

# ISNTE-4

Padua, 5-7 July 2023



## 4<sup>th</sup> International Symposium on Negative Thermal Expansion and Related Materials (ISNTE-4)



**ABSTRACT BOOK**



**4<sup>th</sup> International Symposium on  
Negative Thermal Expansion and Related Materials**

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**Padua, 5-7 July 2023**

**Giove Convention Centre – Best Western Plus Hotel Galileo**

**- ABSTRACT BOOK -**



## Organizers

Prof. Andrea Sanson, University of Padua, Italy

Dr. Alessandro Venier, University of Padua, Italy

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Dipartimento  
di Fisica  
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*Microstructures*



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# Conference Program

## DAY 0 – 4<sup>th</sup> July 2023

17:00-19:00	Welcome Desk Opening
19:00-21:00	<b>WELCOME BUFFET DINNER</b>

## DAY 1 – 5<sup>th</sup> July 2023

8:45-9:00	<b>Andrea Sanson</b> – Opening Ceremony with greetings from <b>Flavio Seno</b> , Head of the Physics and Astronomy Department “G. Galilei”
9:00-9:05	Microstructures - Sponsor Video
9:05-9:40	Opening Lecture <b>Jun Chen</b> University of Science and Technology Beijing, China <i>Design of ferroelectric and magnetic functional materials inspired by negative thermal expansion</i>
	<b>Session “MAGNETIC MATERIALS (I)” – Chair: Koshi Takenaka</b>
9:40-10:05	<b>Masahito Mochizuki</b> Waseda University, Japan <i>Theory of magnetism-induced negative thermal expansion in inverse perovskite antiferromagnets</i>
10:05-10:25	<b>Sergii Khmelevskiy</b> Vienna University of Technology, Austria <i>Accurate calculations of the spontaneous volume magnetostriction in Fe-Ni Invar alloys: impact of the spin fluctuations</i>
10:25-10:45	<b>Kun Lin</b> University of Science and Technology Beijing, China <i>Chemical heterogeneity modulated zero thermal expansion alloy over super-wide temperature range</i>
10:45-11:15	<b>COFFEE BREAK</b>
	<b>Session “FRAMEWORK MATERIALS” – Chair: John S. O. Evans</b>
11:15-11:40	<b>Yu Jia</b> Zhengzhou University, China <i>Machine learning guided discovery of new negative thermal expansion materials with open-framework structures</i>
11:40-12:00	<b>Angus P. Wilkinson</b> Georgia Institute of Technology, USA <i>Inserting Helium into ReO<sub>3</sub>-type fluorides which display negative thermal expansion</i>
12:00-12:20	<b>Liam McKinlay</b> University of New South Wales Sydney, Australia <i>The phase transitions of a zero thermal expansion material under pressure</i>
12:20-12:40	<b>Toshihiro Isoe</b> Tokyo Institute of Technology, Japan <i>Synthesis and properties of <math>\alpha</math>-Zr<sub>2</sub>SP<sub>2</sub>O<sub>12</sub> and related substances</i>
12:40-13:00	<b>Lei Hu</b> Xi’an Jiaotong University, China <i>Negative thermal expansion in metallic framework oxide Cd<sub>2</sub>Re<sub>2</sub>O<sub>7</sub> with ultralow thermal conductivity</i>
13:00-14:15	<b>LUNCH</b>

<b>Session “TUNING THERMAL EXPANSION” – Chair: Julien Haines</b>	
14:15-14:40	<p><b>Frederico Alabarse</b> Elettra Sincrotrone Trieste, Italy <i>Tuning negative thermal expansion properties by high pressure insertion of guest molecules</i></p>
14:40-15:00	<p><b>Koshi Takenaka</b> Nagoya University, Japan <i>Negative thermal expansion and related volumetric functionality of pyrovanadate-phosphates</i></p>
15:00-15:20	<p><b>Qiao Li</b> Hong Kong University of Science and Technology, China <i>Large tunable thermal expansion in ferroelastic alloys by stress</i></p>
15:20-15:40	<p><b>Alessandro Venier</b> University of Padova, Italy <i>Tuning the phonon contribution to control thermal expansion</i></p>
15:40-16:00	<p><b>Sofia Gonçalves</b> University of Porto, Portugal <i>Tailoring negative thermal expansion via tunable induced strain in La-Fe-Si-based multifunctional material</i></p>
16:00-	<p><b>POSTER SESSION with refreshments</b></p> <p><b>Aistė Miliūtė</b> Bundesanstalt für Materialforschung und -prüfung, Germany P.01 - <i>High-quality zirconium vanadate samples for negative thermal expansion analysis</i></p> <p><b>Angel J. Ross</b> IGG - National Research Council, Italy P.02 - <i>EosFit: a tool for fitting thermal expansion data and phase transitions</i></p> <p><b>Chunyan Wang</b> Zhoukou Normal University, China P.03 - <i>Spatial modulation and thermal-induced spin phase transition on the negative thermal expansion of ScF<sub>3</sub> with metal dopants</i></p> <p><b>Eliza K. Dempsey</b> University of Edinburgh, UK P.04 - <i>Metal oxyfluorides: a new area for novel, tunable NTE materials</i></p> <p><b>Elodie Harbourne</b> University of Oxford, UK P.05 - <i>Local structure of NTE Prussian blue analogues</i></p> <p><b>Feiran Shen</b> Spallation Neutron Source Science Center &amp; Chinese Academy of Sciences, China P.06 - <i>Magnetic ordering dominated giant negative thermal expansion in Fe-doped MnNiGe compounds</i></p> <p><b>Feixiang Long</b> University of Science and Technology Beijing, China P.07 - <i>Strong negative thermal expansion induced by magnetic field in La(Fe,Al)<sub>13</sub></i></p> <p><b>Feiyu Qin</b> Xi'an Jiaotong University, China P.08 - <i>Enhanced thermoelectric performance and low thermal conductivity in Cu<sub>2</sub>GeTe<sub>3</sub> with identified localized symmetry breakdown</i></p> <p><b>Götz Schuck</b> Helmholtz-Zentrum Berlin für Materialien und Energie, Germany P.09 - <i>Apparent shrinkage of [PbX<sub>6</sub>] octahedra with increasing temperature and anharmonicity of the lead-halide bond in chlorine-substituted MAPbI<sub>3</sub></i></p> <p><b>Hao Lu</b> University of Science and Technology Beijing, China</p>

P.10 - *Lightweight and near-zero thermal expansion ZrW<sub>2</sub>O<sub>8</sub>-SiCnw/Al hybrid composites*

**Hisashi Kino**

Tohoku University, Japan

P.11 - *Developments of negative-thermal-expansion gate electrode formed from manganese nitride compound for transistor performance enhancement*

**Hu Zhang**

University of Science and Technology Beijing, China

P.12 - *Tunable negative thermal expansion in La(Fe, Si)<sub>13</sub>/resin composites with high mechanical property and long-term cycle stability*

**Jiazheng Hao**

Spallation Neutron Source Science Center, China

P.13 - *Realization of ultra-low thermal expansion over a broad temperature interval in (R,R')(Fe,Co)<sub>2</sub> compounds*

**Joao Horta Belo**

University of Porto, Portugal

P.14 - *Optimizing thermal expansion in 3d-printed mortar*

**Meng Xu**

University of Science and Technology Beijing, China

P.15 - *High-temperature zero thermal expansion in HfFe<sub>2+δ</sub> from added ferromagnetic paths*

**Minjun Ai**

University of Science and Technology Beijing, China

P.16 - *Unconventional magnetovolume effect induced negative thermal expansion*

**Nikita Zhadnov**

Lebedev Physical Institute, Russian Academy of Sciences, Russia

P.17 - *Ultrastable optical cavities with natural and artificial zero thermal expansion*

**Peixi Zhang**

University of Science and Technology Beijing, China

P.18 - *Strain-induced ferroelectric order in nanosized SrTiO<sub>3</sub>*

**Qiang Li**

University of Science and Technology Beijing, China

P.19 - *Chemical order-disorder nanodomains in Fe<sub>3</sub>Pt bulk alloy*

**Soumya Mondal**

Indian Association for the Cultivation of Science, India

P.20 - *Negative thermal expansion induced in several graphene and graphyne analogues*

**Yanming Sun**

University of Science and Technology Beijing, China

P.21 - *Structure, magnetism and low thermal expansion in Tb<sub>1-x</sub>Er<sub>x</sub>Co<sub>2</sub>Mn<sub>y</sub> intermetallic compounds*

**Yili Cao**

University of Science and Technology Beijing, China

P.22 - *Quantified zero thermal expansion in the magnetic intermetallic R<sub>2</sub>Fe<sub>17</sub>-based (R =rare earth) materials*

**Ying Sun**

Beihang University, China

P.23 - *Strategies for obtaining negative/near zero thermal expansion materials with wide temperature range in antiperovskite compounds*

**Yuzhu Song**

University of Science and Technology Beijing, China

P.24 - *Mechanism and control of negative thermal expansion in metal-based magnetic compounds*

**Zhanning Liu**

Shandong University of Science and Technology, China

P.25 - *Anomalous thermal expansion in metal-sulfate frameworks*

## DAY 2 – 6<sup>th</sup> July 2023

	<b>Session “MAGNETIC MATERIALS (II)” – Chair: Andrew Goodwin</b>
9:00-9:25	<b>Hena Das</b> Tokyo Institute of Technology & Kanagawa Institute of Industrial Science and Technology, Japan <i>Understanding the mechanisms responsible for the anisotropic thermal expansion in Ca<sub>2</sub>RuO<sub>4</sub> ruthenates through quantum mechanical calculations</i>
9:25-9:45	<b>Xianran Xing</b> University of Science and Technology Beijing, China <i>Magnetic structure in kagomé magnets and Invar phenomenon</i>
9:45-10:05	<b>Takashi Mizokawa</b> Waseda University, Japan <i>Charge/Orbital disordered states with smaller volume and higher entropy in transition-metal oxides</i>
10:05-10:25	<b>Filomena Forte</b> National Research Council, CNR-SPIN, Italy <i>Spin-orbital mechanisms for negative thermal expansion in Ca<sub>2</sub>RuO<sub>4</sub></i>
10:25-10:45	<b>Zhao Pan</b> Institute of Physics, Chinese Academy of Sciences, China <i>Magnetic-field-induced sign changes of thermal expansion in DyCrO<sub>4</sub></i>
10:45-11:15	<b>COFFEE BREAK</b>
	<b>Session “NTE AND PHONONS” – Chair: Angus P. Wilkinson</b>
11:15-11:40	<b>Naike Shi</b> University of Science and Technology Beijing, China <i>Abundant negative thermal expansion in A<sub>2</sub>M<sub>2</sub>O<sub>7</sub> family</i>
11:40-12:00	<b>Ayan Datta</b> Indian Association for the Cultivation of Science, India <i>Negative thermal expansion in two-dimensional monoatomically thin layers: T-graphene, Tri-graphene and Graphyne</i>
12:00-12:20	<b>Qiang Sun</b> Zhengzhou University, China <i>Influence of A/B element substitution on negative thermal expansion in AB(CN)<sub>6</sub> (A=Al, Ga, In; B=Co, Fe, Mn, Cr, V, Ti)</i>
12:20-12:40	<b>Toshihiko Yokoyama</b> Institute for Molecular Science, Japan <i>Thermal vibration and expansion from the view point of local structure</i>
12:40-13:00	<b>Quentin Guérout</b> University of Oxford, UK <i>NTE in diamond networks: from Si to Cd(CN)<sub>2</sub></i>
13:00-14:30	<b>LUNCH</b>
14:45	<b>GROUP PHOTO</b>
15:00-19:15	<b>SOCIAL TOUR “Padova Urbs Picta”</b>
19.30-22.00	<b>SOCIAL DINNER at the historical “Café Pedrocchi”</b> Return to the Hotel BW Plus Galileo at around 22.30

## DAY 3 – 7<sup>th</sup> July 2023

<b>Session “THEORY AND FUNDAMENTALS” – Chair: Jun Chen</b>	
9:00-9:25	<b>Zi-Kui Liu</b> Pennsylvania State University, USA <i>Theory and parameter-free prediction of positive and negative derivatives of volume to temperature and their positive and negative divergencies at critical points</i>
9:25-9:45	<b>Ashish Chainani</b> National Synchrotron Radiation Research Center, Taiwan <i>Dual Kondo effect coupled charge ordering and zero thermal expansion in a correlated intermetallic YbPd</i>
9:45-10:05	<b>Takuro Katsufuji</b> Waseda University, Japan <i>Novel aspects of orbital ordering in Ba-V-O with V triangular lattice</i>
10:05-10:25	<b>Jason Hancock</b> University of Connecticut, USA <i>Strain soliton generation in negative thermal expansion materials</i>
10:25-10:45	<b>Yue Chen</b> The University of Hong Kong, China <i>Anharmonic lattice dynamics of materials containing diffusive constituents: a computational study based on the machine learning potential</i>
10:45-11:15	<b>COFFEE BREAK</b>
<b>Session “PEROVSKITES” – Chair: Masaki Azuma</b>	
11:15-11:40	<b>Igor Zaliznyak</b> Brookhaven National Laboratory, USA <i>Negative thermal expansion, entropic elasticity, and colossal softening in ScF<sub>3</sub>-type empty perovskites</i>
11:40-12:00	<b>Cong Wang</b> Beihang University, China <i>Isotropic negative/zero thermal expansion in a broad temperature range in antiperovskite Mn<sub>3</sub>XN(C)</i>
12:00-12:20	<b>Yuki Sakai</b> Kanagawa Institute of Industrial Science and Technology & Tokyo Institute of Technology, Japan <i>Systematic charge distribution change in perovskite-type Bi<sub>0.5</sub>Pb<sub>0.5</sub>MO<sub>3</sub> (M = 3d transition metal)</i>
12:20-12:40	<b>Dmitry Bocharov</b> Institute of Solid State Physics, University of Latvia, Latvia <i>Exploring the mechanisms of negative thermal expansion in scandium trifluoride: a combined theoretical and experimental analysis</i>
12:40-13:00	<b>Sihao Deng</b> Spallation Neutron Source Science Center, China <i>Spin dependent electronic transport properties of Mn-based antiperovskites</i>
13:00-14:15	<b>LUNCH</b>
<b>Session “DESIGN &amp; APPLICATIONS” – Chair: Xianran Xing</b>	
14:15-14:40	<b>Zheshuai Lin</b> Tech. Institute of Physics and Chemistry, Chinese Academy of Sciences, China <i>Zero thermal expansion and good optical transparency in the crystals with sodalite cage structures</i>
14:40-15:00	<b>Xingxing Jiang</b> Tech. Institute of Physics and Chemistry, Chinese Academy of Sciences, China <i>Integration of negative, zero and positive linear thermal expansion enables light transmission in borate optical crystals to be temperature-independent</i>

15:00-15:20	<b>Carl P. Romao</b> ETH Zurich, Switzerland <i>Data mining and machine learning of NTE materials from the ICSD</i>
15:20-15:40	<b>Takumi Nishikubo</b> Kanagawa Institute of Industrial Science and Technology & Tokyo Institute of Technology, Japan <i>Domain structure observation and design of phase transition-type negative thermal expansion materials</i>
15:20-15:40	<b>Chang Zhou</b> University of Science and Technology Beijing, China <i>Design of zero thermal expansion and high thermal conductivity in machinable xLFCS/Cu metal matrix composites</i>
16:00-16:30	<b>COFFEE BREAK</b>
16:30-17:00	<b>BEST POSTER AWARDS &amp; CLOSING REMARKS</b>

**DAY 1**

**5<sup>th</sup> July 2023**

## Design of ferroelectric and magnetic functional materials inspired by negative thermal expansion

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Negative thermal expansion (NTE) refers to the abnormal contraction of the lattice with increasing temperature. It is well known that the properties of a compound are usually determined by its crystal structure. Abnormal lattice changes can induce novel ferroelectric and magnetic properties of compounds. For example, there is a strong coupling between the ferroelectric polar unit and lattice strain, which allows lattice strain to be used to control the polar functional unit and thus improve the properties. Through the new method of "interphase strain", a large lattice strain is introduced to increase the polar displacement, and the ferroelectrics with giant polarization are achieved. Based on the multi-element characteristics of the high-entropy method, the multi-state local lattice strain is introduced to form the flexible polar functional unit configuration, greatly enhancing the piezoelectric and capacitive energy storage performances [1-4]. The magnetic field induces the rotation of the magnetic spin of  $\text{La}(\text{Fe,Al})_{13}$ , successfully achieving a huge transition from weak NTE to strong NTE. Simultaneously, due to the spin-lattice coupling effect, the lattice is greatly elongated when the ferromagnetic component increases, and giant magnetostriction occurs. NTE magnetic materials undergo sharp magnetic transition and large lattice thermal contraction at the same time, resulting in large magnetic entropy changes and lattice entropy changes. Magnetic NTE systems are likely to produce a giant magnetocaloric effect [5-8]. Therefore, NTE research provides feasible ideas for the design of novel properties of giant polarization ferroelectrics, high-entropy ferroelectrics, giant magnetostriction, and giant magnetocaloric effect.

- [1] L. X. Zhang, *et al.*, *Science*, 361, 494 (2018).
- [2] L. Cheng, *et al.*, *Nat. Commun.* 13, 3089 (2022).
- [3] Y. Liu, *et al.*, *Acta Mater.* 236, 118115 (2022).
- [4] H. Qi, *et al.*, *Nat. Rev. Mater.* doi.org/10.1038/s41578-023-00544-2 (2023).
- [5] Y. Song, *et al.*, *Prog. Mater. Sci.* 121, 100835 (2021).
- [6] Y. Song, *et al.*, *J. Am. Chem. Soc.* 140, 602 (2018).
- [7] Y. Song, *et al.*, *Chem. Mater.* 32, 7535 (2020).
- [8] Y. Song, *et al.*, *Sci. China Mater.* 64, 1238 (2021).

