The role of average atomic volume in predicting negative thermal expansion: The case of $REFe(CN)_6$

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Negative thermal expansion (NTE), as an abnormal physical behavior, has been followed by scientists' attention over the past 30 years, due to its fascinating physical mechanisms and the prospect of high-precision thermal expansion control [1–5]. Although some NTE materials (alloys [6], cyanides [7], fluorides [8–10], nitrides [11], oxides [12,13], MOFs [14–16], etc.) have been found, their number and variety are still very small, limiting their applications. Exploring and designing new NTE materials is an important and challenging topic for the development of the field of NTE. Researchers have been continually reviewing and summarizing obtained results to look to the future of NTE [17–23]. It is known that the NTE behavior in open-framework materials is related to the low-frequency phonons, while the NTE behavior in functional materials with magnetic or electronic transitions comes from the electronic structure, but it is still difficult for us to find new NTE materials. Interestingly, there has been some studies which tried to construct new NTE materials, for example fabricating microstructures in Ca_2RuO_4 systems to achieve colossal NTE [24], designing three-dimensional metamaterials to tailor the thermal expansion from negative to positive continuously [25] or exploiting the nanosizing effect in Au [26] or CuO [27] to obtain the NTE, even super NTE behavior. Hence, it is strongly necessary to develop or introduce new ways to explore NTE materials.

Recently, Gao *et al.* [28] proposed a new concept of average atomic volume (AAV) by summarizing the structural characteristics of isotropic framework NTE materials and successfully discovered the NTE material $AgB(CN)_4$. The concept of AAV is a simple parameter to indicate the average volume of atoms in a unit cell. In other words, it means that the unit volume is divided by the atom number in a lattice cell. The formula is $AAV = V/(Z \times N)$, where V is the unit cell volume, Z is the cell formula units, and N is the number of atoms in the chemical formula. Here, with the help of AAV, one could evaluate the thermal expansion behavior [28]. It should be noted that the number of anisotropic materials is much larger than that of isotropic ones. If we extend this concept to anisotropic materials, it will be possible to seek much more potential NTE

materials. Due to their flexible networking architecture, many cyanides/Prussian blue analogues (PBAs), such as $Zn(CN)_2$ [29], $ZnPt(CN)_6$ [30], $LaCo(CN)_6$ [31] and $ScCo(CN)_6$ [32], display a fascinating NTE behavior. Gao *et al.* [33] reported the large NTE behavior in $YFe(CN)_6$, whose AAV is $22.58 \text{ \AA}^3$, well above the critical point (assessed to $\sim 16 \text{ \AA}^3$ by Gao *et al.* [28]). The framework structure of isostructural materials with formula $REFe(CN)_6$ consists of REN_6 trigonal prisms alternating with FeC_6 octahedra, as shown in Fig. 1a. The values of AAV for $REFe(CN)_6$ materials range from $22 \text{ \AA}^3$ ($LuFe(CN)_6$) to $24.7 \text{ \AA}^3$ ($LaFe(CN)_6$), much larger than $16 \text{ \AA}^3$. It seems natural to us to ask whether the $REFe(CN)_6$ shows NTE behavior. Interestingly, the intrinsic thermal expansions of $REFe(CN)_6$ ($RE = La, Sm, Ho, Lu$), which were determined by synchrotron X-ray diffraction (SXRD) at Advanced Photon Source (APS) (Fig. 1b), show larger volume NTE behavior in the temperature range of 100–525 K than expected. One can clearly see that the negative coefficient of thermal expansion (CTE) has a linear relationship with the AAV, thus providing a way to predict the CTE of similar systems and also showing that they have similar NTE mechanism.

In order to investigate the NTE mechanism of $REFe(CN)_6$, we selected two representative NTE materials, $LaFe(CN)_6$ (strong NTE) and $LuFe(CN)_6$, to be studied from the lattice and local structure perspectives. Here, we combined temperature-dependent neutron powder diffraction (NPD) and extended X-ray absorption fine structure (EXAFS) data to extract information regarding thermal vibrations. The anisotropic atomic displacement parameter (ADP) is an important parameter to reflect the structural properties of crystals. Under the temperature field, the ADP could display the thermal ellipsoids of atoms, which reflects the information of thermal vibrations [34]. Here, the shape and size of displacement ellipsoids of the bridge CN atoms were extracted to reveal the vibrational information in the required directions. As shown in Fig. 2a, b, the bridge CN atoms show large anisotropy (the values of transverse ADPs in $LaFe(CN)_6$ (strong NTE) and $LuFe(CN)_6$ are many times larger than the longitudinal ones). As for other PBAs, the transverse ADPs of N atoms are much larger than those of C atoms. This

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Figure 1 (a) The structure of $REFe(CN)_6$ ($RE = La, Sm, Ho, Lu$), possessing hexagonal symmetry ($P6_3/mmc$) owing to the combination of REN_6 trigonal prisms alternating with FeC_6 octahedra; (b) the linear relationship between the volume CTE (experimental values from SXRD) and AAV for $REFe(CN)_6$.

