Singh, B., et al, J. Phys. Chem. C, 2018, 122, 15575-15581
Hester, B. R., et al, J. Sol. State Chem. 269 (2019) 428–433
Cairns, A. B., et. al, Phys.Chem.Chem.Phys., 2015, 17, 20449
Barnes, D. L., University of Exeter (Doctoral dissertation)., 2017
Miller, W., et al., Appl. Phys. Lett. 2015, 106 231903
Coates, C. S., et al., Mater. Horiz., 2019, 6, 211-218
Feyman, R., et al., The Fey. Let. On Phys. Volume II
Duyker, S. G. et al., Nature Chem., 2016, 8
Kamali, C. et al., J. Phys. Chem. C, 2013, 117, 25704–25713
Singh, B., et al., Front Chem., 2018, 6, 544
Fortes, A. D., et al., Science., 2011, 331
Hester, B. R., et al, Inorg. Chem. 2018, 57, 11275–11281
Bins, J., et. al, Chem. Commun., 2016, 52, 7486
Munn, R., J. Phys. Chem. C: Solid State Physics, 2001, 5, 535
Baughman, R.H., et al., Science, 1998, 279
Coudert, F., Chem. Matter, 2015, 27, 1905-1916
Huang, C.W., et al., Adv. Mater. 2012, 24, 4170-4174

The Strategy:
3rd Step – Compare Structures for Similarities

Survey The
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Look for Negative Linear Compressibility

List & Orga e
Mate s

Look for Materials with Existing Structures and Organize

Compare Structure & Chemistry

Similarities in Structure and Chemistry

List and Organization of Materials: Structural Similarities

What Do These Materials Have in Common?

