Examining the Link Between Anomalous Mechanical and Thermal Properties in Crystals

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Abstract:

Materials that exhibit anomalous mechanical or thermal properties, like negative linear compressibility (NLC) and negative thermal expansion (NTE), allow for the design of composite materials with tailored properties. NTE has impactful use in engineering applications where temperature variation poses problems. However, there remains need for materials options that show NTE. Most research has focused on predicting NTE by calculating Grüneisen parameters, where thermal expansion is related to linear compressibility and Grüneisen parameters. A material is selected for further study if the Grüneisen parameters are *negative* since linear compressibility is assumed positive. Because deriving the Grüneisen parameters are cumbersome, finding structural correlation between materials that exhibit both NLC and NTE may help narrow down possible NTE candidates. The focus of this project is to examine the relationship between materials exhibiting both NLC and NTE to facilitate the findings NTE materials options. Survey of the literature found nineteen materials exhibiting both properties. Silver hexacyanocobaltate, silver tricyanomethanide, and $KMn[Ag(CN)_2]_3$ share a similar layering of "hinge-like" bonds along their c-axis. First principle calculations are suggested for further insight.

Summary of Research:

Most materials expand as temperature increases and contract as pressure increases (Figure 1). In some anomalous materials, one or two cell dimensions expand under hydrostatic pressure-negative linear compressibility (NLC) [1]. Some cell dimensions shrink under rising temperatures-negative thermal expansion (NTE) [2].

NLC is a consequence of structure [1,2,7]. Materials that show "wine-rack" bonding, recently seen in metal-organic frameworks (Figure 2), polyhedral tilting networks seen in some ferroelastics, and helical bonding like those seen in selenium, exhibit NLC [2].

Thermal expansion is proportionally related to linear compressibility and Grüneisen parameters. To predict NTE in materials, most research focuses on calculating the Grüneisen parameters — how the vibrational free-energy of the system changes with strain [3]. A *negative* Grüneisen parameter likely indicates NTE [3]. However, materials with *positive* Grüneisen parameters may also exhibit NTE if they show NLC [3]. Since, calculating Grüneisen parameters requires a complex understanding of the vibrational spectrum, a more straightforward approach to predicting materials that exhibit NTE could be the study of NLC, since NLC likely indicates NTE. Establishing an understanding of a link between NLC and NTE through structural and/or chemical similarities may help focus the search for new NTE materials. Are there materials with both anomalous properties?

A survey of the literature found 19 materials exhibiting both NTE and NLC. Structural information was examined for similarities. Three materials were found to have similar collapsible "hinges". Further study using first principle calculations is suggested to gain more insight.

Results and Conclusions:

By surveying the literature, 49 NLC materials were found. Twenty-eight of them had available thermal expansion information. Within that collection, 19 materials exhibited both NTE and NLC, with 14 having detailed numerical data. Eight materials (Table 1) had detailed structural information used for the evaluation of the following structural motifs: porosity, long or short atomic chains along the axis where NLC or NTE was exhibited, atomic layering, and polyhedral shape.

Silver hexacyanocobaltate-I, silver tricyanomethanide, and $KMn[Ag(CN)_2]_3$ showed similarities in layering and polyhedral shape. All three had "hinge-like" bond layering along their c-axis (Figure 2). These "hinge-like" bonds were attributed to the "wine-rack" atomic structure of the system. For example, silver hexacyanocobaltate-I (Figure 3) has a "hinge" mechanism created by its silver-nitrogen bonds below each polyhedral layering. This "hinge" collapses along the c-axis under hydrostatic and thermal pressures resulting in NLC and NTE, expanding the a and b axes [7]. The extent of the importance of chemistry in these materials on NLC or NTE remains unknown.

Future Work:

The chemical similarity of the three materials with layering commonality is suggested to be investigated in order to gain further insight of their NLC and NTE behavior. First principle calculations could be applied in order to understand the implications of their elastic constants, Grüneisen parameters, and chemistry on NLC and NTE.

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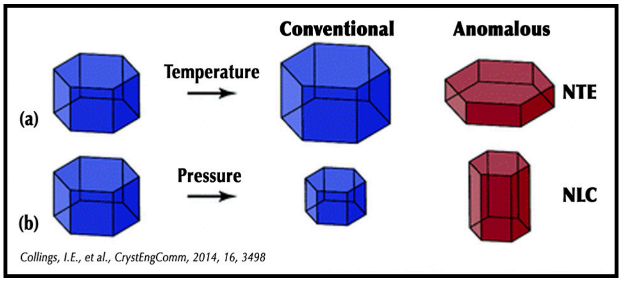

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Figure 1: Illustration of a conventional and anomalous thermal (a) and pressure (b) response.

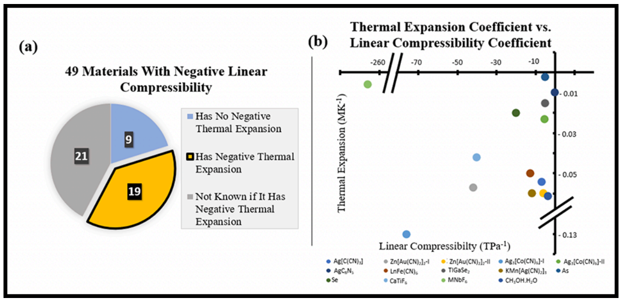

Figure 2: (a) Fourteen of 19 materials have numerical data for both anomalous properties, plotted in (b) [4,5,6,7,8,9,10,11,12,13,14,15].

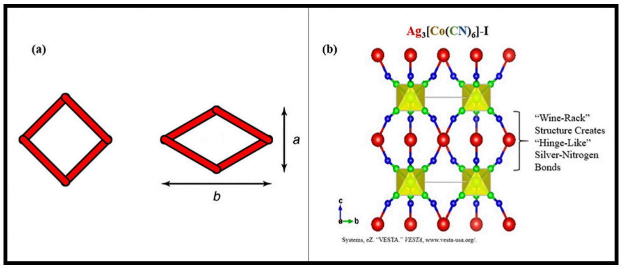

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Figure 3: (a) Illustration of "wine-rack" structure exhibiting NLC [2]. (b) Structure of silver hexacyanocobaltate [7]. Under pressure, the "hinge-like" bond will collapse along the c-axis.

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