## Theory of magnetism-induced negative thermal expansion in inverse perovskite antiferromagnets

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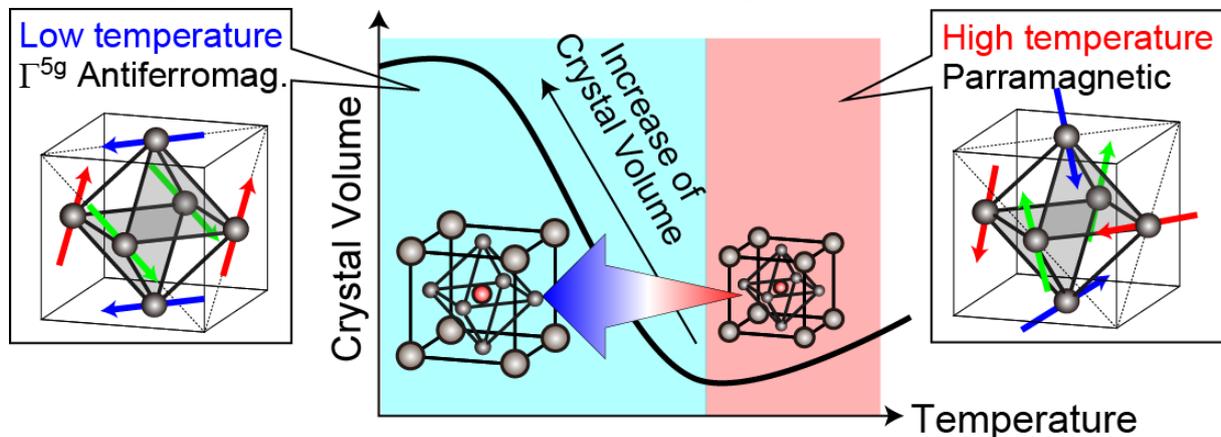
Department of Applied Physics, Waseda University, Okubo, Shinjuku-ku, Tokyo, Japan

We will discuss our recent theoretical study on a physical mechanism of the magnetism-induced negative thermal expansion observed in the inverse-perovskite antiferromagnets  $Mn_3AN$  ( $A=Zn, Ga, \text{etc.}$ ). These compounds exhibit crystal-volume expansion upon cooling, triggered by a non-coplanar antiferromagnetic order [1-3].

The mechanism had remained as a puzzle for 50 years. This puzzle was recently solved by constructing a microscopic spin-lattice model through considering the microscopic electronic and magnetic structures and the coupling between the magnetism and the crystal lattice in this class of materials [4].

By analyzing the constructure model using the Monte-Carlo technique, we reproduced the crystal-volume expansion upon cooling triggered by a non-coplanar antiferromagnetic order and show that the expansion occurs so as to maximize an energy gain of the nearest-neighbor antiferromagnetic interactions [5].

This mechanism is not specific to the inverse perovskite magnets and might also be expected in magnets with other crystal structures. Therefore, our work provides a general guiding principle to search for new magnetism-induced negative thermal expansion materials and will significantly contribute to the development of this research field. We also propose other candidate crystal structures that might exhibit NTE through this mechanism.



**Figure:** Schematics of the magnetism-induced negative thermal expansion in the inverse perovskite  $Mn_3AN$ . When the system enters the special antiferromagnetic phase with lowering temperature, the crystal volume expands to maximize an energy gain of the exchange interactions.

- [1] K. Takenaka, K. Asano, M. Misawa, and H. Takagi, *Appl. Phys. Lett.* 92, 011927 (2008).
- [2] K. Takenaka, *Sci. Technol. Adv. Mater.* 13, 013001 (2012).
- [3] K. Takenaka *et al.*, *Sci. Technol. Adv. Mater.* 15, 015009 (2014).
- [4] M. Mochizuki *et al.*, *Phys. Rev. B* 97, 060401(R) (2018).
- [5] M. Kobayashi, and M. Mochizuki, *Phys. Rev. Mater.* 3, 024407 (2019).

## **Accurate calculations of the spontaneous volume magnetostriction in Fe-Ni Invar alloys: impact of the spin fluctuations**

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The Invar anomaly, a phenomenon observed in the canonical INVAR alloys Fe-Ni, has been investigated on a first-principles basis, with the inclusion of longitudinal spin fluctuations in the paramagnetic region. We obtained an almost perfect quantitative description of the spontaneous volume magnetostrictions and their dependence on the alloy's chemical composition. With an increase in the Ni concentration, the Invar anomaly vanishes in Fe-Ni, and spontaneous magneto-volume magnetostrictions even reach slightly negative values in compositions with over 50% of Ni (anti-Invar). This feature is readily reproduced in our calculations, being a consequence of the longitudinal spin fluctuations (LSF) that increase the local atomic moment as temperature increases. We will provide an overview of the history of the methodology that allows for an effective handling of LSF on a first-principles basis and its impact on the theory of magnetism in transition metal alloys.

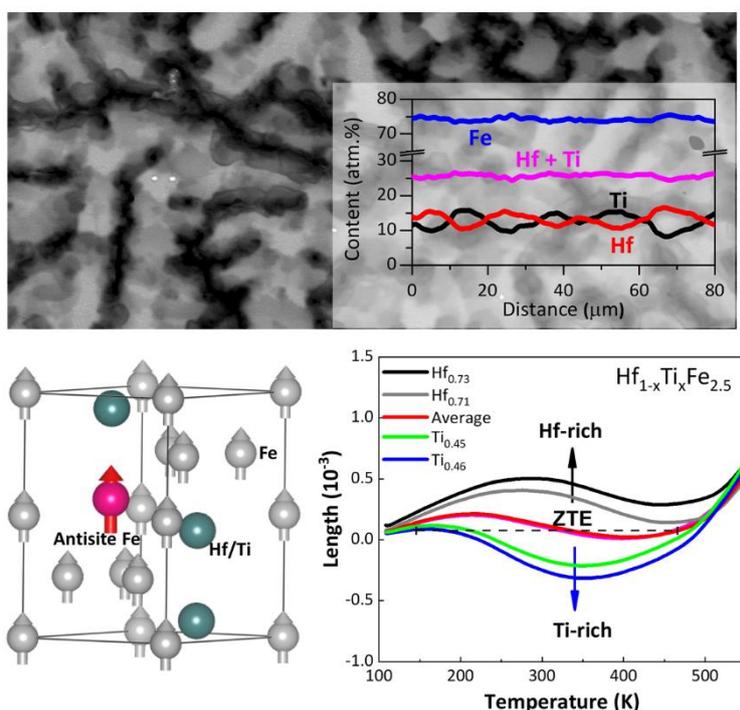
## Chemical heterogeneity modulated zero thermal expansion alloy over super-wide temperature range

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Chemical heterogeneity is usually avoided in solution chemistry, but it sometimes still occurs, with sometimes dramatic effects on target materials and their properties. Here we propose chemical heterogeneity as a counterintuitive strategy to design high-performance zero thermal expansion (ZTE) alloys. We apply this approach in a Hf-Ti-Fe alloy with excess Fe in the Hf/Ti sublattice and produce Hf/Ti concentration alternations at a micro level. Such chemical heterogeneity regulates local magnetic interactions in the alloy and triggers a dispersed magnetic phase transition that modulates the thermal expansions at the micro level and hence results in a remarkable ZTE behavior over a super-wide temperature window from 10 to 480 K. This novel mechanism is supported by comprehensive studies on morphological microstructure, crystal and magnetic structure, and theoretical calculations. The strategy of local chemical heterogeneity opens up an avenue to design ZTE and the related functional materials via microstructure engineering directly.



[1] K. Lin, X. Xing, *et al.*, Cell Rep. Phys. Sci. Vol. 4, Issue 2, 101254 (2023).

[2] W. Li, K. Lin, X. Xing, *et al.*, Adv. Mater., 2109592 (2022).

[3] C. Yu, K. Lin, X. Xing, *et al.*, Nat. Commun. 12, 4701 (2021).

## Machine learning guided discovery of new negative thermal expansion materials with open-framework structures

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The unique thermal expansion characteristics of materials have had attractive prospects in practice since 1996[1]. Yet, to date the number of negative thermal expansion(NTE) materials found in nature is very limited, which greatly limits the growing application. Therefore, design and discovery of new NTE materials is the challenge in this promising field. In this talk, taking the discovered 204 NTE materials between 1996 and 2022 both in experimental and theoretical studies as the basic data set, we will discuss the machine learning method for predicting the NTE properties of materials from the Inorganic Crystal Structure Database(ICSD) and Material Projects Database(MPD)[2]. To do this, the element composition, atomic radius, electronegativity of element, void ratio, crystal structure and crystal symmetry of each material are considered as input vectors and the different machine learning algorithms(linear regression (LR), support vector regression(SVR) and random forest regression(RF)) are checked to identify which is more reliable in the prediction processes. We have shown that the random forest algorithm has the highest prediction accuracy of ~95% and the smallest error of ~6%(see Figure 1). For all materials with the open-framework structures from ICSD and MPD, we have predicted a total of 976 materials as the potential candidates with obviously NTE property, and among them 866, 22, and 82 belong to oxides, cyanide and fluorides, respectively. Further, the NTE range of temperature of these new candidates are also predicted by further machine learning methods. Finally, we carried out the first-principles calculations of the coefficients of NTE of the predicted candidate materials to verify the validity of machine learning prediction. It is found that the results of machine learning prediction are in good agreement with that of the first-principles calculations, suggesting our prediction results are reliable[3]. This work has greatly expanded the number of NTE materials with open-framework structures and plays a guiding role in finding new NTE materials in future experiments.

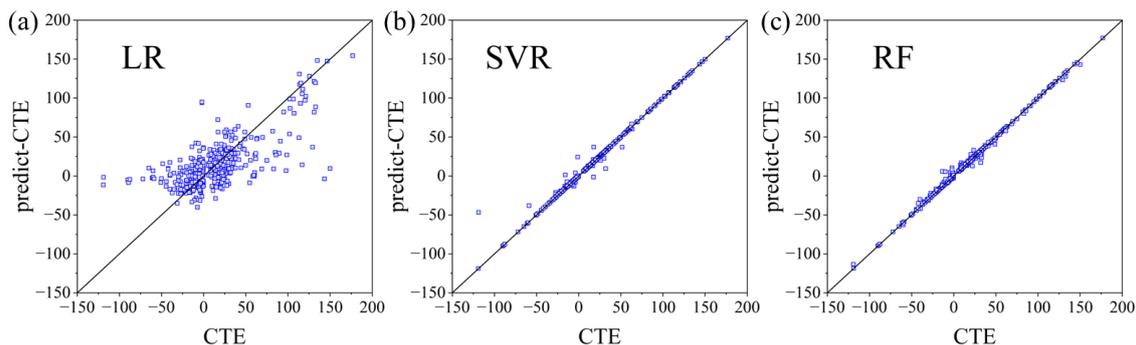


Figure 1: Predicted results of coefficient of thermal expansion (CTE) by using different machine learning algorithms.

[1] T. A. Mary, J. S. O. Evans, A. W. Sleight, *et al.* Science, 272: 90-92(1996).

[2] Database website: <https://icsd.products.fiz-karlsruhe.de/>; <https://materialsproject.org/>.

[3] Y. Cai, Y. Jia, *et al.* (2023)(to be published).

## Inserting Helium into $\text{ReO}_3$ -type fluorides which display negative thermal expansion

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Framework negative thermal expansion (NTE) materials typically show a rich behavior on modest compression, as the softening of low frequency vibrational modes on volume reduction, which drives their NTE, predisposes them to structural phase transitions. This rich behavior, combined with potential applications in composites where they could be subject to significant stress, has led to many studies of their response to pressure. However, the pressure medium for these experiments should be chosen carefully, as it is not always inert. In 2017, we reported that the compression of  $\text{CaZrF}_6$  in helium at room temperature, and pressures of less than 0.5 GPa, led to the formation of the defect perovskite  $[\text{He}_{2-x}\square_x][\text{CaZr}]F_6$ , and the incorporation of helium modified the material's negative thermal expansion.[1] Our subsequent work on this material revealed that the perovskite  $[\text{He}_2][\text{CaZr}]F_6$  likely forms at pressures  $\sim 1$  GPa and that this material is stable to high pressures unlike  $\text{CaZrF}_6$ . [2] Remarkably, this perovskite still shows negative thermal expansion and, on compression at low temperature, it shows a tilting transition typical of perovskites. We have recently shown that other  $\text{ReO}_3$ -type fluorides showing NTE can readily incorporate helium under pressure, and that the helium modifies their properties. We will present work on two examples of this material's class. Our efforts to prepare perovskite  $\text{HeWO}_3$  have not yet been successful, but we will present work showing that helium can be incorporated under pressure into both hexagonal and pyrochlore  $\text{WO}_3$ .

[1] B.R. Hester, A.M. dos Santos, J.J. Molaison, J.C. Hancock, A.P. Wilkinson, *J. Am. Chem. Soc.*, 139, 13284 (2017).

[2] A.J. Lloyd, B.R. Hester, S.J. Baxter, S. Ma, V.B. Prakapenka, S.N. Tkachev, C. Park, A.P. Wilkinson, *Chem. Mater.*, 33, 3132 (2021).

## The phase transitions of a zero thermal expansion material under pressure

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Zero thermal expansion materials have a unique ability to withstand thermal shock over varied temperature ranges; because of this, they have potential applications as components of high precision devices. The zero thermal expansion material  $\text{Sc}_{1.5}\text{Al}_{0.5}\text{W}_3\text{O}_{12}$  exhibits zero thermal expansion over the largest temperature range reported to date, from 4 to 1400 K[2]. In this work, the pressure stability of this material is investigated using high-pressure neutron and X-ray powder diffraction, as well as Raman spectroscopy.  $\text{Sc}_{1.5}\text{Al}_{0.5}\text{W}_3\text{O}_{12}$  has an orthorhombic to monoclinic phase transition above 3.4 GPa, ten times higher than the end members  $\text{Sc}_2\text{W}_3\text{O}_{12}$  and  $\text{Al}_2\text{W}_3\text{O}_{12}$  [3-5], followed by a pressure-induced amorphization above 5.7 GPa. The stable orthorhombic phase has a bulk modulus of 20(6) GPa, as determined by neutron powder diffraction (Figure 1). An amorphous-to-amorphous phase transition is further evidenced around 20 GPa (Figure 2). This work demonstrates the importance of understanding structural changes under pressure for zero thermal expansion materials, as changes in pressure impart a more significant impact on the crystallographic volume compared to temperature.

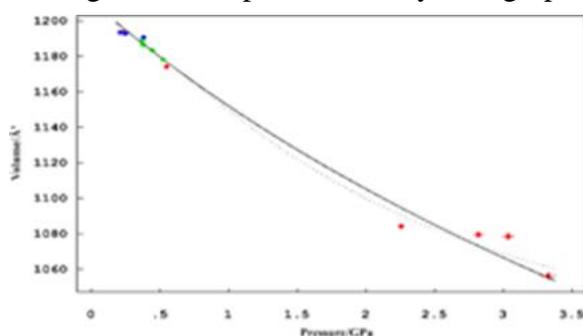


Figure 1. Volume evolution of the orthorhombic phase of scandium aluminium tungstate to near 3.5 GPa. Equations of state determined using EOSFit software[1]

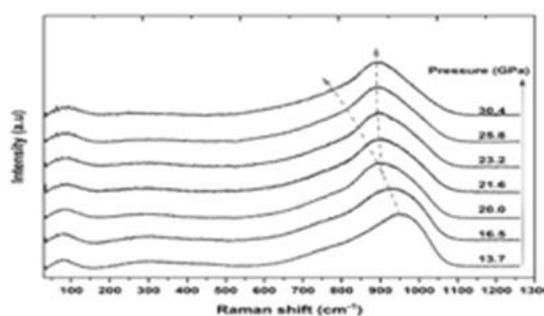


Figure 2. Amorphous to amorphous change evident in the high-pressure Raman spectra

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## Synthesis and properties of $\alpha$ -Zr<sub>2</sub>SP<sub>2</sub>O<sub>12</sub> and related substances

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Substances with negative coefficients of thermal expansion (CTEs) can be used to prepare composites with specific CTE values. The negative thermal expansion behavior can be primarily attributed to two types of mechanisms: phase transition- and framework-type mechanisms.  $\alpha$ -Zr<sub>2</sub>SP<sub>2</sub>O<sub>12</sub> has the NASICON structure with the  $R\bar{3}c$  space group, and involved both mechanisms [1]. Figure 1 shows the relationships between temperature and lattice volume. It exhibits a framework-type mechanism at temperatures below 393 K or above 453 K and an isomorphic phase transition mechanism at 393–453 K. The volumetric CTE of  $\alpha$ -Zr<sub>2</sub>SP<sub>2</sub>O<sub>12</sub> is approximately  $-70$  ppm/K during the isosymmetric phase transition, and this value can be improved by decreasing the proportion of sulfur. The maximum volumetric CTE of  $\alpha$ -Zr<sub>2</sub>S<sub>0.9</sub>P<sub>2</sub>O<sub>12- $\delta$</sub>  is approximately  $-108$  ppm/K in the temperature range of 393–453 K. To investigate the origin of the phase transition, XRD was measured at each temperature and atomic coordinates were refined using the Rietveld method. As a results, it was revealed that the phase transition is related to the deformation of the ZrO<sub>6</sub> octahedron. Based on these results, Zr<sub>2-x</sub>M<sub>x</sub>S<sub>y</sub>P<sub>2</sub>O<sub>12- $\delta$</sub>  with zirconium (IV) ion (Zr<sup>4+</sup>) partially substituted by aliovalent ions were synthesized [2-4]. Table 1 lists the CTEs calculated using the lattice volumes. At 303 – 373 K, the CTEs of the Fe-substituted sample were less than those of the Zr<sub>2</sub>SP<sub>2</sub>O<sub>12</sub>. At 373 – 453 K, the CTEs of the Y- or Fe- substituted samples (minimum  $-117$ ,  $-105$  ppm/K) were less than those of Zr<sub>2</sub>SP<sub>2</sub>O<sub>12</sub>. At 453 – 673 K, the CTEs of all substituted samples were reduced. It is proposed that element substitution can be used to control the CTEs of Zr<sub>2</sub>SP<sub>2</sub>O<sub>12</sub> for each temperature range of 303 – 673 K.

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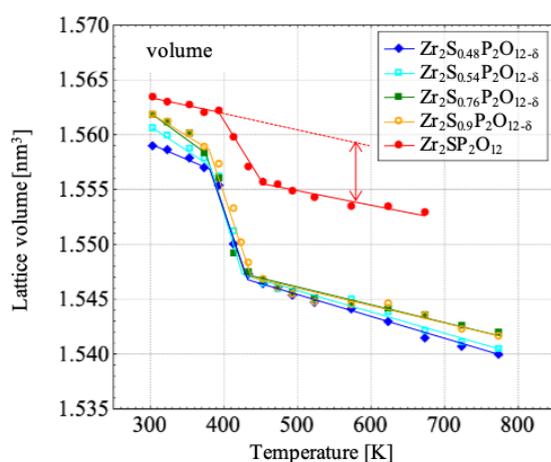


Figure 1. Lattice volume of  $\alpha$ -Zr<sub>2</sub>S<sub>x</sub>P<sub>2</sub>O<sub>12- $\delta$</sub>  calculated using the Rietveld method as functions of temperature [1].