Porous Material

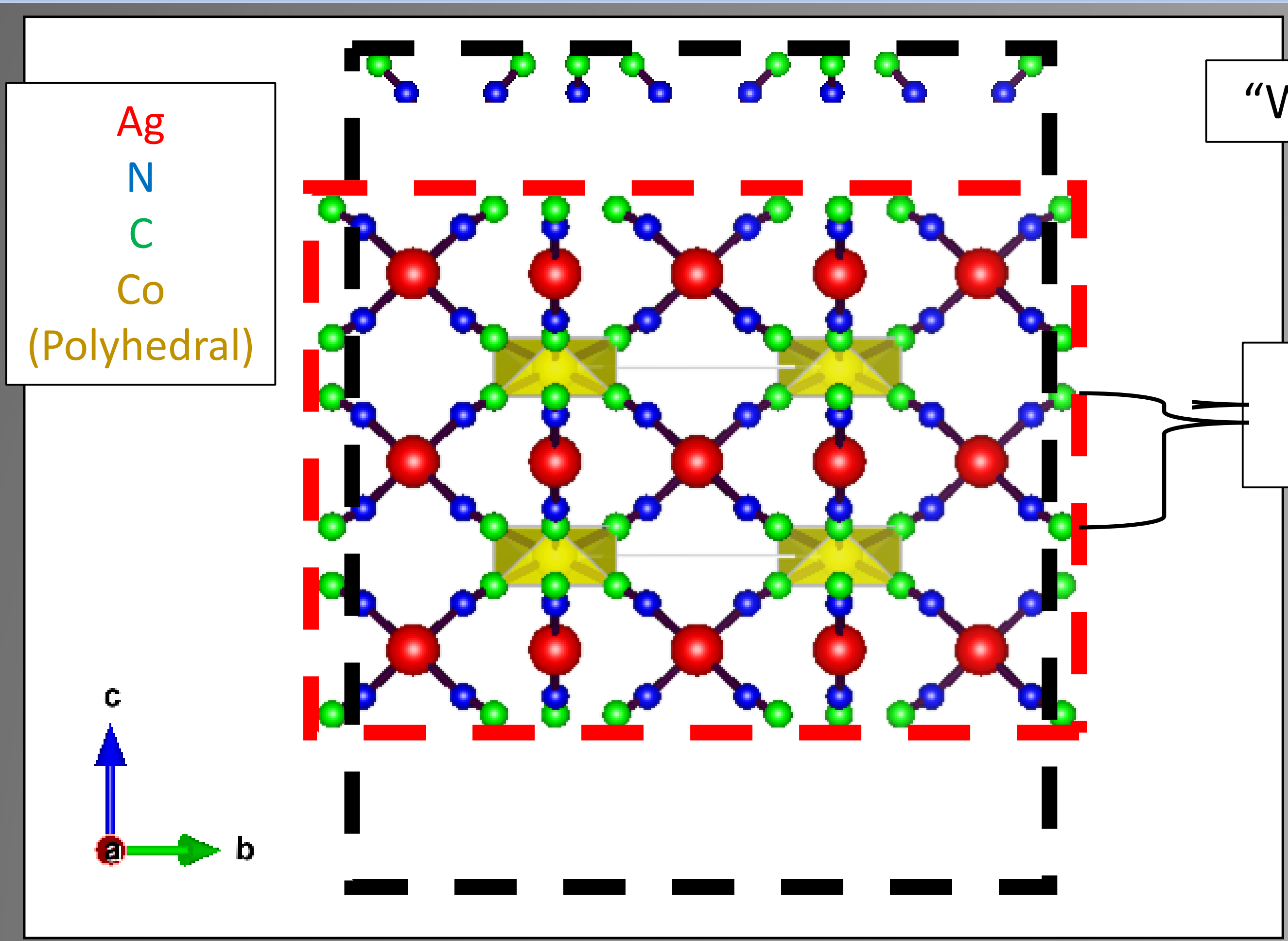
Long or Short Atomic Chains

Layering

Polyhedral Shape

Some Materials Showed This

Collapsible "Hinges" in:
Silver Hexacyanocobaltate - $Ag_3[Co(CN)_6]$-I



"Wine-Rack" Structure

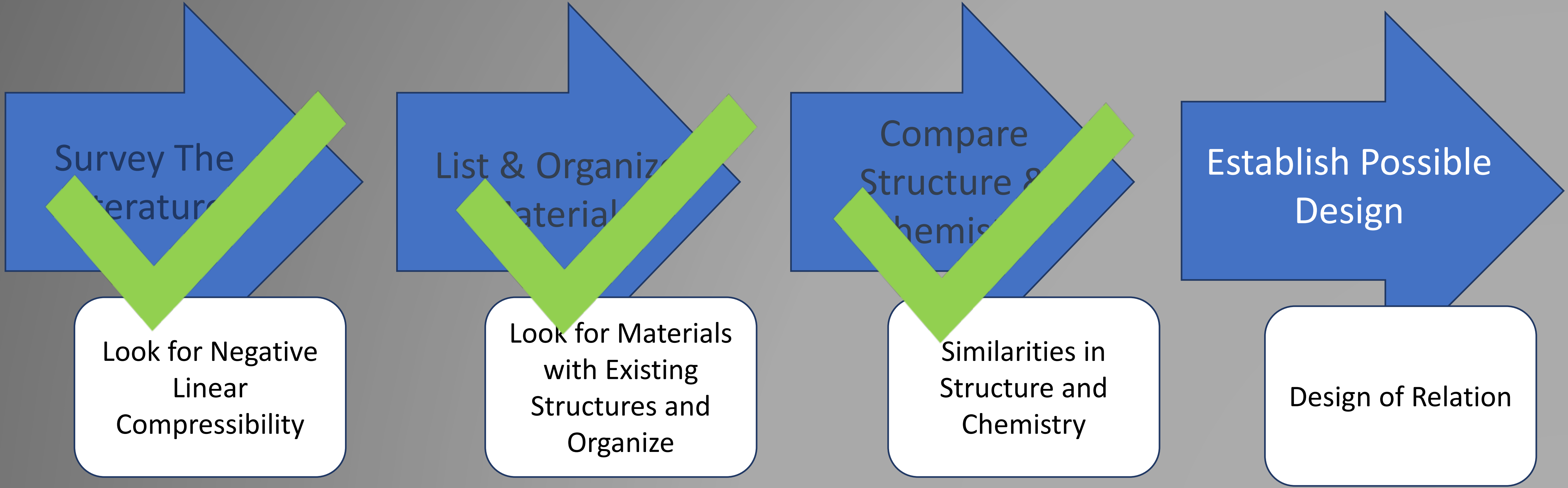
Silver to Nitrogen Bond Create "**Hinges**"

Compress -> Structure Collapses on C-Axis
Heat-Up -> Structure Shrinks on C-Axis

Also Seen in:
- $KMn[Ag(CN)_2]_3$
- Silver Tricyanomethanide

Systems, eZ. "VESTA." *VESTA*, www.vesta-usa.org/.