Figure 2 The thermal vibrational information of $REFe(CN)_6$. Temperature dependence of ADPs of the N and C atoms derived from NPD in (a) $LaFe(CN)_6$ and (b) $LuFe(CN)_6$. (c) The true and apparent Lu–N and Fe–C bond lengths extracted, respectively, from EXAFS and NPD, (d) perpendicular ($\perp$) and parallel ($\parallel$) MSDs of Lu–N and Fe–C bonds in $LuFe(CN)_6$.

also suggests that the transverse thermal vibration of N and C atoms is the driving force for NTE in $REFe(CN)_6$. Compared with the value of ADPs between $LaFe(CN)_6$ (strong NTE) and $LuFe(CN)_6$, the transverse ADPs of CN atoms in strong NTE $LaFe(CN)_6$ are much larger than those in $LuFe(CN)_6$ (the detailed information of NPD structure refinements of $LaFe(CN)_6$ and $LuFe(CN)_6$ is shown in Fig. S1, Tables S1 and S2). This directly indicated the relevant difference between $LaFe(CN)_6$ (strong NTE) and $LuFe(CN)_6$ and also suggested that in same NTE systems with open-framework structure the larger the AAV, the larger the transverse ADPs of bridge atoms, and thus a stronger NTE. To further illustrate the local structure

vibrational information, we conducted the EXAFS experiment with variable temperature. Due to the energy of La L3-edge and Fe K-edge having partial overlapping, we collected only the EXAFS data of $LuFe(CN)_6$ (the detail experiments and data analysis information please see Figs S2–S5, Tables S3 and S4). Here, we adopted NPD measurements to extract the “apparent” bond lengths of Lu–N and Fe–C in $LuFe(CN)_6$ (Fig. 2c), which display contraction. The “true” bond lengths of Lu–N and Fe–C, which interestingly show PTE behavior, were determined from EXAFS (Fig. 2c). Such opposite thermal expansion behavior through similar experimental measurements is also observed in other NTE materials such as ZrW_2O_8 [35], $TiCo(CN)_6$ [36] and

$\text{Cu}_2\text{P}_2\text{O}_7$ [37]. In order to further study the thermal vibrations, we also extracted the atomic mean square relative displacements (MSRDs) [38] of Lu–N and Fe–C atomic pairs. The temperature dependence of Lu–N and Fe–C MSRDs shows that the perpendicular ones are both much larger than the parallel ones (Fig. 2d). As shown in Fig. S5, the anisotropy of thermal vibrations of Lu–N is much larger than that of the Fe–C ones. This indicates that the contribution to the NTE behavior of $\text{LuFe}(\text{CN})_6$ mainly originates from the Lu–N atom pairs, which is in good agreement with the result of ADPs.

To further investigate the NTE mechanism and reveal the reason for the differences in NTE among the $\text{REFe}(\text{CN})_6$ system, we selected $\text{LaFe}(\text{CN})_6$ (strong NTE) and $\text{LuFe}(\text{CN})_6$ as representative samples to obtain further lattice dynamics information by density functional theory (DFT) calculations. As shown in Fig. 3a, b, the phonon dispersion of C and N atoms shows that the vibrations of N atoms play a leading role below 200 cm^{-1} , and most vibrational modes in the low-frequency region have negative Grüneisen parameters (Fig. 3c, d). This indicates that the NTE driving force of $\text{REFe}(\text{CN})_6$ is the thermal vibration of C and N atoms in low-frequency modes. The insets in Fig. 3c, d show vibrational mode with the same transverse direction for N and C atoms, which has the largest negative Grüneisen parameters. These results also confirmed that the mode with the same transverse vibration direction for C and N atoms gives a contribution to NTE greater than the other modes in the PBA NTE system of materials. Interestingly, the frequency of this mode in the strong-NTE material $\text{LaFe}(\text{CN})_6$ is 49 cm^{-1} , which is lower than in the case of the NTE material $\text{LuFe}(\text{CN})_6$ (53 cm^{-1}).