Table 1. CTE of Zr<sub>2-x</sub>M<sub>x</sub>S<sub>y</sub>P<sub>2</sub>O<sub>12- $\delta$</sub>

Temp. /K	The volumetric CTE / ppm · K <sup>-1</sup>		
	303 – 373	373 – 453	453 – 673
Zr <sub>2</sub> SP <sub>2</sub> O <sub>12</sub>	-14.4	-70	-27.4
Zr <sub>1.9</sub> Al <sub>0.2</sub> S <sub>0.9</sub> P <sub>2.0</sub> O <sub>12-<math>\delta</math></sub>	-10.3	-97.3	-15.0
Zr <sub>1.8</sub> Al <sub>0.3</sub> S <sub>0.9</sub> P <sub>2.0</sub> O <sub>12-<math>\delta</math></sub>	-16.4	-95.8	-17.7
Zr <sub>1.8</sub> Y <sub>0.2</sub> S <sub>1.0</sub> P <sub>2.0</sub> O <sub>12-<math>\delta</math></sub>	-25.6	-103	-20.1
Zr <sub>1.7</sub> Y <sub>0.3</sub> S <sub>1.0</sub> P <sub>2.0</sub> O <sub>12-<math>\delta</math></sub>	-27.2	-117	-16.2
Zr <sub>1.8</sub> Nb <sub>0.3</sub> S <sub>0.8</sub> P <sub>2.0</sub> O <sub>12-<math>\delta</math></sub>	-24.0	-101	-18.5
Zr <sub>1.6</sub> Nb <sub>0.6</sub> S <sub>0.7</sub> P <sub>2.0</sub> O <sub>12-<math>\delta</math></sub>	-23.6	-75.4	-23.3
Zr <sub>2.0</sub> Gd <sub>0.1</sub> S <sub>1.1</sub> P <sub>2.0</sub> O <sub>12-<math>\delta</math></sub>	-26.7	-89.4	-17.0
Zr <sub>1.9</sub> Fe <sub>0.2</sub> S <sub>1.2</sub> P <sub>2.0</sub> O <sub>12-<math>\delta</math></sub>	-27.1	-105	-16.5

## Negative thermal expansion in metallic framework oxide $\text{Cd}_2\text{Re}_2\text{O}_7$ with ultralow thermal conductivity

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Negative thermal expansion (NTE) materials are desirable for cutting-edge devices serving in extreme environments. However, it is a grand challenge to integrate tunable NTE, low thermal conductivity, and sufficient electrical conduction into a single-phase structure. Here, a high-performance  $\text{Cd}_2\text{Re}_2\text{O}_7$  oxide is reported, which shows the unconventional NTE ( $\alpha_V = -5.0 \times 10^{-6}/\text{K}$ ) in a broad temperature range of 5 - 210 K, ultralow thermal conductivity ( $\kappa = 0.38 \text{ W/mK}$  at 300 K) and also a metallic state. The overall, local, and phonon structural characteristics of  $\text{Cd}_2\text{Re}_2\text{O}_7$  were identified through a combination of synchrotron X-ray diffraction, total scattering, inelastic X-ray scattering, aberration-corrected scanning transmission electron microscope, and corresponding theoretical calculations. The unconventional NTE is presumably related to soft acoustic phonons with large negative Grüneisen parameters of -21, distinguished from classical NTE triggered by low-energy optical phonons. Moreover, this low  $\kappa$  is comparable to the lowest values achieved in insulating NTE materials and numerous common solids, which also correlates to the soft anharmonic acoustic phonons. These multiple functionalities integrated into a pure  $\text{Cd}_2\text{Re}_2\text{O}_7$  framework oxide could open up a frontier to design state-of-the-art devices

## Tuning negative thermal expansion properties by high pressure insertion of guest molecules

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Microporous aluminophosphate AlPO<sub>4</sub>-17 with a hexagonal erionite structure is the oxide which exhibits the highest coefficient of negative thermal expansion. The NTE mechanism in this material is rationalized by a structural contraction around the empty pores and cages that occurs with increasing temperature. The insertion of small molecules into the empty cages of AlPO<sub>4</sub>-17 offers a means to modify its thermal expansion and mechanical properties. High quality, single-crystal and powder x-ray diffraction (XRD) measurements were used to monitor the NTE and the respective structural response to pressure in AlPO<sub>4</sub>-17. The insertion of oxygen molecules at high pressure into the empty cages of AlPO<sub>4</sub>-17 was found to tune its very strong NTE. The experiments were performed at the Xpress beamline of Elettra Synchrotron Facility, using a diamond anvil cell (DAC) in a closed-cycle He-cryostat with very precise control of the pressure and temperature.

The structure of the oxygen-filled material was determined *in situ* at high-pressure by single-crystal XRD. Powder XRD allowed us to determine the thermal expansion coefficient upon cooling at a pressure of 0.38 GPa. Whereas the volumetric thermal expansion only exhibits a small change with respect to AlPO<sub>4</sub>-17 (empty pores) at ambient pressure, the thermal expansion for the oxygen-filled material along the two main crystallographic directions are surprisingly different. While the thermal expansion along the *a* direction decreases almost to zero upon molecular insertion, the negative expansion along *c* becomes 7 times larger ( $-2.2 \cdot 10^{-5} \text{ K}^{-1}$ ). Such highly anisotropic thermal expansion properties are of great interest for mechanical and optical applications.

Molecular guest insertion is thus a very powerful tool for tuning the thermal expansion properties of porous materials with close to zero thermal expansion. High-pressure, variable temperature XRD is the technique of choice to determine the effect of guest content on the thermal expansion properties of these porous materials. The insertion of non-volatile guest species or the polymerization of a guest molecule under pressure can be used as a strategy to recover composites (after high pressure processing) for potential applications.

## Negative thermal expansion and related volumetric functionality of pyro-vanadate-phosphates

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An explosive progress in research has led to the successive discovery of negative thermal expansion (NTE) materials. However, for industrial use as a thermal expansion compensator, it is still required to develop a material with low environmental load in addition to high functionality. One promising class of materials is pyro-vanadate-phosphates  $A_2V_{2-x}P_xO_7$  ( $A$ : alkaline earth metals, transition metals). We have achieved giant NTE using the structural phase transition of  $Zn_2P_2O_7$  [1]. We have also explored how the structure and NTE functionality vary according to phosphorus content  $x$  in  $Cu_{1.8}Zn_{0.2}V_{2-x}P_xO_7$  [2].

A pyrophosphate  $Zn_2P_2O_7$  exhibits a first-order phase transition from the low-temperature (low- $T$ )  $\alpha$ -phase ( $I2/c$ ) to the high- $T$   $\beta$ -phase ( $C2/m$ ) at 405 K, which accompanies contraction of the unit-cell volume by 1.8%. By substituting Zn with Mg, the abrupt volume change became gradual. The operating- $T$  window was expanded. In fact,  $Zn_{1.6}Mg_{0.4}P_2O_7$  exhibits a large negative coefficient of linear thermal expansion  $\alpha_L$  exceeding  $-60$  ppm/K at 280–350 K ( $\Delta T=70$  K). It is expected to be of practical use because it contains no toxic or expensive elements. We also discovered that the NTE properties of  $Zn_{2-x}Mg_xP_2O_7$  can be tuned sensitively by the third dopant like Al or Mn onto the Zn site (Fig. 1, [3]).

A pyrovanadate  $Cu_{1.8}Zn_{0.2}V_2O_7$  exhibits large NTE with  $\alpha_L = -14.4$  ppm/K in a wide temperature  $T$  range of 100–700 K, which is assisted by the material microstructural effect peculiar to ceramic bodies. We recently found that P-doping of this pyrovanadate improves the insulating properties while maintaining the NTE functionality, which makes this class of materials more suitable as a thermal expansion compensator for electronic devices. We have clarified that  $Cu_{1.8}Zn_{0.2}V_{2-x}P_xO_7$  transforms from  $C2/c$  to  $C2/m$  symmetries by P doping exceeding  $x=1.0$ . On the other hand, it seems that the NTE characteristics are not drastically affected by this compositional change. A more detailed structural analysis is now underway, particularly in terms of relations to the microstructural effects. We also report the electrical field-induced volume change recently found in this system.

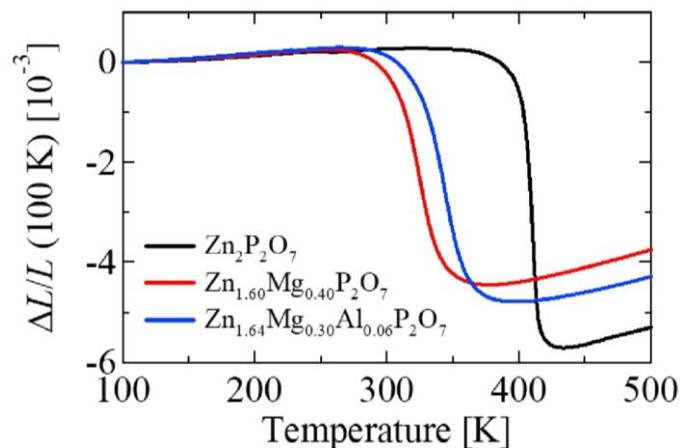


Fig. 1 Linear thermal expansion of  $Zn_{2-x-y}Mg_xAl_yP_2O_7$ . Data were collected during warming.

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## Large tunable thermal expansion in ferroelastic alloys by stress

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Metallic materials inherently possess small coefficients of thermal expansion (CTE). Engineering the CTEs of metals to achieve large values is demanded in many applications but has proved challenging. In this talk, we will show a strategy to achieve large tailored CTEs in ferroelastic alloys through uniaxial stress state control by utilizing the alloys' inherently strong temperature dependence of Young's modulus ( $dE/dT$ ). In nanostructured NiTi alloy with large elastic limit and large  $dE/dT$ , we tune the CTE from large negative  $-53.2 \times 10^{-6} \text{ K}^{-1}$  to large positive  $+40.4 \times 10^{-6} \text{ K}^{-1}$  through applying uniaxial tensile stresses up to 1 GPa. Such stress dependence of the CTE is 40 times stronger than those of non-phase-transformable metals and the created tunable CTE span is one order of magnitude larger than the typical value ( $10 \times 10^{-6} \text{ K}^{-1}$ ) obtained via the existing chemical modification and hydrostatic pressure control. Through in-situ neutron diffraction experiment and theoretical calculation based on Reuss approximation, we show that the observed large thermal expansion under stress mainly comes from the large elastic strain change with temperature due to the large  $dE/dT$  of the NiTi and can be generally achieved in ferroelastic alloys. In contrast to the stress-insensitive thermal expansion of most metals, the unique stress-responsive thermal expansion of ferroelastic alloys may enable new solutions for engineering arising from thermal expansion.

## Tuning the phonon contribution to control thermal expansion

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Since its discovery, anomalous thermal expansion has attracted great interest for its outstanding technological applications. In the last decades, it has been found that materials displaying large Negative Thermal Expansion (NTE) could be engineered in several ways to tune their thermal expansion properties [1]. In this regard, the following methods are worth mentioning: intercalation with small chemical species, chemical modification and nanostructuring. In all these cases, the local dynamics of specific atomic pairs can change drastically; thus, the phononic contribution to NTE can be investigated by temperature dependent EXAFS spectroscopy [2]. By comparing the “true” distance of specific atomic pairs, obtained fitting the XAFS signals, with the “apparent” one, measured by diffractometric means (neutron and/or X-ray Bragg diffraction) it is possible to extract the transverse Mean Square Relative Displacement (MSRD). This, together with the longitudinal MSRD that can be also estimated by the EXAFS analysis, allows a study of the anisotropy of the thermal vibrations and in particular its correlation with thermal expansion among a family of materials. In this work, we considered in this sense relevant examples ranging over the promising methods of tuning thermal expansion previously mentioned. Prussian blue analogues (with formula  $MM'(CN)_6$ ) are compounds in which the M-C and M'-N atomic pairs display significantly different roles in the contribution to anomalous thermal expansion, as exemplified by the effect of intercalation with water molecules on  $TiCo(CN)_6$  [3]. Crystal structure and thermal expansion properties of copper pyrophosphate analogues of the type  $A_2M_2O_7$ ,  $A=Zn,Cu$ ,  $M=V,P$  and solid mixtures thereof strongly depend on the stoichiometry of the sample [4-6], while zirconium alloys of the type  $Zr_2M$  (with M transition metal) have been recently recognized to display an anomalous uniaxial thermal expansion strongly dependent on the transition metal employed [7]: despite the challenging nature of the complicated local structures, in both cases the EXAFS analysis can still provide precious information regarding the mechanism underlying the anomalous thermal expansion. Molecular dynamics simulations have also been performed to elucidate how the phononic contribution to thermal expansion changes upon nanostructuring in the simple yet non-trivial case of spherical gold nanoparticles.

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## Tailoring negative thermal expansion via tunable induced strain in La–Fe–Si-based multifunctional material

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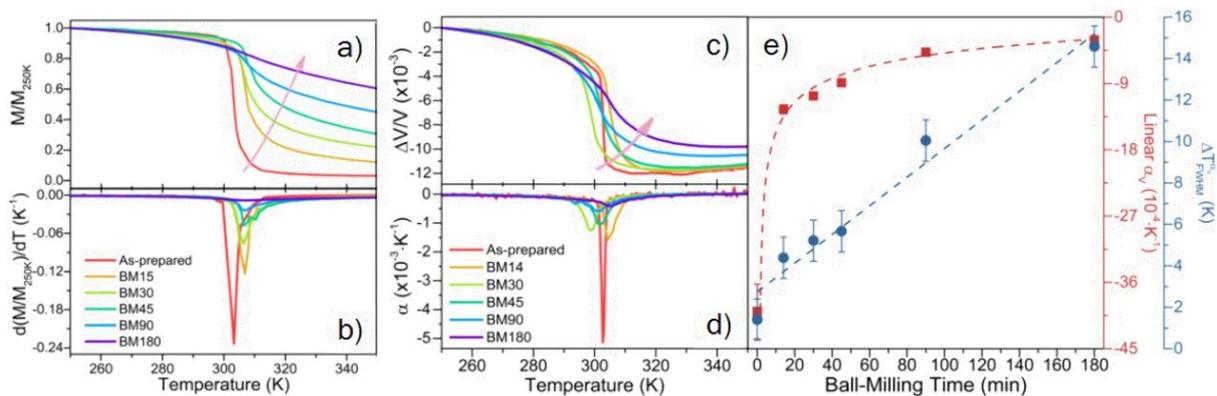
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The La(Fe,Si)<sub>13</sub> are multifunctional materials with remarkable properties, such as giant magnetocaloric effect and giant negative thermal expansion (NTE) at room-temperature, being these properties linked via strong magnetovolume coupling [1,2]. These materials present very sharp magnetic and volume variations across first-order phase transitions, which makes them unsuitable for near-zero thermal expansion (ZTE) applications that undergo thousands of cyclic thermal changes. In this work, a novel method to tune the NTE of materials is presented as an alternative to other strategies [3], namely ball-milling. This method allows simultaneously to decrease particles, crystallite sizes and linearly increase crystal strain. The evolution of these parameters with  $t_{BM}$  broadens the LaFe<sub>11.9</sub>Mn<sub>0.27</sub>Si<sub>1.29</sub>H<sub>x</sub> transitions, resulting in increasingly smeared magnetic and volume transitions (Figure 1) and a drastic 85% reduction of the NTE peak value (for  $t_{BM} = 180$  min.). Hence, this work demonstrates that the control of microstructure parameters with ball-milling can optimize these materials towards ZTE applications.



**Figure 1:** a) Normalized magnetization, b) its corresponding derivative, c) relative volume variation, d) its corresponding derivative ( $\alpha_V$ ) for the samples as-prepared, and ball-milled for 0, 15, 30, 45, 90 and 180 minutes. e) Evolution of  $T_c$  distribution width and linear  $\alpha_V$  (red squares) analyzed in the  $\Delta T_{FWHM}$ , for all samples.

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## High-quality zirconium vanadate samples for negative thermal expansion analysis

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Zirconium vanadate ( $\text{ZrV}_2\text{O}_7$ ) is a well-known negative thermal expansion (NTE) material which exhibits significant isotropic contraction over a broad temperature range ( $\sim 150^\circ\text{C} < T < 800^\circ\text{C}$ ). The linear thermal expansion coefficient of  $\text{ZrV}_2\text{O}_7$  is  $-7.1 \times 10^{-6} \text{ K}^{-1}$  [1]. Therefore, it can be used to create composites with controllable expansion coefficients and prevent destruction by thermal shock [2].

Material characterization, leading to application, requires pure, homogenous samples of high crystallinity via a reliable synthesis route. While there is a selection of described syntheses in the literature, it still needs to be addressed which synthesis route leads to truly pure and homogenous samples. Here, we study the influence of the synthesis methods (solid-state, sol-gel, solvothermal) and their parameters on the sample's purity, crystallinity, and homogeneity. The reproducibility of results and data obtained with scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry, and thermogravimetric analysis (DSC/TGA) were analyzed extensively. The sol-gel method proves superior to the solid-state method and produces higher-quality samples over varying parameters. Sample purity also plays an important role in NTE micro and macro-scale characterizations that explain the impact of porosity versus structural changes.

Moreover, we implement *ab-initio*-based vibrational computations with partially treated anharmonicity (quasi-harmonic approximation [3], temperature-dependent effective harmonic potentials [4]) in combination with experimental methods to follow and rationalize the negative thermal expansion in this material, including the influence of the local structure disorder, microstructure, and defects. Khosrovani et al. [5] and Korthuis et al. [6], in a series of diffraction experiments, attributed the thermal contraction of  $\text{ZrV}_2\text{O}_7$  to the transverse thermal motion of oxygen atoms in V-O-V linkages. In addition to previous explanations, we hypothesize that local disorder develops in  $\text{ZrV}_2\text{O}_7$  crystals during heating.

