# Why do solids expand when heated? Can we design a solid that doesn't expand?

## *Negative Thermal Expansion Behavior in Cyanide-Bridged Frameworks*

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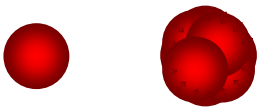
Most solids expand when heated and contract when cooled; behavior referred to as ***positive thermal expansion (PTE)***. As the atoms in the material heat up, they vibrate more, taking up more room, and thereby forcing the material to expand. Consequently, engineers building bridges install expansion joints to accommodate atoms vibrating on hot days and trains run slower because the rails can buckle in the heat.

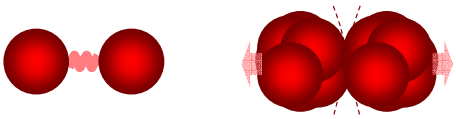
We have discovered materials that seem to breach this law of nature by shrinking when heated and expanding when cooled; so-called ***negative thermal expansion (NTE)*** behavior. The origin of this remarkable behavior lies in the atomic-scale structure of the solid, that is, how the atoms are "holding hands". In these special materials, two metal atoms are joined by a molecular 'jump rope' which is the key to this unusual phenomenon.

**A single atom**



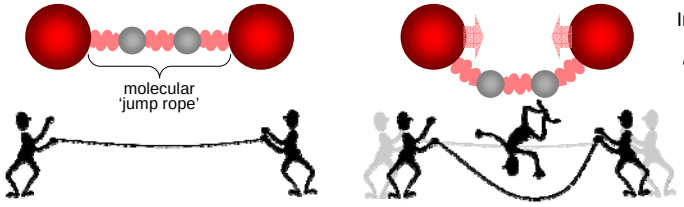
As the temperature is increased, the atom gains energy, causing it to vibrate more and to take up extra space.

**Normal solids**



In solids, which consist of arrays of chemically bonded atoms, this forces the individual bond lengths and the bulk solid to expand.

**Negative thermal expansion**




In solids where heavier atoms (e.g. metals) are connected by a light atom chain, a molecular 'jump rope', the opposite behavior is possible.

*At absolute zero* (-459ºF) the rope is straight holding the metal atoms apart.

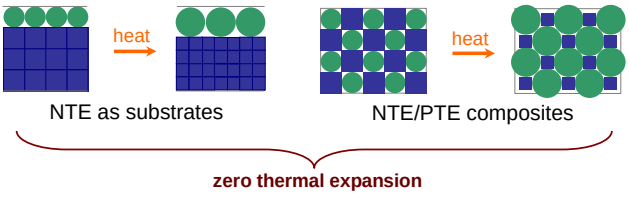
*When heated*, the rope bends, pulling the metal atoms closer together

**Thermal expansion –** a real world problem e.g.:

- *Train rails* get longer and can buckle on hot days
- Water/gas/oil *pipes* change length with the weather
- Failure in *electronics* is associated with thermal cycling
- If *dental fillings* expanded more than *teeth,* a hot coffee could be like a kick in the teeth.
- ... and many more

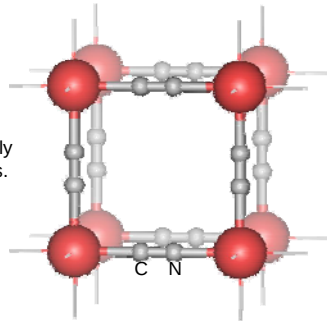
### How could a NTE materials be used?

By combining a NTE material with a PTE material it is possible to compensate for the expansion behavior of 'normal' materials to give overall ***zero thermal expansion (ZTE***) behavior.

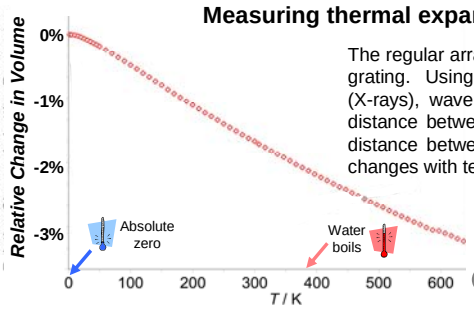



**Metal cyanides –**
excellent NTE materials

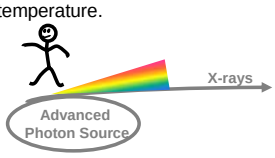
The cyanide anion ($CN^-$) binds strongly to connect metal ions in infinite arrays.




### Measuring thermal expansion




The regular array of atoms acts like a diffraction grating. Using light with short wavelengths (X-rays), wavelengths of a similar size to the distance between atoms, we can see how the distance between atoms, and material volume changes with temperature.




For further information about negative thermal expansion behavior or materials chemistry contact chapmank@aps.anl.gov

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