Moreover, it should be noted that the number of low-frequency modes with negative Grüneisen parameters (≤ -5) for the strong-NTE $\text{LaFe}(\text{CN})_6$ is greater than that for $\text{LuFe}(\text{CN})_6$. These results confirm that the frequency and negative Grüneisen parameter of the thermal vibrations are the factors relevant to the difference in NTE behaviors in the $\text{REFe}(\text{CN})_6$ system.

Back to the concept of AAV, the discovery of NTE in the $\text{REFe}(\text{CN})_6$ system suggested that it is applicable to anisotropic materials. As shown in Fig. 4, it covers most classical NTE open-framework materials among oxides, fluorides, cyanides and PBAs (Table S5). One can clearly see that there seems to be a strong correlation between CTE and AAV, especially for the same type of materials. As the value of AAV increases, NTE enhances (Fig. 4). This is also corroborated by the relationship between thermal expansion and the length of the lattice parameter observed in Ref. [39]. In the case of $\text{REFe}(\text{CN})_6$, the larger the AAV, the larger the transverse ADPs of CN atoms, and thus a much stronger NTE appears. The DFT results for $\text{REFe}(\text{CN})_6$ indicated that the larger the AAV, the lower the frequency and the larger the value of negative Grüneisen parameter for the NTE contributing phonon modes. Hence, it not only provides one possible way to predict thermal expansion in inorganic open-framework materials, but also brings new insight into the design of super NTE materials, thus promoting further developments of NTE.

In summary, we have introduced the concept of AAV to predict the NTE of materials in the $\text{REFe}(\text{CN})_6$ system. A combined study of NPD, EXAFS and DFT results was performed to reveal the mechanism of thermal expansion. The $\text{REFe}(\text{CN})_6$

Figure 3 The results of DFT calculations. Phonon dispersion curves and phonon DOS for (a) $\text{LaFe}(\text{CN})_6$ and (b) $\text{LuFe}(\text{CN})_6$. The mode Grüneisen parameters as a function of vibrational frequency for (c) $\text{LaFe}(\text{CN})_6$ and (d) $\text{LuFe}(\text{CN})_6$. Insets: the transverse vibrational modes with the same direction of vibration for N and C atoms showing the largest negative Grüneisen parameters at the low frequencies of 49 cm^{-1} ($\text{LaFe}(\text{CN})_6$) and 53 cm^{-1} ($\text{LuFe}(\text{CN})_6$). The direction and size of arrows reflect the directions and amplitudes of vibrations of N and C atoms.

Figure 4 The strong relationships between thermal expansion and the AAV of open-framework fluorides, oxides and PBAs.

system has large NTE behavior in the temperature range of 100–525 K. The ADPs and MSDs resulting from the analysis clearly indicated that the NTE of the $REFe(CN)_6$ system is determined by the transverse thermal vibrations of CN groups, which is also reflected in the low-frequency phonon modes with negative Grüneisen parameters. This work not only reported new NTE materials with chemical formula $REFe(CN)_6$, but also gave us some insight into the prediction of NTE behavior for most framework materials, such as oxides, fluorides, PBAs and many others.

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Author contributions Gao Q and Chen J conceived the idea and designed the experiments. Gao Q prepared the samples and performed the measurements. Sanson A analyzed and discussed the data of the X-ray absorption fine structure experiments. Sun Q performed density functional theory (DFT) calculations. Huang Q assisted in the neutron powder diffraction experiments. All authors contributed to the discussions. Gao Q and Chen J wrote the manuscript with help for the revision from all coauthors.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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平均原子晶格体积在预测负热膨胀材料中的作用: 以 $REFe(CN)_6$ 为例

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摘要 面对高精尖仪器或设备的热膨胀控制的需求, 探索新的负热膨胀材料显得尤为重要。本文采用“平均原子晶格体积”概念预测各向异性新的负热膨胀材料体系, 据此发现了 $REFe(CN)_6$ ($RE = La, Sm, Ho, Lu$) 负热膨胀材料家族。我们采用原位中子粉末衍射(NPD)、X射线吸收精细结构谱(EXAFS)和第一性原理计算揭示了其负热膨胀来源于低频声子振动模式中的CN原子的横向热振动, 进一步发现“平均原子晶格体积”越大, 其对应的低频声子模式频率越低, 格林艾森常数越负, CN原子的横向热振动越强。本工作为定性预测负热膨胀材料提供了新的方法, 对热膨胀控制与设计具有重要意义。