We are working on the experimental  $\text{ZrV}_2\text{O}_7$  development and discuss difficulties one might face in the process as well as high-quality sample significance in further investigation. The obtained samples are currently used in the ongoing research of structure analysis and the negative thermal expansion mechanism.

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## EosFit: a tool for fitting thermal expansion data and phase transitions

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EosFit is a freeware software suite for calculations involving both thermal expansion and equations of state, available at [www.rossangel.net](http://www.rossangel.net) and [www.mineralogylab.com](http://www.mineralogylab.com). EosFit7-GUI [1] is a full graphical user interface designed to simplify the analysis of thermal expansion and equations of state (EoSs). The software allows users to easily perform least-squares fitting of EoS parameters to diffraction data collected as a function of varying pressure, temperature or both. It has been especially designed to allow rapid graphical evaluation of both parametric data and the EoS fitted to the data, making it useful both for data analysis and for teaching. The EosFit7c console program [2] is our development platform and includes many advanced features not available in the GUI, including the fitting of phase transition data with Landau-type models and simultaneous fitting of both diffraction and elasticity data. Data from NTE materials can be fitted with one of the many polynomial expansions used in the literature, or with thermal-pressure EoS based on models for the phonon density of states, such as Mie-Grünesien-Debye, Einstein oscillators, Kieffer acoustic modes, or combinations of these.

Both programs run under Windows, Mac-OSX and Linux. Further programs are available to perform various calculations with EoS. The EosFit program suite is built on a publicly available Fortran subroutine library CrysFML [3] allowing other researchers to develop their own programs, including web applications [e.g. 4].

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## **Spatial modulation and thermal-induced spin phase transition on the negative thermal expansion of $\text{ScF}_3$ with metal dopants**

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Negative thermal expansion (NTE) is an intriguing physical property of solids, which is often related to the lattice, phonons, charges, and spin. However, most of the studies are mainly focused on the phonons, and the spin-related mechanism in open framework compounds remains unclear owing to the lack of more experimental pieces of evidence. Here, based on the first-principles calculations combined with the quasi-harmonic approximation, we carried out studies of the NTE properties of  $\text{ScF}_3$  with metal dopants to reveal the roles in NTE of both the spatial effects and spin states. For most of the dopants, the NTE coefficient decreases with the decrease of ionic radius, obeying a linear scaling relationship. Interestingly, for magnetic impurities with a spin phase transition from a high spin state to a low spin state, we show that they will exhibit a Jahn–Teller distortion behavior and enhance the longitudinal vibration mode. In turn, the longitudinal vibration mode has a large positive Grüneisen parameter, which can offset the NTE obviously. This work not only proposes a new insight into the NTE mechanism about impurities in  $\text{ScF}_3$  but also provides an approach to tailor the NTE properties for fluorides with magnetic impurities as well as oxides.

## Metal oxyfluorides: a new area for novel, tunable NTE materials

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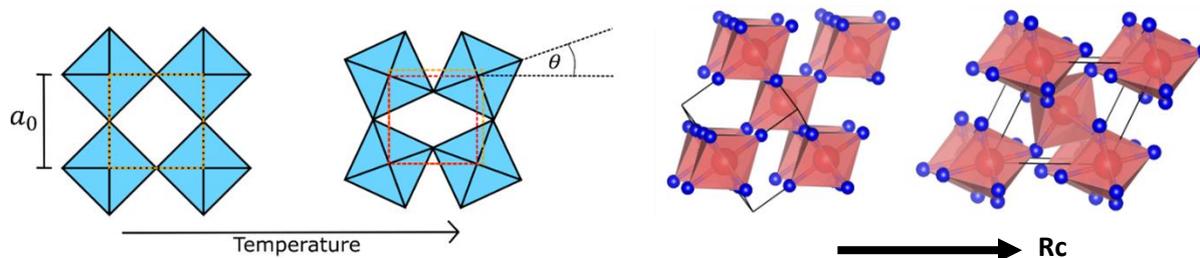
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The role of rigid unit modes (RUMs) in negative thermal expansion (NTE) materials is frequently explained by the simple  $\text{ReO}_3$ -type structure consisting of corner-sharing octahedra (Fig. 1).  $\text{ScF}_3$ , however, is the only  $\text{ReO}_3$ -type structure to exhibit NTE over a broad temperature range.[1] Other trifluoride structures, with less electropositive cations, have a tendency to collapse into a rhombohedral ( $R\bar{3}c$ ) structure.[2] This octahedral-tilting phase transition occurs under decreasing temperature or increasing pressure and leads to strong positive thermal expansion.

In order to overcome this issue, we have explored the effect of substituting oxide with fluoride anions on the cubic to rhombohedral phase transition of  $\text{NbO}_{2-x}\text{F}_{1+x}$ , and have found that the cubic ( $Pm\bar{3}m$ ) structure can be stabilized by the addition of fluoride.[3] Oxide linkages also appear to be less flexible than fluoride linkages which indicates that increasing fluoride content is beneficial for NTE. This accounts for the observed difference in NTE properties of  $\text{ReO}_3$  and  $\text{ScF}_3$ . [4, 5] In addition, increasing the oxygen content of  $\text{NbO}_{2-x}\text{F}_{1+x}$  causes it to be less air sensitive and simpler to synthesise, giving oxyfluorides an advantage over single anion fluoride materials.

Metal oxyfluorides present a novel solution to many of the issues with both oxide and fluoride NTE materials but to date no oxyfluoride NTE material has been identified and the effects of mixed-anions on thermal expansion have been under-explored.  $\text{NbO}_{2-x}\text{F}_{1+x}$  is an ideal material to expand our understanding of anionic effects as anions have a significant impact on thermal expansion through tuning of bond flexibility and structural stability. We believe this work will drive forward a new area of novel, tunable NTE oxyfluorides.



**Figure 1.** (a) a 2D representation of the rigid unit mode model of negative thermal expansion. (b) the cubic to rhombohedral phase transition observed in metal trifluorides.

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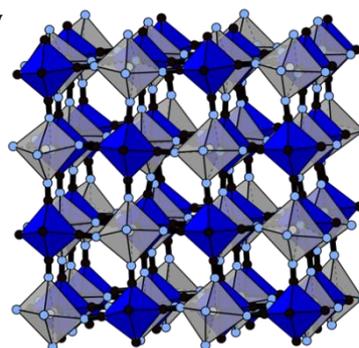
## Local structure of NTE Prussian blue analogues

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Negative thermal expansion (NTE) has been identified in several cyanide-based molecular framework materials, including in the Prussian blue analogues (PBAs) [1-4]. The parent structure of PBAs is a cubic net assembled from transition-metal ions at the octahedral nodes, connected by linear M–CN–M linkages. The NTE mechanism in PBAs is usually described in terms of thermal population of transverse vibrations of M–CN–M linkers coupled to rotations of the transition-metal coordination octahedra [1-3]. Relatively recently, an alternative mechanism involving correlated translations of columns and sheets of linked octahedra was also proposed [5].



In order to provide experimental insight into the NTE mechanism, we have carried out X-ray pair distribution function (PDF) measurements, which are sensitive to local fluctuations, including correlated thermal motion. Analysis of PDF data is particularly tricky for PBA materials, and this talk will summarise some of the key challenges involved. The newly-developed ‘big-box’ approach we have taken allows also the calculation of single-crystal diffuse scattering, which can be compared directly against experiment. Our analysis provides the first microscopic insight into thermal fluctuations in PBA materials and is helping resolve our understanding of NTE in these canonical systems.

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## Magnetic ordering dominated giant negative thermal expansion in Fe-doped MnNiGe compounds

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The intrinsic positive thermal expansion (PTE) properties of conventional materials can seriously affect the performance of some precise devices or instruments, such as printed circuit boards, optical fiber reflective grating devices, and high-precision optical mirrors. The undesired PTE behavior can be effectively modified by mixing with a negative thermal expansion (NTE) material. Therefore, NTE has emerged as one of the intense research topics to meet the demands of precision industry. The adjustment of NTE behavior, which includes the amplitude and the temperature region of NTE, becomes the key of NTE research. Currently, the NTE behavior can be effectively tuned by chemical modification and particle size effect<sup>[1]</sup>. However, the amplitude and temperature region of NTE is normally limited by the crystallographic contribution whatever the dominated mechanism is phonon induced type, such as tension effect, or electronic transition induced one, such as magnetic, ferroelectric, or charge order.

It has been reported that the martensite of the stoichiometric MnNiGe displays spiral antiferromagnetic (AFM) structure, and the substitution of Mn with Fe can introduce ferromagnetic (FM) coupling in Fe–6Mn configurations<sup>[2]</sup>, which would disintegrate the intrinsic AFM coupling. The neutron powder diffraction (NPD) studies reveal that the Fe-doped MnNiGe displays a cone-spiral incommensurate magnetic structure. And the first-principles calculations results indicate that the cone-spiral magnetic state is more stable than the spiral AFM (showing an energy gain of 0.8 meV/f.u.) in the present Mn<sub>0.87</sub>Fe<sub>0.13</sub>NiGe, which is consistent with the NPD results. More importantly, we found that, due to the distinct magnetic coupling, the MnCoGe<sub>0.99</sub>In<sub>0.01</sub> with linear FM structure<sup>[3]</sup> shows a lattice distortion about 7.49%, smaller than those of Mn<sub>0.87</sub>Fe<sub>0.13</sub>NiGe (8.68%) by 12% in average. By utilizing the magnetic structure controlled lattice distortion, giant NTE is achieved in Fe-doped MnNiGe. The maximal linear expansion reaches  $\Delta L/L \sim -23690 \times 10^{-6}$  in a wide temperature window of 195K (80-275K)<sup>[4]</sup>, which exceeds the performance of almost all other NTE materials reported to date. This work paves a new way for exploring NTE materials, which is of great significance for developing novel NTE materials to meet various desires in modern industries.

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## Strong negative thermal expansion induced by magnetic field in $\text{La}(\text{Fe},\text{Al})_{13}$

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The control of thermal expansion in materials is of great importance for various applications, and negative thermal expansion (NTE) has emerged as a promising strategy in this regard. [1,2] However, the discovery of strong NTE materials, which is rare, remains challenging. In this study, a strong NTE ( $\alpha_1 = -14.01 \times 10^{-6} \text{ K}^{-1}$ ) has been achieved in  $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$  by a new method of loading magnetic field, which is different from the conventional method of chemical modification. The strong NTE of  $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$  originates from the enhanced ferromagnetic (FM) component induced by the magnetic field-driven spin-moment rotation of the canting structure, which has been revealed by the magnetic field and temperature dependence of neutron powder diffraction and small-angle neutron scattering. Furthermore, the hidden short-range FM order facilitates a wider NTE temperature range in  $\text{La}(\text{Fe}_{11.5}\text{Al}_{1.5})$ . [3] This study provides the possibility that an external environment, such as a magnetic field, can be an effective approach to control or achieve strong NTE in functional materials.

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## Enhanced thermoelectric performance and low thermal conductivity in $\text{Cu}_2\text{GeTe}_3$ with identified localized symmetry breakdown

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Highly efficient and eco-friendly thermoelectric generators rely on low-cost and non-toxic semiconductors with high symmetry and ultralow lattice thermal conductivity  $\kappa_L$ . We report the rational synthesis of the novel cubic (Ag, Se)-doped  $\text{Cu}_2\text{GeTe}_3$  semiconductors. A localized symmetry breakdown (LSB) was found in the composition of  $\text{Cu}_{1.9}\text{Ag}_{0.1}\text{GeTe}_{1.5}\text{Se}_{1.5}$  (i.e., CAGTS15) with an ultralow  $\kappa_L$  of 0.37 W/mK at 723 K, the lowest value outperforming all  $\text{Cu}_2\text{GeCh}_3$  (Ch = S, Se, and Te). A joint investigation of synchrotron X-ray techniques identifies the LSB embedded into the cubic CAGTS15 host matrix. This LSB is an Ångström-scale orthorhombic symmetry unit, characteristic of multiple bond lengths, large anisotropic atomic displacements, and distinct local chemical coordination of anions. Computational results highlight that such an unusual orthorhombic symmetry demonstrates low-frequency phonon modes, which become softer and more predominant with increasing temperatures. This unconventional LSB promotes bond complexity and phonon scattering, highly beneficial for extraordinarily low lattice thermal conductivity.

## Apparent shrinkage of [PbX<sub>6</sub>] octahedra with increasing temperature and anharmonicity of the lead–halide bond in chlorine-substituted MAPbI<sub>3</sub>

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We report studies on three samples of chlorine-substituted MAPbI<sub>3</sub> using combined temperature-dependent synchrotron X-ray diffraction (XRD) and Pb L<sub>3</sub>-edge extended X-ray absorption fine structure (EXAFS) to analyse the bond expansion, tension effects and anharmonicity of the lead–halide bond.[1] From the results of the XRD and EXAFS analyses, the perpendicular MSR<sub>D</sub> was determined, allowing a comparison of the tension and bond expansion effects in the compounds studied. In the orthorhombic phase, the positive bond expansion and the negative tension effects of the lead-halide bond were approximately equal in all three samples. However, after the transition to the disordered tetragonal/cubic phase, the balance shifted in favour of the negative tension effects in MAPbI<sub>3</sub> and MAPbI<sub>2.94</sub>Cl<sub>0.06</sub>, but in MAPbCl<sub>3</sub> the positive bond expansion seemed to predominate towards higher temperatures. The negative tension effects observed by EXAFS in the tetragonal phase of MAPbI<sub>3</sub> and MAPbI<sub>2.94</sub>Cl<sub>0.06</sub> are correlated with the behaviour of the apparent shrinking [PbX<sub>6</sub>] octahedra observed by XRD. This correlation suggests that these two compositions have stiffer Pb–X bonds and that the [PbX<sub>6</sub>] octahedra are less rigid in the tetragonal phase.

The EXAFS parameters in the orthorhombic phase were described by an Einstein or T<sup>2</sup>-type behaviour, which was then compared with the experimental EXAFS parameters of the tetragonal/cubic phase. In the orthorhombic phase, it was observed that the asymmetry of the pair distribution function (cumulant C<sub>3</sub>) is much lower in MAPbCl<sub>3</sub> than in MAPbI<sub>3</sub>. Compared to the behaviour in the orthorhombic phase, the anharmonicity changed after the phase transition to the room temperature phase, with MAPbCl<sub>3</sub> showing an increase in anharmonicity and MAPbI<sub>3</sub> showing a decrease. The differences between MAPbI<sub>3</sub> and 2% chlorine substitution were small in both the orthorhombic and tetragonal phases.

By determining the structural parameters required to convert the effective force constants k<sub>0</sub> and k<sub>3</sub> obtained from the EXAFS analysis into the Morse potential parameters α and D, we found that our results are in agreement with other experimental results.

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## Lightweight and near-zero thermal expansion ZrW<sub>2</sub>O<sub>8</sub>-SiC<sub>nw</sub>/Al hybrid composites

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Negative thermal expansion particles can compensate metal matrix composites to achieve near-zero thermal expansion materials. However, there are huge thermal residual mismatch stresses in the particles due to the thermal expansion mismatch between matrix and reinforcement. The use of hybrid reinforcement is required to solve the stress concentration problem. In this study, the hybrid Al matrix composites reinforced with ZrW<sub>2</sub>O<sub>8</sub> and SiC reinforcements (SiC<sub>p</sub>, SiC<sub>nw</sub>) were fabricated by the pressure infiltration process. The effect of SiC content on microstructure, phase composition, thermal expansion and mechanical properties were examined by a combination of XRD, SEM, thermal dilatometer and bending tests. The results showed that the high-pressure phase ( $\gamma$ -ZrW<sub>2</sub>O<sub>8</sub>) content of hybrid metal matrix composites decreased with increasing SiC fraction. Among them, the composites containing 61.7 vol%ZrW<sub>2</sub>O<sub>8</sub> and 3.3vol%SiC<sub>nw</sub> achieved the best performance with a bending strength of 100–150 MPa and a near-zero thermal expansion ( $2.0\text{--}3.0\times 10^{-6}\text{K}^{-1}$ ) in a wide range of  $-50\text{--}120\text{ }^{\circ}\text{C}$ , which was attributed to the synergetic hybrid effects of SiC<sub>nw</sub> and ZrW<sub>2</sub>O<sub>8</sub>. This work opens up a new frontier for the design and preparation of lightweight zero-thermal expansion materials.

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## Developments of negative-thermal-expansion gate electrode formed from manganese nitride compound for transistor performance enhancement

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The sophisticated information society is supported by integrated circuits (ICs) composed of semiconductor devices. The performance of ICs has been improved by scaling semiconductor devices. In recent years, the technology node of semiconductor devices has reached 10 nm or less. The scaling of semiconductor devices has been performed by introducing various new materials. For instance, Cu interconnections have been used instead of Al interconnections from the 130 nm technology node. High-k gate dielectric and metal gate had been used from the 45 nm technology node. The scaling of semiconductor devices has been advanced due to the introduction of new material systems, as shown above. In this study, we proposed the field-effect transistor (FET) with negative thermal expansion (NTE) materials as a gate electrode to enhance the performance.

Tensile strain along the current direction can improve electron mobility in the FET channel. Therefore, various strain-introduction technologies have been developed as technology boosters [1,2]. However, the strain that existing technologies can introduce is becoming saturated. We proposed a structure that can introduce tensile strain into the channel by using an NTE material for the gate electrode of the FETs, as shown in Figure 1 [3,4]. The strain introduction technique with the gate electrode can be combined with other strain technologies, such as the stress liner. Therefore, it is possible to introduce further strain into the FET.

This study used a manganese nitride compound as a material for an NTE gate electrode. Manganese nitride compounds can exhibit large NTE characteristics near room temperature and a resistivity equivalent to polycrystalline silicon, commonly used as a gate electrode material [5]. Thus, manganese nitride compounds are promising materials as gate electrodes. First, we estimated the amount of strain that

can be introduced by a gate electrode using an NTE material by finite element method (FEM) simulation. FEM simulation results indicate that the NTE gate electrode can introduce a uniaxial tensile strain of 0.06% into the FET channel. Then, we fabricated the FETs with the NTE gate electrode. We observed that the NTE gate electrode could enhance electron mobility via the fabricated FETs with the NTE gate electrode. The NTE gate electrode structure is promising to enhance the performance of semiconductor devices.