The Strategy:
4th Step – Suggesting Further Study of Relationship



Examining Linkage Between Negative Linear Compressibility & Negative Thermal Expansion Facilitates Findings of More Materials with Properties,

Found Common "Hinge" Mechanisms in Materials ,

Suggested Calculations To Further Examine Materials

Acknowledgements

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AN NSF MATERIALS INNOVATION PLATFORM

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CNF Group

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Free-Energy

Free- Energy = Elastic Free Energy + Vibrational Free Energy

F = B (delta V)^2 + (Grunisen)(T) (delta V)

- Elastic energy refers to strains and stresses in system
- Strain tensor = distance between point A & B in a solid
- Equilibrium Volume at a given T is the Volume -> lowest free-energy

Grüneisen Parameter (Cubic Systems)

A system always wants to be at a low free-energy state: its equilibrium volume is the lowest free-energy

Gruneisen Parameter = How the Vibrational Free Energy Changes with Strain

$$\Upsilon = \left(\frac{V}{C}\right)\left(\frac{dP}{dT}\right)_v$$

V = Volume

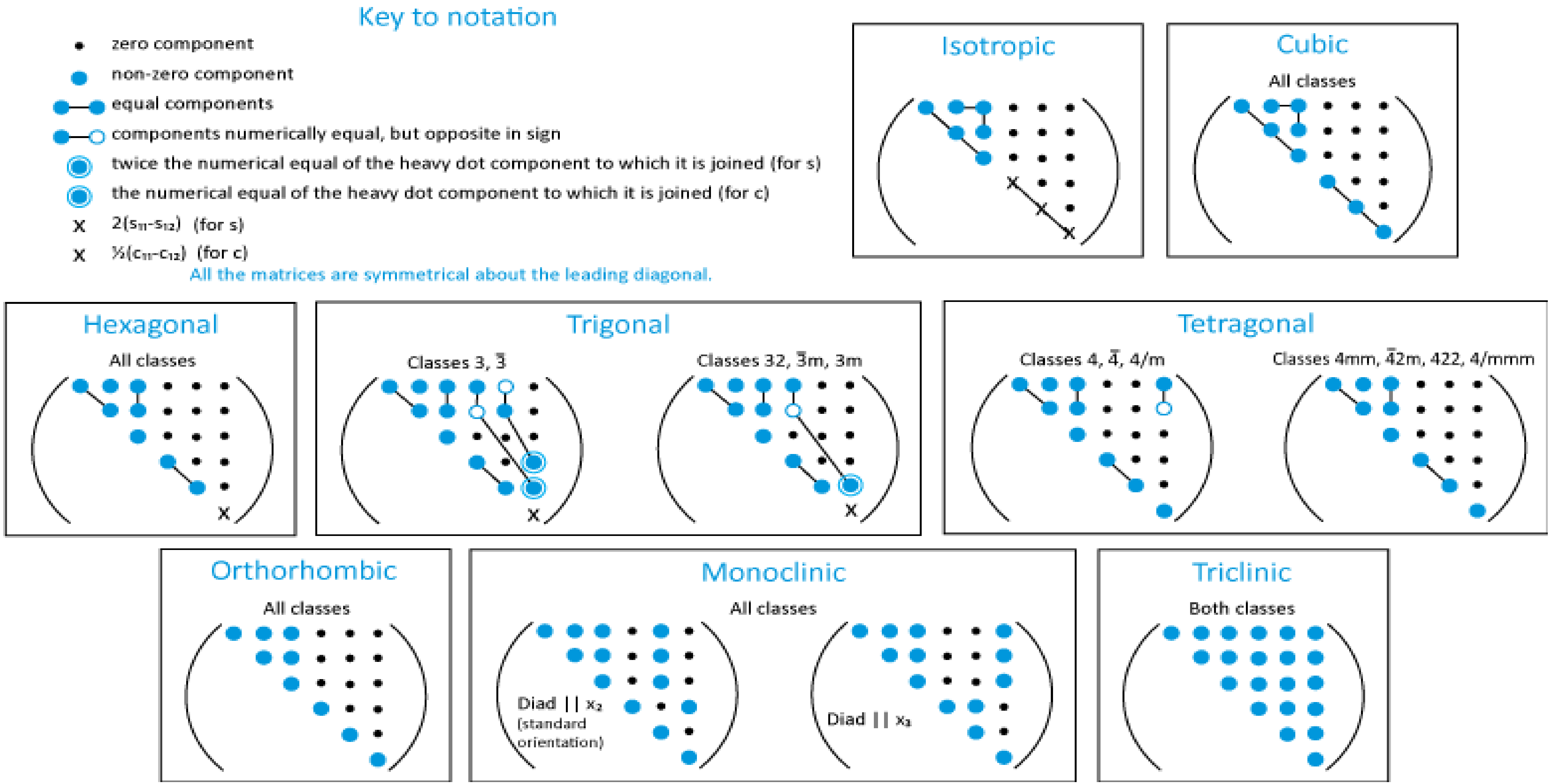
C = Heat capacity at Constant Volume

dP/dT = Change in pressure with respect to temperature at constant Volume

Positive G. Parameter = Positive Thermal Expansion

Negative G. Parameter = Negative Thermal Expansion

Form of the (s_{ij}) and (c_{ij}) matrices

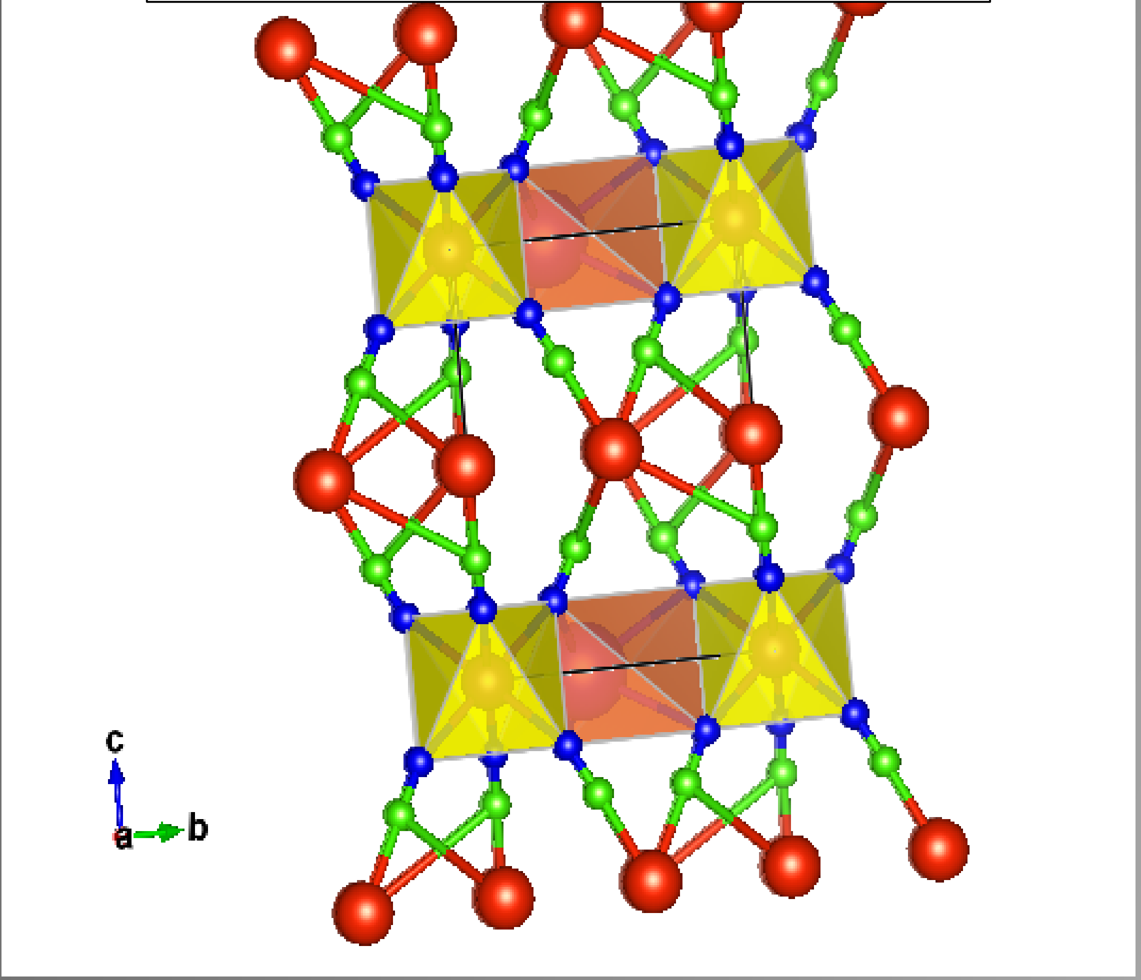


After Nye, 1959

$$\mathbf{K} = -\frac{\partial}{\partial p}\begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{bmatrix}.$$

$$K_i = \sum_{j=1}^{3} S_{iijj}$$

$KMn[Ag(CN_2)]_3$



$Ag_3[Co(CN)_6]$-I