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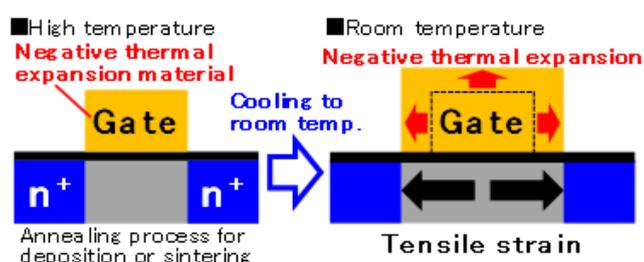


Fig. 1: Cross-sectional schematic illustration of the FET with the NTE gate electrode.

# Tunable negative thermal expansion in La(Fe, Si)<sub>13</sub>/resin composites with high mechanical property and long-term cycle stability

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Materials with tunable negative thermal expansion (NTE) are highly demanded in various functional devices. La(Fe, Si)<sub>13</sub>-based compounds are promising NTE materials due to their outstanding NTE properties[1]. However, their poor mechanical properties and related short service life restrict the practical applications[2]. In this work, epoxy resin with positive thermal expansion is used to synthesize La-Fe-Si/resin composites. The NTE of La-Fe-Si/resin composites can be manipulated by optimizing La-Fe-Si particle sizes and resin contents, and tailoring resin content could tune the NTE more effectively. The composites' average linear coefficient of thermal expansion decreases from  $-275.0 \times 10^{-6} \text{ K}^{-1}$  to  $-4.9 \times 10^{-6} \text{ K}^{-1}$  over the magnetic transition temperature range as the resin content increases from 3 wt.% to 80 wt.%. Additionally, zero thermal expansion is achieved in La-Fe-Si/resin composite with 20 wt.% resin. The resin would reinforce the binding force by filling the pores between the particles. The La-Fe-Si/resin composite with 80 wt.% resin exhibits a highly improved mechanical property, e.g., the compressive strength of 205 MPa is 75% higher than that of La-Fe-Si/resin composite with 3 wt.% resin. The obtained La-Fe-Si/resin composites can be machined into different shapes for practical applications, such as thin plates, strips, and rods. Furthermore, the La-Fe-Si/resin composites can undergo 1000 thermal cycles without NTE performance degradation and mechanical integrity loss, which means durable cycle stability. Hence, largely tunable NTE with high mechanical property and long-term cycle stability makes the La-Fe-Si/resin composites present great application potentials as NTE materials.

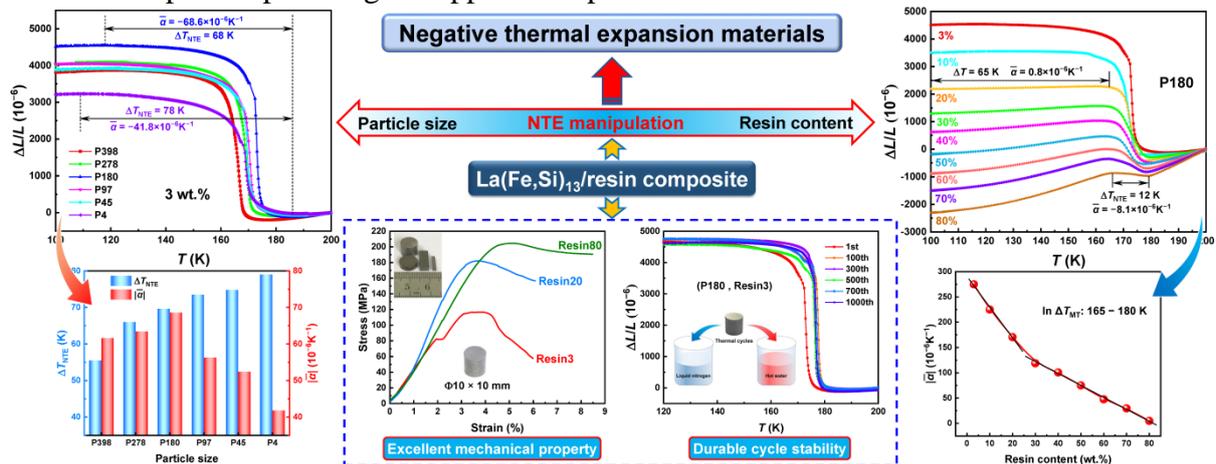


Fig. 1. Graphic Abstract: Tunable negative thermal expansion in La(Fe, Si)<sub>13</sub>/resin composites with high mechanical property and long-term cycle stability.

[1] R. J. Huang, Y. Y. Liu, W. Fan *et al.*, Journal of The American Chemical Society 135, 11469 (2013).

[2] Y. X. Wang, H. Zhang, E. K. Liu *et al.*, Advanced Electronic Materials 4, 1700636 (2018).

## Realization of ultra-low thermal expansion over a broad temperature interval in $(R,R')(\text{Fe,Co})_2$ compounds

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Zero thermal expansion (ZTE) materials, particularly metals, have important applications in precision manufacturing. Recently, the rare-earth-based magnetic phase transition material  $R\text{Co}_2$  ( $R$ =rare earth) with abnormal thermal expansion properties has attracted widespread attention[1-2]. Our previous research has shown that ultra-low thermal expansion over a significantly broadened temperature interval is realized by tuning Gd content in ferrimagnetic(FIM)  $\text{Gd}_x(\text{Dy}_{0.5}\text{Ho}_{0.5})_{1-x}\text{Co}_2$  compounds. The achieved coefficients of thermal expansion  $\alpha_1 \sim +1.3 \times 10^{-6}\text{K}^{-1}$  (5-220K),  $-1.5 \times 10^{-6}\text{K}^{-1}$  (220-280K) for  $x=0.5$  are even better than the well-known ZTE Invar alloy  $\text{Fe}_{0.65}\text{Ni}_{0.35}$ , while the operation temperature interval is much wider[1]. Here, we also obtained near zero expansion properties in  $R(\text{Fe}_x\text{Co}_{1-x})_2$  compounds over a wide temperature range by adjusting the Fe/Co ratio of compounds. The results show that with the increase of Fe content, the phase transition temperature shifts to higher temperature, and the nature of the first-order phase transition gradually weaken(Fig 1a).The XRD results indicate that the achieved coefficients of thermal expansion of the compound is  $\alpha_1 \sim +1.2 \times 10^{-7}\text{K}^{-1}$  (20-200K),  $-2.1 \times 10^{-6}\text{K}^{-1}$  (200-280K)(Fig 1b). For  $R\text{Co}_2$ , with the increase of temperature, the compound undergoes a structural transition from rhombohedral R-3m to cubic Fd-3m, accompanied by a magnetic phase transition from ferrimagnetic to paramagnetic. There are two Co sites(Co1:(0.5,0,0.5) and Co2:(0,0,0)) in the rhombohedral structure of compounds at low temperatures. Therefore, using the advantage of in situ variable temperature neutron diffraction technology for sensitive resolution of adjacent elements, we systematically studied the intrinsic relationship between the occupancy of Fe ions at the two Co sites in compounds with different Fe content and the crystal and magnetic structure phase transitions of the compounds(Fig 1c and 1d). The results show that Fe ions tend to occupy the Co1 site between the rare earth element layers, affecting the magnetic exchange of rare earth elements while changing the crystal field exchange of rare earth elements. That is, we obtain excellent performance of near zero expansion in a wide temperature range by changing the balance between magnetovolume effect and general anharmonic lattice vibration in the FIM region of the compound. This work highlights the advantageous ways to generate ultra-low thermal expansion in magnetocaloric materials.

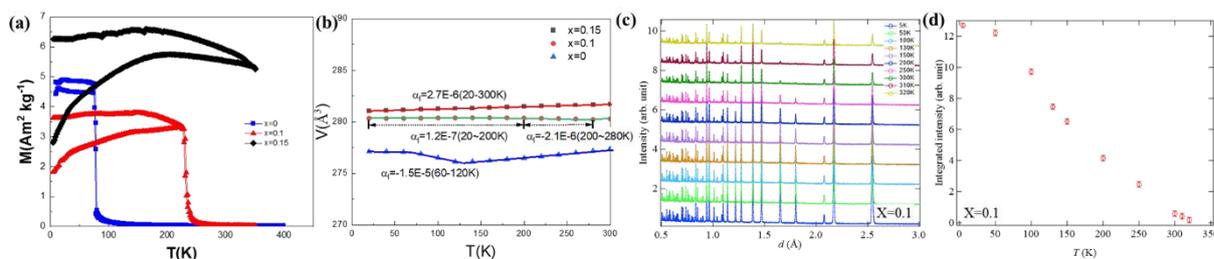


Fig. 1 (a) The thermomagnetic curve, (b) crystal volume vs temperature curves, (c) neutron diffraction patterns at different temperatures, and (d) (311) peak intensity vs temperature curve of  $R(\text{Fe}_x\text{Co}_{1-x})_2$  compounds.

[1] J.Z. Hao, F.X. Hu, L.H. He, J. R. Sun, B. G. Shen, *et al.*, *Scr. Mater.*, 185:181–186 (2020).

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## Optimizing thermal expansion in 3d-printed mortar

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The number of reports detailing negative thermal expansion (NTE) materials, which exhibit a contraction in response to heat and an expansion when cooled, has substantially risen over the past few years. These materials play a crucial role in the production of composites with zero thermal expansion (ZTE) when combined with the conventional positive thermal expansion (PTE) materials that have the opposite effect, and find practical application in various fields, including space telescopes, micro-electronic components, and dental fillings [1]. Moreover, NTE materials could potentially benefit the construction sector by optimizing the thermal expansion of mortars to minimize micro-fissures and cracks induced by natural cooling and heating cycles. As the development and optimization of ZTE composites for construction purposes is in a preliminary state, this work aims to fill the gap in the literature, while also improving the thermal behaviour of 3D printed structures [2].

Amongst the materials that exhibit isotropic NTE behaviour, this work has been focused on La-Fe-Si based materials. Tailoring their thermal expansion by tuning their particle size and strain via ball milling, as well as changing their chemical composition allows them to be used in room-temperature ZTE applications [3]. Complementary and considering lower-cost solutions, studies were also made with materials with low PTE, such as silica powder. All their properties were characterized using various methods, including Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD), and SQUID magnetometry. To optimize the ZTE of the composite, analytical and numerical [4] models were used to determine the optimal concentration and particle size of the compensator in the final composite, as well as the effects of its distribution in the composite's matrix.

Finally, the mechanical properties and thermal expansion of the final composites will be studied.

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[2] S. Pessoa *et al.*, *Renewable and Sustainable Energy Reviews*, 141, p. 110794 (2021).

[3] R. O. Fleming, S. Gonçalves, A. Davarpanah, I. Radulov, L. Pfeuffer, B. Beckmann, J. H. Belo *et al.*, *ACS Applied Materials & Interfaces*, 14(38), 43498-43507 (2022).

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## High-temperature zero thermal expansion in $\text{HfFe}_{2+\delta}$ from added ferromagnetic paths

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Deformation caused due to thermal expansion of a material at high temperature impairs the functioning of the device. Hence, high-temperature zero thermal expansion (ZTE) compounds are widely used in many high-precision devices. However, domination of magnetic behavior over thermal expansion of magnetic compounds makes it difficult to display ZTE at high temperatures. Herein, we report a high-temperature ZTE in Fe-rich  $\text{HfFe}_{2+\delta}$  compound, whose ZTE operating temperature could reach 583 K, the highest temperature reached by ZTE metal-based compounds. Synchrotron X-ray diffractometry, neutron powder diffractometry, Mössbauer spectroscopy, first-principles calculations, and macroscopic magnetic measurements revealed that the additional Fe atoms occupy the Hf sites and introduced extra ferromagnetic exchange interaction paths with the neighboring Fe atoms, thereby enhancing the magnetic transition temperature and the ZTE temperature region. Moreover, it was experimentally shown that the generation of ZTE by  $\text{HfFe}_{2.5}$  was due to the mutual cancellation of lattice shrinkage caused by the transformation of magnetic moments of Fe from ordered to disordered state and lattice expansion caused by lattice vibration. This study not only reports a high-temperature ZTE material, but also provides an unusual method to modulate the magnetic systems to obtain high-temperature ZTE compounds.[1]

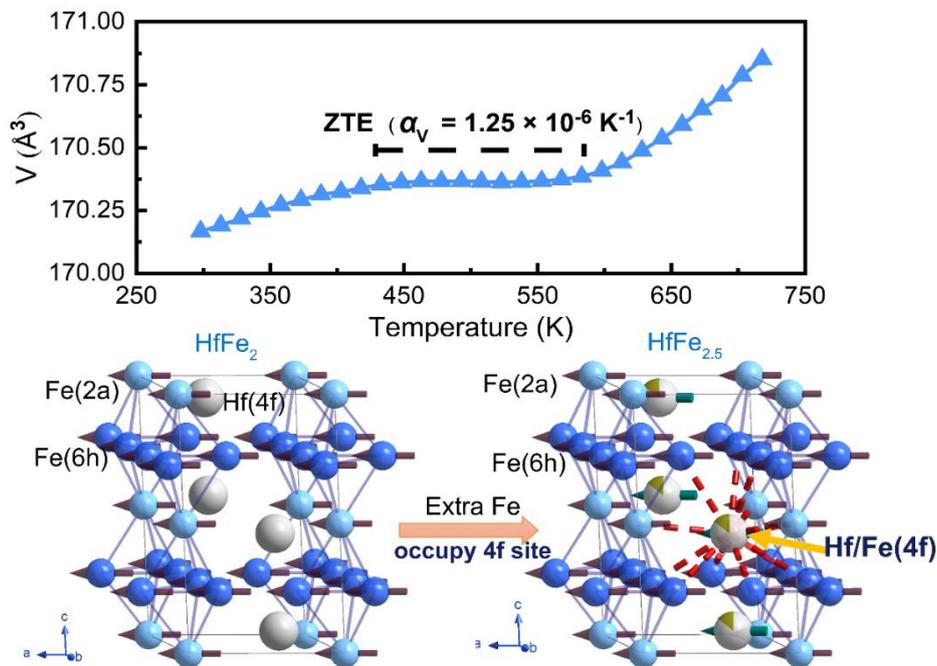


Figure 1. Temperature dependence of  $\text{HfFe}_{2.5}$ , and the magnetic structure of  $\text{HfFe}_{2+\delta}$ .

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## Unconventional magnetovolume effect induced negative thermal expansion

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Among the very rare negative thermal expansion materials, magnetic ones play a unique role due to their intriguing magnetic structure. Generally, they exhibit anomalous negative thermal expansion owing to the magnetovolume effect (MVE) according to the theory of MVE and magnetic NTE materials that has been reported [1]. However, here we introduce an unconventional MVE, which can induce a crossover from normal PTE of both ScFe<sub>2</sub> and TiFe<sub>2</sub> to NTE ((Sc<sub>0.4</sub>Ti<sub>0.6</sub>)Fe<sub>2</sub>,  $\alpha_V = -28.36 \times 10^{-6} \text{K}^{-1}$ , 125–205 K) and ZTE ((Sc<sub>0.55</sub>Ti<sub>0.45</sub>)Fe<sub>2</sub>,  $\alpha_V = 1.24 \times 10^{-6} \text{K}^{-1}$ , 10–250 K) in (Sc,Ti)Fe<sub>2</sub> solid solutions [2]. In such a case, almost no change happens in the direction order of the spin alignment, but in the magnitude of the magnetic spin, which can be regarded as an unconventional MVE because previous studies on MVE are all correlated to ferromagnetic-to-paramagnetic, ferromagnetic-to-antiferromagnetic or antiferromagnetic-to-paramagnetic transitions. The direct evidence of neutron powder diffraction and first-principles calculations discloses that the decrease of intrinsic magnetic moments at the Fe(2a) site results in the ferromagnetic transition from one to another, which causes a stronger negative contribution to thermal expansion than the conventional MVE. The pair distribution function analysis verifies that the decrease in the nearest distance of Fe(6h)–Fe(6h) lying in the ab plane results in the shrinkage of the a(b) axis. The analysis of anisotropic atomic displacement parameters excludes the phonon induced NTE mechanism. The present finding provides an approach to achieve NTE or controllable thermal expansion, which may be used to enhance other magnetic-related effects, such as the magnetocaloric and barocaloric effect.

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[2] Y Song, Q. Sun, M. Xu *et al.*, Mater. Horiz. 7, 275 (2020).

## Ultrastable optical cavities with natural and artificial zero thermal expansion

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Ultrastable optical cavities are essential in modern time, frequency, and length metrology, as well as precision laser spectroscopy and interferometry. One of the primary applications of these cavities is laser frequency stabilization, where the light wavelength is locked to the cavity length using the Pound-Drever-Hall technique. Typically, such cavities consist of mirrors and a spacer that fixes the distance between the mirrors. Developing reference cavities requires careful consideration of their sensitivity to temperature fluctuations. Our work focuses on ultrastable lasers based on two types of cavity materials: ultra-low expansion glass [1] and monocrystalline silicon [2,3]. These materials exhibit zero thermal expansion at room and cryogenic temperatures, respectively. By measuring the cavities' eigenfrequencies using lasers, we can determine the materials' thermal expansion coefficient with an uncertainty of  $10^{-9}$  K<sup>-1</sup> [4]. We will present such measurements for monocrystalline silicon.

In addition, we propose an alternative method of creating cavities with zero thermal expansion without relying on materials with this property. Composite Fabry-Perot and whispering-gallery-mode cavities are described in [5].

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- [4] M. G. Zahedi *et al.*, Conference on Lasers and Electro-Optics Europe & European Quantum Electronics Conference (CLEO/Europe-EQEC) 174117 (2019).
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## Strain-induced ferroelectric order in nanosized SrTiO<sub>3</sub>

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Ferroelectric order in nanostructures arouses interest in next-generation electronic devices applications.[1,2] However, the depolarization field at low-dimensional systems shields ferroelectricity[3] and maintaining ferroelectricity and inducing ferroelectric order in nanostructures is of great difficulty.

Herein, an intrinsic-strain-induced ferroelectric order in quantum paraelectric 0D freestanding SrTiO<sub>3</sub> nanoparticles (NPs) was achieved. By high-angle annular dark-field (HAADF) STEM images, atomic displacement vector mapping reveals that 2-4 nm polar nanoregions (PNRs) arrange ordered, connected end-to-end like fluid water and resulting in macroscopic polarization. Integrated differential phase-contrast (IDPC) STEM analysis proved the concurrence of antiferrodistortive and Ti atom displacement, which is the structure origin of SrTiO<sub>3</sub> NPs. Geometric phase analysis found that ferroelectricity and structure distortion were induced by intrinsic strain in three-direction restricted nanoparticles. The present work demonstrates a unique way to regulate ferroelectric order in nanostructures, expanding the family of functional materials for electronic device applications.

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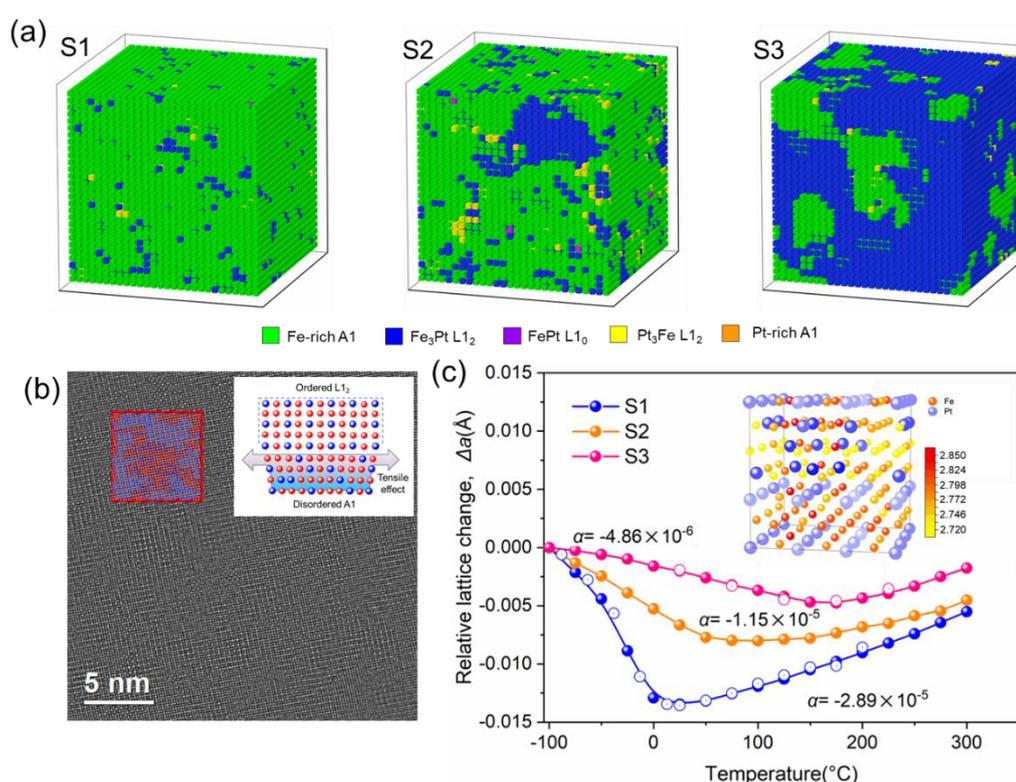
## Chemical order-disorder nanodomains in Fe<sub>3</sub>Pt bulk alloy

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Chemical ordering is a common phenomenon and highly correlated with the properties in solid materials. By means of the redistribution of atoms and chemical bonds, it invokes the effective lattice adjustment and tailors corresponding physical properties. To date, however, a direct probe to the 3D interfacial interactions of chemical ordering remains a big challenge. In this work, we deciphered the interlaced distribution of the nanosized domains with chemical order/disorder in Fe<sub>3</sub>Pt bulk alloy. HAADF-STEM images evidence the existence of such nanodomains. The reverse monte carlo method with the X-ray pair distribution function data reveal the 3D distribution of local structures and the tensile effect in the disordered domains at the single-atomic level. The chemical bonding around the domain boundary changes the bonding feature in the disordered side and reduces the local magnetic moment of Fe atoms. This results in a suppressed negative thermal expansion and its extended temperature range in Fe<sub>3</sub>Pt bulk alloy with nanodomains. Our study demonstrates an elaborate local revelation for the chemical order/disorder nanodomains in bulk alloy. The understanding gained from the atomic short-range interactions within the domain boundaries provides useful insights to design new functional compounds.



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## Negative thermal expansion induced in several graphene and graphyne analogues

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Materials which contract on heating (negative thermal expansion, NTE) are of significant interest for advanced applications. Graphene has shown NTE up to 1000 K, which motivates further improvements in two-dimensional carbon to attain superior performance. Very large negative thermal expansion coefficients are reported for tri-graphene (TrG) and T-graphene (TG), all carbon atoms having  $sp^2$  hybridization. Carbon atoms having both  $sp$  and  $sp^2$  hybridization i.e. graphynes (Gys) also show good NTE behavior. Also, they are very stable under very high temperatures. Quasi-harmonic approximation calculations show that  $\alpha_T$  remains negative until 4200 K and 2900 K for TrG and TG, respectively. Graphynes also show NTE even beyond 1000K. The effect of substitution in particular sites by other atoms is also studied along with their periodic trends. The high NTE for these systems is understood on the basis of the soft phonon modes, which induce inter-unit rotations, and ab-initio molecular dynamics simulations. The local distortions for the 3–12 rings (in TrG) and 4–8 rings (in TG) have structural resemblance with the rigid-unit modes that are usually envisioned for bulk systems.

S. Mondal and A. Datta, *J. Am. Chem. Soc.* 144, 16703 (2022).

## Structure, magnetism and low thermal expansion in $Tb_{1-x}Er_xCo_2Mn_y$ intermetallic compounds

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Cubic Laves phase  $RECo_2$  ( $RE =$  rare earth) have been studied intensively due to its relatively simple crystal structure and magnetic structure, and it is a class of magnetostrictive and magnetocaloric materials.<sup>1</sup> It is composed of two magnetic sublattices. One is the local magnetic moment of rare earths and the other Co sublattice has a long-range magnetic ordering induced by the molecular field of  $RE$  atoms.<sup>2</sup>

In this study, we obtain a series of different thermal expansion alloys  $Tb_{1-x}Er_xCo_2Mn_y$  ( $x = 0-0.5$ ,  $y = 0-0.4$ ) by double rare earth doping and the introduction of non-stoichiometric Mn elements. By varying the amount of Er or Mn, a low thermal expansion is achieved in  $Tb_{0.6}Er_{0.4}Co_2Mn_{0.1}$  (TECM,  $\alpha_1 = 1.23 \times 10^{-6} K^{-1}$ , 125~236 K). The macroscopic linear expansion and magnetic properties reveal that the anomalous thermal expansion is closely related to the magnetic phase transition. Synchrotron X-ray powder diffraction results show that TECM is a cubic phase (space group:  $Fd-3m$ ) at high temperatures and that a structural transition to a rhombohedral phase (space group:  $R-3m$ ) occurs as the temperature decreases. The  $c$ -axis expands with temperature, yielding the volumetric low thermal expansion. This study provides a new metallic and magnetic LTE material.

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## Quantified zero thermal expansion in the magnetic intermetallic $R_2Fe_{17}$ -based (R =rare earth) materials

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Zero thermal expansion (ZTE) has been a fascinating task over the last few decades due to its high scientific and practical merits. To realize ZTE, negative thermal expansion was usually tailored by chemical substitutions and tuning structure features. Here, we report on exploring quantification of thermal expansion with magnetic ordering in an intermetallic class of  $R_2Fe_{17}$  (R = rare earth), which can be employed to well identify the ZTE composition using a documented database. By joint investigations of magnetization and neutron powder diffraction, it is evidenced that the magnetic ordering of Fe-sublattice contributes to the thermal expansion anomaly. Alternative elements can be manipulated on Fe-sublattice to control both the total ordered magnetic moments of Fe-sublattice and Curie temperature, which tailors the temperature variation of the magnetic contributions on thermal expansion. The present study may indicate a perspective for high throughput ZTE searching, anticipated to benefit applications.

## **Strategies for obtaining negative/near zero thermal expansion materials with wide temperature range in antiperovskite compounds**

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In recent years, some magnetic metallic compounds have been found to exhibit negative thermal expansion (NTE) or nearly zero thermal expansion (NZTE) behaviors with great application prospects in aerospace, microelectronic devices, precision optical devices and other modern industries. However, it is a big challenge for applications because the responding temperature range for these compounds is not broad enough or far away from room temperature. The application requirement and the bottlenecks encountered during regulation of NTE/NZTE temperature range make it necessary to design the isotropic ZTE materials over a wide temperature range. As the typical NTE material, Mn-based anti-perovskites nitrides  $Mn_3AN$ , where A is usually a transition metal, possess the colossal magnitude of NTE due to magnetic order-driven volume constriction. In this work, the strategies are put forward to design the wide temperature range of NTE/NZTE behaviors in antiperovskite compounds. Firstly, we utilized a series of NTE components responding at several adjacent temperature ranges to realize the broadening effect. Then a concordant collaboration of multi-phase in thermal expansion could be achieved by an optimized volume fraction for every component and an apropos counteraction in the thermal expansion was realized at the whole connected temperature ranges. Secondly, high-performance ZTE materials were achieved by nanodomain coherent coupling between negative and positive thermal expansion phases based on microstructure design. Thirdly, we regulated the unique sluggish effect of phase transition by introducing large lattice distortion, which brings about effective relaxation of sharp phase transition and thus broadens the NTE temperature range. The obtained results demonstrated that the strategies are effective for broadening the operation temperature range of NTE/NZTE behaviors.

## Mechanism and control of negative thermal expansion in metal-based magnetic compounds

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Small shape changes caused by thermal expansion during solid heating may reduce its excellent performance. Thermal expansion coefficient mismatches have important effects on materials, aerospace, precision instruments, and other fields. Negative thermal expansion (NTE) has attracted widespread attention in basic research and application fields due to its unique advantages in compensating and controlling positive thermal expansion (PTE). The earliest research on NTE can be traced back to the discovery of magnetic invar alloys in 1897. Due to the complexity and variability of magnetism, the research on NTE magnetic compounds has a history of more than 120 years, but scientists' interest in the study of NTE has not diminished [1]. Here, a variety of new NTE magnetic systems have been discovered, and a variety of zero thermal expansion compounds with excellent performance have been obtained through chemical substitution methods. The mechanism of NTE induced by magnetic order-disorder transition and intrinsic magnetic moment reduction has been studied with the aid of advanced large scientific devices, covering almost all common magnetic transitions, such as FM-PM, FIM-PM, AFM-PM, FM-FM, Canting-PM, and short-range magnetic order transitions. A new method of magnetic phase coexistence and in-situ magnetic field for controlling the NTE of magnetic compounds has been developed. This study is conducive to deeply revealing the complex mechanism of magnetic NTE, developing and designing new compounds of NTE, and promoting their application in high-tech fields [2-8].

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- [8] Y. Song, J. Chen\* *et al.*, J. Phys. Chem. Lett. 11, 1954 (2020).

## Anomalous thermal expansion in metal-squarate frameworks

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Metal-organic frameworks (MOFs), as a new type of inorganic-organic hybrid crystalline materials, have attracted considerable interest not only owing to their diverse chemical properties but also some anomalous physical properties, such as negative thermal expansion (NTE). The squaric acid is a typical carboxylate ligand, which possesses a diverse coordination mode. The central four-membered aromatic ring endows the molecule with strong structural rigidity. Recently, we found that a series of metal-squarate frameworks (termed as M-sq) can exhibit anomalous thermal expansion. Intriguingly, the lattice vibration behavior is highly correlated with the coordination mode of squarate ligand, thus leading to different thermal expansion properties. For instance, in the  $\mu_4$ -connected Cd-sq, the squarate ligand can adopt either staggered or eclipsed packing mode, which possess volumetric zero thermal expansion (ZTE) and NTE, respectively.[1] In the planar  $\mu_5$ -connected Ca-sq, the squarate ligand tends to exhibit strong trampoline-like transverse vibration, giving rise to volumetric NTE.[2] Similarly, the planar  $\mu_5$ -connected Sr-sq can also exhibit transverse vibration, leading to the contraction of distance between bridged Sr atoms.[3] As for the  $\mu_3$ -connected Ag-sq, owing to the high  $D_{4h}$  molecular symmetry and low coordination number, the squarate ligand tends to rotate under thermal stimuli, resulting in the in-plane NTE[4]. However, for the  $\mu_8$ -connected Ba-sq or Pb-sq, the squarate ligand is tightly bonded by eight metal ions along all directions, which largely frustrate the vibration behaviors of the squarate ligand.[5]

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**DAY 2**

**6<sup>th</sup> July 2023**

## Understanding the mechanisms responsible for the anisotropic thermal expansion in $\text{Ca}_2\text{RuO}_4$ ruthenates through quantum mechanical calculations

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Thermal strains in functional materials can seriously impede their device applications. It is thus a technological imperative to minimize the thermal expansion of materials. Negative thermal expansion (NTE), a rare and interesting phenomenon observed in certain materials which contract upon heating, can be effectively harnessed to this end. Layered ruthenate  $\text{Ca}_2\text{RuO}_4$  is one such material endowed with this phenomenon. A giant NTE within a 200 K temperature window with a value of  $\alpha_L \sim -115 \times 10^{-6} / \text{K}$  of the linear coefficient of thermal expansion was reported in this system [1], and the phenomenon was attributed to the observed anisotropic thermal expansion of the system. Recent observations also lead to the possibility of tuning the thermal expansion of this system from a negative to a positive value by varying its oxygen content and chemical substitutions [1,2]. While these observations were attributed to the modulation in the Ru  $4d$  orbital ordering and rotation of the  $\text{RuO}_6$  octahedra as a function of temperature and chemical doping, the exact microscopic mechanisms responsible for anisotropic thermal expansion and the subsequent NTE behavior of  $\text{Ca}_2\text{RuO}_4$  and related systems remains unclear. The aim of the present work is to develop further insights in this direction by means of the first-principles density functional theory (DFT) calculations.

$\text{Ca}_2\text{RuO}_4$ , which crystallizes in a layered distorted  $\text{K}_2\text{NiF}_4$  structure [2,3] undergoes multiple phase transitions as a function of temperature with the metal-insulator transition below 357 K [4,5]. Formation of Ru  $4d$  orbital and antiferromagnetic orders were observed below 260 K and 110 K [6,7], respectively. In my presentation, I will elaborate upon the couplings between various order parameters and their impacts on the thermal expansion properties of this system. I will discuss the electronic and phononic contributions to the thermal expansion properties of  $\text{Ca}_2\text{RuO}_{4\pm\delta}$  in general. Our findings will expectedly contribute to the development of methods of systematic control of the thermal expansion properties of  $\text{Ca}_2\text{RuO}_4$  and to the search for new NTE materials within layered  $\text{K}_2\text{NiF}_4$  lattice framework.

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## Magnetic structure in Kagomé magnets and Invar phenomenon

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The Invar anomaly is a century-old enigma arising from isotropic spin-lattice coupling in face-centered cubic lattice. In this work, we extend the Invar behavior to Kagomé analogue with single magnetic element Fe by utilizing thermodynamic phase stability rather than by altering chemical composition. On transforming from hexagonal to cubic symmetry, the magnetic ordering changes from antiferromagnetic to ferromagnetic. Due to the resulting lifting of the interplanar magnetic frustration, magnetic ordering is enhanced which enables strong temperature-induced longitudinal spin fluctuations, leading to large magnetic compensation for lattice thermal expansion. Outcome from this work demonstrates the interplanar spin-lattice correlation in a cubic symmetry and will be essential to gain insight into the nature of Invar anomaly.

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## Charge/Orbital disordered states with smaller volume and higher entropy in transition-metal oxides

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In magnetic transition-metal oxides with charge or orbital degrees of freedom, magnetic ordering temperature is usually lower than the charge or orbital ordering temperature [1]. In the present work, we focus on charge/orbital disordered states in  $\text{Ca}_2\text{RuO}_4$ ,  $\text{BiNiO}_3$  and  $\text{V}_2\text{OPO}_4$  which show interesting interplay between magnetism and charge/orbital order. In the paramagnetic phase of  $\text{Ca}_2\text{RuO}_4$  with the Ru 4d orbital ordering, spin entropy tends to be suppressed due to the Ru 4d spin-orbit interaction [2]. Most of the spin and orbital entropy is released at the orbital melting transition temperature, which may help the negative thermal expansion (NTE) discovered in  $\text{Ca}_2\text{RuO}_4$  [3]. In NTE  $\text{BiNiO}_3$ , the  $\text{Ni}^{2+}$ -O- $\text{Ni}^{2+}$  superexchange interaction is enhanced due to the relatively small O-to-Ni charge-transfer energy (about 4 eV), and the magnetic order (or short range order) can survive until the Ni-to-Bi charge transfer transition under pressure or with chemical substitution [4]. Here the high temperature phase of  $\text{BiNiO}_3$  can be viewed as a charge disordered state of the ligand hole charge disproportionated  $\text{RNiO}_3$  ( $R$ =rare-earth) [5]. The charge degrees of freedom of the ligand hole may contribute to stabilizing the high temperature phase of  $\text{BiNiO}_3$ .  $\text{V}_2\text{OPO}_4$  exhibits NTE above the  $\text{V}^{2+}/\text{V}^{3+}$  charge ordering temperature [6]. Since the strong  $\text{V}^{2+}$ -O- $\text{V}^{3+}$  superexchange interaction stabilizes short range spin order in the face-sharing  $\text{VO}_6$  octahedra [7], most of the spin and orbital entropy is released above the charge melting transition, supporting the NTE.

The present work has been performed in collaboration with Prof. D. I. Khomskii, Prof. L. H. Tjeng, Prof. G. A. Sawatzky, Prof. M. Azuma, Prof. J. P. Attfield, Prof. S. Nakatsuji, Prof. Y. Maeno, and the members of their research groups.

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## Spin-orbital mechanisms for negative thermal expansion in $\text{Ca}_2\text{RuO}_4$

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The phenomenon of negative thermal expansion (NTE) deals with the increase of the lattice parameters and the volume of the unit cell when the material is thermally cooled. The NTE is typically associated with thermal phonons and anomalous spin-lattice coupling at low temperatures. However, the underlying mechanisms in the presence of strong electron correlations in multi-orbital systems are not yet fully established. We investigate the role of Coulomb interaction in the presence of lattice distortions in setting out the NTE effect, by focusing on the physical case of layered  $\text{Ca}_2\text{RuO}_4$  with  $d^4$  configuration at each Ru ion site. We employ the Slater-Koster parametrization to describe the electron-lattice coupling through the dependence of the  $d - p$  hybridization on the Ru-O-Ru bond angle. The evaluation of the minimum of the free energy at finite temperature by fully solving the multi-orbital many-body problem on finite size cluster allows us to identify the regime for which the system is prone to exhibit NTE effects. The analysis shows that the nature of the spin-orbital correlations is relevant to drive the reduction of the bond angle by cooling, and in turn the tendency towards a NTE. This is confirmed by the fact that a changeover of the electronic and orbital configuration from  $d^4$  to  $d^3$  by transition metal substitution is shown to favor the occurrence of NTE in  $\text{Ca}_2\text{RuO}_4$ . This finding is in agreement with the experimental observations of a NTE effect which is significantly dependent on the transition metal substitution in the  $\text{Ca}_2\text{RuO}_4$  compound.

## Magnetic-field-induced sign changes of thermal expansion in DyCrO<sub>4</sub>

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The anharmonicity of lattice vibration is mainly responsible for the coefficient of thermal expansion (CTE) of materials [1,2]. External stimuli, such as magnetic and electric fields, thus cannot effectively change the CTE, much less the sign variation from positive to negative or vice versa. Herein, we report significant magnetic field effects on the CTE of zircon- and scheelite-type DyCrO<sub>4</sub> prepared at ambient and high pressures, respectively [3]. At zero field, the zircon-type DyCrO<sub>4</sub> exhibits a negative CTE below the ferromagnetic-order temperature of 23 K. With increasing field up to  $\geq 1.0$  T, however, the sign of the CTE changes from negative to positive. In the scheelite phase, magnetic field can change the initially positive CTE to be negative with a field up to 2.0 T, and then a reentrant positive CTE is induced by enhanced fields  $\geq 3.5$  T. Both zircon and scheelite phases exhibit considerable magnetostrictive effects with the absolute values as high as  $\sim 800$  ppm at 2K and 10 T. The strong spin-lattice coupling is discussed to understand the unprecedented sign changes of the CTE caused by applying magnetic fields. The current DyCrO<sub>4</sub> provides the first example of field-induced sign change of thermal expansion, opening up a way to readily control the thermal expansion beyond the conventional chemical substitution.

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## Abundant negative thermal expansion in $A_2M_2O_7$ family

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Thermal expansion is a conventional phenomenon in solid materials, which seriously affects the performance and lifespan of facilities and devices. Negative thermal expansion (NTE) is an abnormal thermal behavior closely related to the coupling between phonons, charges, and crystal structures. A series of NTE materials were discovered in the  $A_2M_2O_7$  family. Represented by  $Cu_2P_2O_7$ , it exhibits strong NTE in 5K ~ 375K,  $\alpha_v \sim -27.69 \times 10^{-6} K^{-1}$ . Through chemical substitution, its NTE temperature range and thermal expansion coefficient can be effectively regulated. By replacing Cu with Zn, it can be adjusted from NTE to near zero expansion; By replacing V with P, the NTE temperature range can be greatly broadened. Especially, in  $Cu_2PVO_7$ , the  $\alpha_v \sim -26.0 \times 10^{-6} K^{-1}$  in the range of 100K to 650K. The direct experimental evidence revealed that the NTE property in these materials is induced by the transverse vibrations of oxygen atoms. Phase transition and microstructure effect also arouses giant NTE in the  $A_2M_2O_7$  family. An  $\alpha$  to  $\beta$  phase transition occurs in  $Zn_2P_2O_7$  and  $Co_2P_2O_7$  at around 473K and 563K, respectively, which induces lattice thermal contraction. Interesting, in the  $Zn_{1.96}Cu_{0.04}P_2O_7$  ceramic body, the linear contraction measured by dilatometry reaches to 0.9% ( $3\Delta L/L = 2.7\%$ ) when heated from -30 °C to 125 °C, while the intrinsic crystallographic volume contraction derived by X-ray diffraction is only 1.68%. A similar phenomenon is present in  $Co_{1.95}Zn_{0.05}P_2O_7$  as well. An apparent shrinkage of the voids in the ceramic body has been observed by in-situ atomic force microscope (AFM). Accordingly, the remarkable NTE enhancement in the ceramic sample is attributed to the microstructure effect.

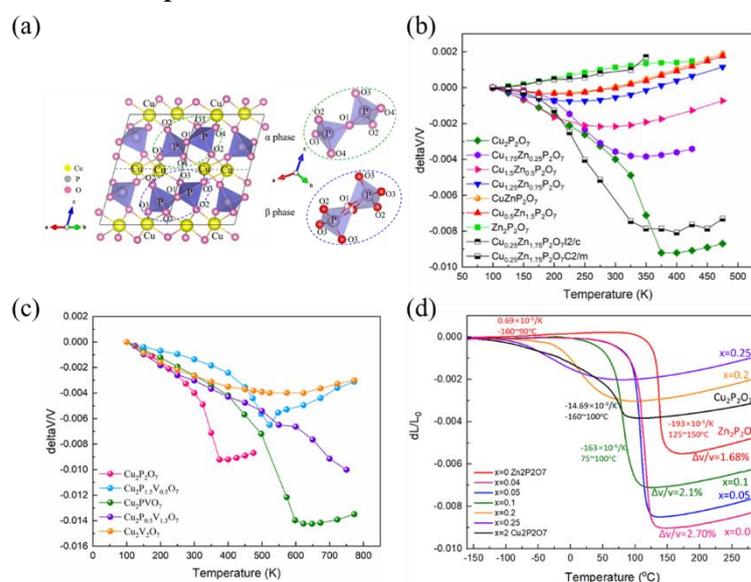


Fig.1 (a) Crystal structure of  $Cu_2P_2O_7$ . (b) Lattice thermal expansion of  $Cu_{2-x}Zn_xP_2O_7$ ; (c) Lattice thermal expansion of  $Cu_{2-x}P_{2-x}V_xO_7$ . (d) Linear thermal expansion of  $Zn_{2-x}Cu_xP_2O_7$ .

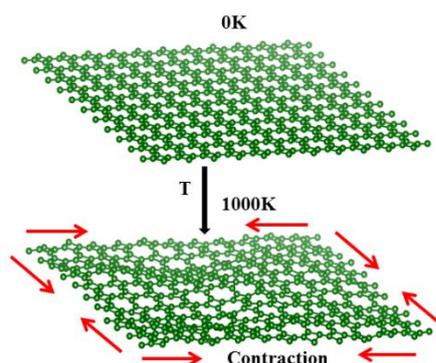
## Negative thermal expansion in two-dimensional monoatomically thin layers: T-graphene, Tri-graphene and Graphyne

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Materials which contract on heating (negative thermal expansion, NTE) are of significant interest for advanced applications. Graphene has shown NTE till 1000 K which motivates further improvements in two-dimensional carbon to attain superior performance [1,2]. Our calculations show a very large negative thermal expansion coefficient (TEC,  $\alpha_T$ ) for tri-graphene (TrG) and T-graphene (TG) both of them being allotropes for graphene. Quasi-harmonic approximation (QHA) calculations show that  $\alpha_T$  remains negative till 4200 K and 2900 K for TrG and TG respectively. The results are in agreement with NPT-ensemble average *ab-initio* molecular dynamics (AIMD) simulations. The high NTE for these systems is understood on the basis of the soft phonon modes which induce rotation of the 3-membered and the 4-membered rings in TrG and TG respectively. The local distortions for the 3-12 rings (in TrG) and 4-8 rings (TG) have structural resemblance with the rigid-unit modes (RUMs) that are usually envisioned for bulk systems.[3] Moving into more rigid systems like graphynes with  $sp^2$ - $sp$  and  $sp$ - $sp$  networks provide a control to chemically tune the NTE properties of 2D-carbon materials [4].



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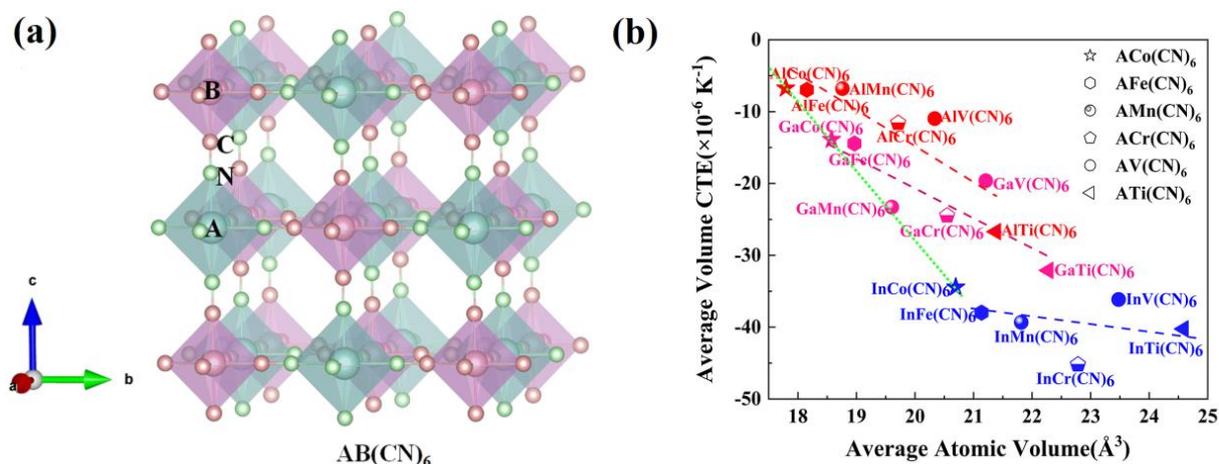
## Influence of A/B element substitution on negative thermal expansion in $AB(CN)_6$ (A=Al, Ga, In; B=Co, Fe, Mn, Cr, V, Ti)

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Negative thermal expansion (NTE) as abnormal physical behavior is promising in precision applications, but such materials are rare. It is important and valuable to hunt new NTE materials and to tune their NTE property [1]. Here, we report our recent work, in which the first principles calculation based on density functional theory (DFT) combined with the recently developed average atomic volume (AAV) [2] rule was adopted to predict the large isotropic NTE materials of Prussian blue analogues (PBAs)  $AB(CN)_6$  (A=Al, Ga, In; B=Co, Fe, Mn, Cr, V, Ti) in a wide temperature range. Our results showed clearly that the coefficient of the NTE of the PBAs has a near linear relationship with the AAV and is also influenced by the element substitution at A or B site. Lattice dynamic simulations indicate that the main contribution of the NTE comes from the low frequency transverse vibration of the  $-C\equiv N-$  groups, especially the transverse vibration of the N atoms. Thus, the element substitution at the A site can more effectively tune the NTE behavior of the systems than that at the B site, indicating the different roles of bonds on the NTE. Our present work not only expands the kinds of isotropic NTE materials, but also gives some insight into the relationship between AAV and NTE.



**Figure 1.** (a) The cubic structure of  $AB(CN)_6$  PBAs with  $AN_6$  and  $BC_6$  octahedrons. (b) The calculated average volume CTE vs. the AAVs of  $AB(CN)_6$  (A=Al, Ga, In; B=Co, Fe, Mn, Cr, V, Ti). The four dashed lines (green, red, pink, blue in colors) represent  $ACo(CN)_6$ ,  $AIB(CN)_6$ ,  $GaB(CN)_6$  and  $InB(CN)_6$ . A nearly linear relationship can be found between the average volume CTE and AAV for the systems.

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## Thermal vibration and expansion from the view point of local structure

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Thermal vibration and expansion of metal alloys and semiconductors were investigated from the viewpoint of local structure using the extended x-ray absorption fine structure (EXAFS) spectroscopic data and the path-integral effective classical potential (PIECP) Monte Carlo computational simulations, including negative and zero thermal expansion materials. EXAFS is believed to be the most suitable experimental technique to investigate local thermal vibration and expansion, because EXAFS is an element specific technique and provides detailed information on radial distribution function including asymmetry. On the other hand, the PIECP technique is a practical computational method that allows us to estimate quantum mechanical vibrational amplitude and thermal expansion with rather high accuracy. In this presentation, I will show several experimental/computational results such as FeNi Invar alloy, MnNi martensitic alloy, Elinvar alloy, CuZn brass alloy, and semiconductors with diamond structure like CdTe, studied by EXAFS and PIECP. Similarities and dissimilarities between local and macroscopic thermal expansion will be discussed. It is emphasized that the vibrational quantum effect is of great importance for the understanding of low-temperature thermal vibration, expansion, and elasticity.

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**NTE in diamond networks: from Si to Cd(CN)<sub>2</sub>**

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The diamond net has long been known to support phonon branches with negative Grüneisen parameters, with the corresponding modes reducing thermal expansion in diamond itself and even leading to NTE in cubic silicon at low temperatures [1]. There is an appealing geometric link between the energies of zone-boundary transverse acoustic (TA) modes and the Grüneisen parameter that is general to any system with the diamond structure. This relationship shows that the magnitude of NTE depends on the ratio of the stiffness of the bonds in the diamond net to the stiffness of the network angles [2].

The family of materials Zn<sub>1-x</sub>Cd<sub>x</sub>(CN)<sub>2</sub> have long been known to show exceptionally strong isotropic NTE [3,4], and this behaviour is usually rationalised in terms of correlated rotations of M(C/N)<sub>4</sub> tetrahedra that draw the structure in on itself [4,5]. Since the crystal structure of this family involves two interpenetrated diamond nets, we have sought to re-examine its NTE behaviour in terms of a mapping onto the parent diamond structure. This talk will focus on this mapping, showing explicitly how the dynamical behaviour of the cyanides is related to that of C and Si themselves. Exploiting the geometric relationship developed in [2] we are then able to rationalize the strong NTE behaviour of tetrahedral cyanide frameworks in new and very simple terms.

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**DAY 3**

**7<sup>th</sup> July 2023**

## Theory and parameter-free prediction of positive and negative derivatives of volume to temperature and their positive and negative divergences at critical points

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The stability criteria of a system require that the derivatives between conjugate variables in the combined law of thermodynamics must be positive except at the limit of stability where they become zero. However, there is no such requirement for derivatives between non-conjugate variables. The derivative of volume to temperature under constant pressure,  $\partial V/\partial T$ , is thus not required to be positive in a stable system because  $V$  and  $T$  are not conjugate variables. In many natural materials and human-made materials such as water and  $\text{Fe}_3\text{Pt}$ , the volume does decrease with the increase of temperature under certain conditions. While there have been many theories that aim to describe mechanisms in various materials, a fundamental understanding applicable to all materials is still lacking. Based on Maxwell relations, the derivative of  $V$  to  $T$  under constant pressure equals to the derivative of entropy to negative pressure under constant temperature, i.e.,  $\partial V/\partial T = \partial S/(\partial(-P))$ . Therefore, the fundamental understanding of the sign is related to the entropy of the system. While the total entropy of a system can be accurately obtained as a function of temperature from experimentally measured heat capacity, its pressure dependence is more difficult to comprehend, and its theoretical prediction remains elusive. Entropy of a system is counted theoretically by either statistical mechanics in terms of top-down Gibbs distribution or bottom-up quantum mechanics in terms of Fermi-Dirac and Bose Einstein distributions. Our newly termed zentropy theory integrates them into a nested formula from the electronic scale to the macroscopic scale of the system. In this presentation, the zentropy theory is introduced, and its parameter-free predictive capability is demonstrated through prediction of emergent behaviors in magnetic and ferroelectric materials including singularity and positive and negative divergences of  $\partial V/\partial T$  at critical points and the T-P regions where  $\partial V/\partial T$  is negative. It is articulated that the emergent behavior of a system originates from the statistical competition among stable and metastable configurations in the system. When the volumes of dominant metastable configurations are smaller than that of the stable configuration, the system will show negative divergences of  $\partial V/\partial T$  at its critical point if it has one. Negative values of  $\partial V/\partial T$  may thus be observed far away from the critical point when the volume reduction due to the increasing thermal populations of metastable configurations with smaller volumes and the decreasing thermal population of the stable configuration with large volume overpowers the volume increase of individual stable and metastable configurations [1].

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## Dual Kondo effect coupled charge ordering and zero thermal expansion in a correlated intermetallic YbPd

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In this work, we have investigated the electronic structure of YbPd, a strongly correlated f-electron metal which exhibits an incommensurate and commensurate charge-density wave (CDW) ordering below  $T_1 = 130$  K and  $T_2 = 105$  K, respectively. Bulk sensitive electron spectroscopy reveals temperature-independent single-Yb site mixed-valence in the cubic phase above  $T_1$ , and a clear temperature-dependent valence change of the two crystallographic Yb sites in the tetragonal CDW phase below  $T_1$ . The two Yb sites in the tetragonal phase exhibit a distinct/dual Kondo effect. Simplified single-impurity Anderson model calculations are developed to validate the dual Kondo effect coupled CDW changes and quantify site-dependent Kondo temperatures. The evolution of dual Kondo temperatures in the CDW phase tracks the lattice parameter changes, indicating a direct coupling to structural properties. The Kondo energy gain is shown to be the origin of the CDW transition which, in turn, leads to zero thermal expansion (ZTE). The ZTE arising from valency changes can be associated with the change in the radii of Yb ions and result in compensating the accompanying structural changes. The study indicates mixed valency of Yb ions is a viable method for developing room temperature intermetallic ZTE materials [1].

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## Novel aspects of orbital ordering in Ba-V-O with V triangular lattice

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Orbital degrees of freedom in degenerate d states can be coupled with the strain of lattice, leading to various fascinating phenomena in transition-metal oxides. Successive phase transitions that occur in BaV<sub>10</sub>O<sub>15</sub> with V quasi-triangular lattice are discussed from this perspective. In particular, we focus on the incommensurate structure arising from the orbital ordering of V t<sub>2g</sub> states, of which the period changes with temperature and is locked to three times the unit cell, as well as the phase transition from the incommensurate to the commensurate state [1]. Furthermore, we discuss the slow dynamics of such a phase transition in BaV<sub>10</sub>O<sub>15</sub>, which is caused by the nucleation-growth process of the phase transition associated with orbital ordering [2].

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## Strain soliton generation in negative thermal expansion materials

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Negative thermal expansion is an unusual physical effect which can be driven directly by phase transitions, or the associated fluctuations of structural motifs near structural instabilities. Here, we pose the following broad question: which physical processes show qualitative differences based on the reversal of the sign of thermal expansion coefficient? We will describe the important role that the CTE plays in generating dynamic strain textures following ultrafast heating by an absorbed femtosecond laser pulse. We will review the theoretical and experimental state of affairs on a particular light-in/sound-out process which results in launching of strain pulses in both the linear and nonlinear strain regimes. We find through computational solution of a nonlinear wave equation that NTE-generated strain pulses are qualitatively different from those of conventional materials, holding particularly high spatial frequency content as a precursor event to shock wave development. Finally, we will show our own efforts to produce solitons in NTE materials and suggest applications of the effect.

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## **Anharmonic lattice dynamics of materials containing diffusive constituents: a computational study based on the machine learning potential**

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Lattice dynamics are of great importance for understanding the different properties of materials. A complete experimental determination of lattice dynamics is challenging and often requires large-scale scientific research facilities. The theoretical study thus becomes paramount for a better understanding of the fundamental dynamics of materials. In this presentation, I will discuss phonon coupling mechanisms in emerging superionic materials for thermoelectric energy conversion applications. Because of the diffusive constituent atoms in these materials, we perform molecular dynamics simulations based on accurate first-principles machine learning potentials to study the lattice dynamical properties at high temperatures. By calculating the current correlation functions, our results suggest strong anisotropic phonon scattering in the superionic state. The thermal transport property of the superionic materials, including contributions from both conduction and convection, will also be thoroughly discussed in this presentation.

## Negative thermal expansion, entropic elasticity, and colossal softening in ScF<sub>3</sub>-type empty perovskites

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Recent analysis of neutron total diffraction measurement in ScF<sub>3</sub> [1], a material that shows large negative thermal expansion from zero temperature to nearly 1,000 K [2], reveals a structural motif where Sc-F bonds are the rigid units, while ScF<sub>6</sub> octahedra are not. This observation leads to a Coulomb Floppy Network (CFN) description [3] where the empty perovskite structure of ScF<sub>3</sub> is considered made of rigid, flexibly jointed Sc-F bonds. This structure forms a floppy network which resembles a three-dimensional version of the celebrated Flory model of a freely jointed polymer chain. In ScF<sub>3</sub> and other cubic empty perovskites, the stability of the floppy network is rendered by the combination of Coulomb forces between Sc and F ions and fluorine steric repulsion. The resulting CFN theory provides an accurate quantitative description of NTE, compressibility, and structural phase diagram, all in excellent agreement with experiment. The entropic stabilization of criticality explains the observed crystalline phases, while significant entropic contribution to elasticity accounts for the marked discrepancy between the *ab initio* calculated and the experimentally observed compressibility. The CFN theory is also in excellent agreement with the equation of state, V(P,T) of ScF<sub>3</sub> measured by neutron diffraction, and in particular, quantitatively explains pressure-induced colossal softening observed in this material [5].

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## Isotropic negative/zero thermal expansion in a broad temperature range in antiperovskite $Mn_3XN(C)$

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The antiperovskite  $Mn_3XN(C)$  (X: Zn, Sn, Ag, etc.) compounds display isotropic negative/zero thermal expansion (NTE/ZTE) properties in the wide temperature ranges. Herein we show the series of NTE/ZTE behaviors in  $Mn_3XN(C)$  compounds, which can be tunable and modified over a wide temperature range by elemental doping, substitution or introduction of vacancies. Some special kinds of non-collinear AFM structures play an important role for the NTE/ZTE effects, such as in  $Mn_3(Zn,Sn)C(N)$ . The origin of abnormal thermal expansion properties in the compounds is discussed based on the strong “spin-lattice” coupling supported by the neutron diffraction results [1-3].

The thermal expansion behaviors were changed from NZTE to PTE, and to NTE by gradual doping of C and N in the cubic body center of the lattice in  $Mn_3Zn_{0.5}Sn_{0.5}C_{1-x}N_x$ , which is corresponding to the different magnetic structures. ZTE behavior was induced by noncoplanar AFM in antiperovskite  $Mn_3Zn_{0.5}Sn_{0.5}C_{1.0}$  as a practical example of directly regulating the magnetic interaction integral  $|J_{FM}|/|J_{AFM}|$ . In combination with numerical calculations using the spin model, the magnetic interaction competition in a noncoplanar AFM ordered system is quantified within  $0.8 < |J_{FM}|/|J_{AFM}| < 1.0$  for producing ZTE behavior. Therefore, an effective regulation of thermal expansion behaviors from conventional PTE to ZTE can be achieved by tuning the magnetic ground state from FM to AFM in the antiperovskite system  $Mn_3Zn_{0.5}Sn_{0.5}C_{1-x}N_x$ .

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## Systematic charge distribution change in perovskite-type $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{MO}_3$ ( $M = 3d$ transition metal)

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Bismuth and lead are the main group elements but have charge degrees of freedom depending on their  $6s^0$  ( $\text{Bi}^{5+}$ ,  $\text{Pb}^{4+}$ ) and  $6s^2$  ( $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ ) electronic configurations. In the perovskite-type  $\text{BiMO}_3$  and  $\text{PbMO}_3$ , systematic changes in charge distribution are found to occur according to the  $M$ 's position in the periodic table because the energies of the  $6s$  orbitals of bismuth and lead are close to those of the  $3d$  orbitals of transition metals and the  $2p$  orbital of oxygen. The valences of  $M$  decrease as increasing  $M$ 's atomic numbers, i.e., as decreasing the energy of the  $3d$  orbital, while those of bismuth and lead increase to compensate for the decrease in the  $M$ 's valence [1]. Moreover, temperature- and pressure-induced charge transfer transition between transition metals and bismuth or lead are observed in these perovskite-type oxides, and  $\text{BiNiO}_3$  derivatives exhibit negative thermal expansion (NTE) owing to the shrinkage of the Ni-O bond by the charge transfer [2]. Recently, we focused on  $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{MO}_3$  with 1:1 mixture of bismuth and lead at the A-site of perovskite  $\text{ABO}_3$ . They are expected to possess more complicated crystal structures and charge distributions because both bismuth and lead have charge degrees of freedom. Therefore, a temperature-induced intermetallic charge transfer accompanied by NTE may also occur in  $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{MO}_3$ .

The polycrystalline samples were prepared by high pressure synthesis, and their crystal structures and charge distributions were investigated by comprehensive studies using synchrotron X-ray and neutron sources.  $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  has the  $\text{Bi}^{3+}_{0.5}\text{Pb}^{2+}_{0.5}\text{Mn}^{3+}_{0.5}\text{Mn}^{4+}_{0.5}\text{O}_3$  charge ordered state with CE-type spin and  $d_{z^2}$  orbital orderings, the same as in  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ , and both bismuth and lead have the  $6s^2$  electronic configurations [3]. In the case of  $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{FeO}_3$ , lead valence is disproportionated into  $2+$  and  $4+$  while bismuth remains trivalent, resulting in the  $\text{Bi}^{3+}_{0.5}\text{Pb}^{2+}_{0.25}\text{Pb}^{4+}_{0.25}\text{Fe}^{3+}\text{O}_3$  charge distribution [4]. Furthermore,  $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{CoO}_3$  shows incredibly complicated charge distribution with the triple charge separation of bismuth, lead and cobalt,  $\text{Bi}^{3+}_{0.25}\text{Bi}^{5+}_{0.25}\text{Pb}^{2+}_{0.25}\text{Pb}^{4+}_{0.25}\text{Co}^{2+}_{0.5}\text{Co}^{3+}_{0.5}\text{O}_3$ . Finally, in  $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{NiO}_3$ , lead valence changes to  $4+$ , resulting in the  $\text{Bi}^{3+}_{0.25}\text{Bi}^{5+}_{0.25}\text{Pb}^{4+}_{0.5}\text{Ni}^{2+}\text{O}_3$  charge distribution [5]. These results indicate that the valence of transition metal  $M$  in  $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{MO}_3$  changes from  $3.5+$  to  $3+$  to  $2.5+$  and finally to  $2+$  from Mn to Fe to Co and to Ni, from left to right in the periodic table as the  $3d$ -level becomes deeper, and lead starts to change from  $6s^2$  to  $6s^0$  before bismuth changes.

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## Exploring the mechanisms of negative thermal expansion in ScF<sub>3</sub>: a combined theoretical and experimental analysis

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This study investigates the negative thermal expansion (NTE) effect and ground state properties of cubic scandium trifluoride (ScF<sub>3</sub>) perovskite over a broad temperature range (10 K to 1600 K) using first-principles calculations, ab initio molecular dynamics (AIMD) simulations, diffraction, extended X-ray absorption fine-structure (EXAFS) spectroscopy, and infrared absorption experiments. The electronic structure of ScF<sub>3</sub> is determined by a linear combination of atomic orbital (LCAO) and plane wave projector augmented-wave (PAW) methods using modified hybrid exchange-correlation functionals within the density functional theory (DFT), with both methods showing good agreement with known experimental valence-band photoelectron and F 1s x-ray absorption spectra.

The temperature dependence of lattice constant, Sc-F-Sc bond angle distributions, Sc-F and Sc-Sc radial distribution functions, and infrared absorption spectra are obtained as a function of supercell size and analyzed using ab initio lattice dynamics simulations within and beyond the quasiharmonic approximation. The origin of NTE in ScF<sub>3</sub> is attributed to the interplay between the expansion and rotation of ScF<sub>6</sub> octahedra. Experimental Sc K-edge EXAFS data at 600 K are used to validate the accuracy of AIMD simulations, demonstrating that a supercell size larger than 2a×2a×2a is necessary to account for dynamic disorder accurately.

Temperature-dependent structural information extracted from the experimental EXAFS spectra is compared with AIMD results using the reverse Monte Carlo method coupled with an evolutionary algorithm. The study reveals that while the quasiharmonic approximation fails to reproduce the temperature dependence of infrared active bands, an approach beyond the quasiharmonic approximation, accounting for the NTE of the lattice and fluorine atom displacements due to strong F atoms vibrational motion perpendicular to the cubic axes, enables qualitative explanation of the temperature behavior of infrared spectra of ScF<sub>3</sub>. A comprehensive comparison of the results obtained by LCAO and PAW methods is also presented.

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## Spin dependent electronic transport properties of Mn-based antiperovskites

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Mn-based antiperovskite compounds with triangular magnetic lattice show a variety of magnetic structures accompanied by some fascinating physical properties, including a large magnetocaloric effect, giant magnetoresistance, giant barocaloric effect, baromagnetic effect, negative thermal expansion, and anomalous hall effect etc. Among them, face-centered magnetic atoms (such as Mn) and body-centered N (C) atoms can form NMn<sub>6</sub> or CMn<sub>6</sub> octahedra, and six magnetic atoms Mn are located at the six corners of the octahedron, which is prone to magnetic frustration. Thereby it generates the abounding magnetic structures. Here, we investigate the chiral spin states and their associated electronic transport properties in antiperovskite materials. For Mn<sub>3.33</sub>Ni<sub>0.67</sub>N, in addition to the  $\Gamma^{5g}$  triangular antiferromagnetic configuration, there is also a weaker ferromagnetic component perpendicular to the  $\Gamma^{5g}$  plane, which in turn shows non-zero scalar spin chirality values. By cooling with an external magnetic field, the ferromagnetic component is frozen, thereby realizing the manipulation of the chirality of the magnetic structure. Experimentally, we have discovered a vertical shift of the magnetization curve and to an asymmetrical magnetoresistance, and observed the chiral Hall effect. Our findings open interesting prospects for tailoring specific materials properties for the development of future chiral spintronic devices.

## **Zero thermal expansion and good optical transparency in the crystals with sodalite cage structures**

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Zero thermal expansion (ZTE) crystals can retain a constant size in a specified temperature range and have been applied in many scientific and technical fields where a high dimensional stability for resisting temperature change is required. The application prospect of the ZTE crystals can be significantly expanded if they also have good optical transparency, e.g. in visible region. In this talk, we summarize the recent progress of the studies on ZTE crystals with good optical transparency in our group. In particular, we focused on the crystals with sodalite cage ( $\beta$ -cage) structure, and several compounds with isotropic ZTE behaviors were designed and synthesized. This series has a very small coefficient of thermal expansion of  $\sim 1 \text{ MK}^{-1}$  from  $\sim 20 \text{ K}$  to  $\sim 300 \text{ K}$  and good optical transparency from  $\sim 230 \text{ nm}$  to  $3500 \text{ nm}$ , covering the ultraviolet, visible to near-infrared spectral region. Further molecular engineering design has been performed to expand the ZTE temperature range in this type of ZTE crystals.

## **Integration of negative, zero and positive linear thermal expansion enables light transmission in borate optical crystals to be temperature-independent**

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Optical path stability is a crucial parameter for the advanced optical apparatus operated in temperature-fluctuating conditions. Regardless of the invariant size, due to variable refractive index resulting from the dynamic lattice dynamics process, conventional zero thermal expansion (ZTE) materials cannot strictly keep the optical path unchanged as temperature varies. Here, we propose a method by taking use of the anisotropy of thermal expansion in non cubic single crystals, with maximal tunability from the integration of linear NTE, ZTE and positive thermal expansion (PTE). We demonstrate this concept in borate optical crystals of  $AEB_2O_4$  ( $AE = Ca$  or  $Sr$ ) to make the light transmission temperature-independent by counterbalancing the thermal expansion and thermo-optics coefficient. We further reveal that such a unique thermal expansion behavior in  $AEB_2O_4$  arises from the synergetic thermal excitation of bond stretching in ionic  $[AEO_8]$  and rotation between covalent  $[BO_3]$  groups. This work has significant implications for understanding the thermal excitation of lattice vibrations in crystals and promoting the functionalization of anomalous thermal expansion materials.

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## Data mining and machine learning of NTE materials from the ICSD

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We have identified the NTE materials reported in the Inorganic Crystal Structure Database (ICSD), using linear regression of the lattice constants of all crystal structures reported therein at multiple temperatures. This analysis identified many known NTE materials and us to classify these according to their chemistry and crystal symmetry. We then used the data to create a machine learning model which attempts to predict whether a material possesses NTE from its chemical composition, lattice vectors, and space group, in order to allow identification of potential NTE materials from Le Bail refinement of a powder diffraction pattern. Several potential materials were then screened by density functional theory calculations.

## Domain structure observation and design of phase transition-type negative thermal expansion materials

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Chemical substitution for the tuning of working temperature of phase-transition type negative thermal expansion (NTE) materials generally reduces the volume shrinkage during the transition. It was found that electron-doped  $\text{PbVO}_3$  undergoes a polar-to-nonpolar transition accompanied by a huge NTE. The parent compound,  $\text{PbVO}_3$ , has a tetragonal perovskite structure with a space group of  $P4mm$  and has a large  $c/a$  ratio of 1.23 due to the ordering of the  $d_{xy}$  orbital in addition to the stereo chemical activity of  $6s^2$  lone pair of  $\text{Pb}^{2+}$ . [1-3] We have investigated the effects of electron doping and reduction of  $6s^2$  lone-pair activity in  $\text{PbVO}_3$  and found that the combination of Bi and Sr substitutions for Pb enables a temperature induced polar to non-polar transition with 11% volume shrinkage, even larger than the pressure-induced volume collapse of  $\text{PbVO}_3$  (~10.6%), and is the largest value among the NTE materials reported so far. The domain structure of the coexisting cubic and tetragonal phases with such a huge volume difference in  $\text{Pb}_{0.82}\text{Sr}_{0.18}\text{VO}_3$  was successfully observed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and the spatial distribution of domains by Bragg coherent X-ray diffraction imaging (BCDI). The temperature hysteresis is reduced by repeated heating/cooling cycle, suggesting that the changes in domain structure dominate the NTE properties.

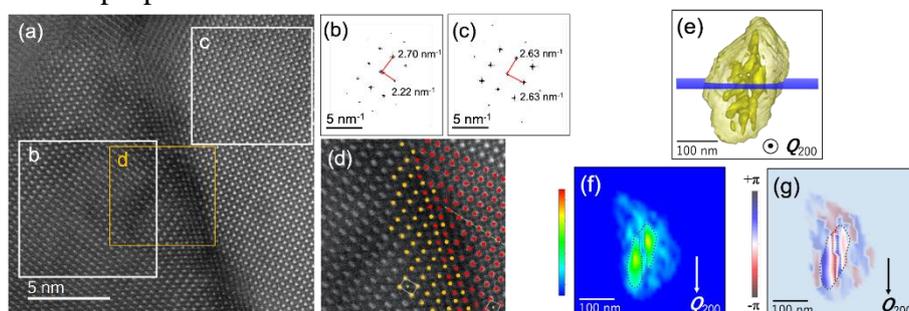


Fig. 1 (a-d) HAADF-STEM image of cubic-tetragonal boundary in  $\text{Pb}_{0.82}\text{Sr}_{0.18}\text{VO}_3$ . FFT image of (b) tetragonal and (c) cubic regions obtained from areas d and e in (a). (d) Magnified view of area d in (a) around phase boundary. (e-g) BCDI of  $\text{Pb}_{0.82}\text{Sr}_{0.18}\text{VO}_3$  sample (e) Reconstructed three-dimensional image of particle (f) Cubic 200 reflection density map in horizontal plane in (e). (g) Phase image of same plane in (e).

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## **Design of zero thermal expansion and high thermal conductivity in machinable xLFCS/Cu metal matrix composites**

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Materials with comprehensively good performances of zero thermal expansion (ZTE), high thermal conductivity, and machinability are in great demand for electronics, precision instruments, and aerospace applications. However, very few materials can meet such conditions, which remains challenging. In this study, a multicomponent negative thermal expansion (NTE) reinforcement is designed for metal matrix composites (MMCs) to achieve wide-temperature-range ZTE, high thermal conductivity, and certain machinability. Benefiting from the giant NTE in the system of  $\text{La}(\text{Fe},\text{Co},\text{Si})_{13}$ , its original narrow NTE temperature range can be broadened in the multicomponent material (xLFCS). When xLFCS is used for the reinforcement of MMCs to combine with copper, the thermal expansion coefficient of the xLFCS/39.7vol.%Cu composite can be adjusted to be nearly zero ( $-0.2 \times 10^{-6} \text{ K}^{-1}$ ) in a wide temperature range of 200-320 K. The thermal conductivity of the composite can reach  $44.1 \text{ W m}^{-1} \text{ K}^{-1}$ , which is about seven times as much as that of LFCS itself. In addition, compared with other ZTE metal-based materials, the present composite has a good machinability. This work provides a metal matrix composite with high thermophysical properties and proposes an easy-to-operate method to broaden the temperature range of NTE or ZTE.



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