Inorganic Chemistry

Isotropic Zero Thermal Expansion and Local Vibrational Dynamics in $(Sc,Fe)F_3$

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S Supporting Information

ABSTRACT: Scandium fluoride (ScF₃) exhibits a pronounced negative thermal expansion (NTE), which can be suppressed and ultimately transformed into an isotropic zero thermal expansion (ZTE) by partially substituting Sc with Fe in $(Sc_{0.8}Fe_{0.2})F_3$ (Fe20). The latter displays a rather small coefficient of thermal expansion of $-0.17 \times$ 10⁻⁶/K from 300 to 700 K. Synchrotron X-ray and neutron pair distribution functions confirm that the Sc/ Fe-F bond has positive thermal expansion (PTE). Local vibrational dynamics based on extended X-ray absorption fine structure indicates a decreased anisotropy of relative vibration in the Sc/Fe-F bond. Combined analysis proposes a delicate balance between the counteracting effects of the chemical bond PTE and NTE from transverse vibration. The present study extends the scope of isotropic ZTE compounds and, more significantly, provides a complete local vibrational dynamics to shed light on the ZTE mechanism in chemically tailored NTE compounds.

he overwhelming majority of materials exhibit positive thermal expansion (PTE) because of the nearly universal increase in the bond length with temperature due to increasing atomic vibration amplitude. Negative thermal expansion (NTE) is counterintuitive and typically results from some other processes. The physical phenomenon leading to NTE is often related to magnetic or electric polarization effects, such as in an Invar alloy,¹ antiperovskite manganese nitrides,² and La- $(Fe,Si,Co)_{13}^{3}$ related closely to magnetic order variation, in $BiNiO_{3'}^{4}$ attributed to intermetallic charge-transfer transition, in PbTiO₃-based solid solutions⁵ originating from spontaneous polarization, etc. NTE framework solids are inherently different because NTE arises only from atomic vibrations. The NTE in these materials is explained by the rigid unit mode model, which involves low-frequency phonon modes intimately coupled with polyhedron motion as found in, e.g., ZrW₂O₈,⁶ ScF₃,⁷ and CaZrF₆.

Zero thermal expansion (ZTE) compounds are rare but critical for practical applications.⁹ For example, high-precision optical instruments requiring 3D stability can accommodate

strong temperature fluctuations using isotropic ZTE structural materials. However, such compounds are documented in only a few species: e.g., $Fe[Co(CN)_6]$,¹⁰ $Zr_{1-x}Sn_xMo_2O_8$,¹¹ nano $Mn_3Cu_{0.5}Ge_{0.5}N$,¹² $(Sc_{0.85}Ga_{0.05}Fe_{0.15})F_3$,^{7b} TaO_2F ,¹³ and $Zn_4B_6O_{13}$.⁴

The strong NTE of ScF₃ tends to be weakened after chemical substitutions of Sc with Ga/Fe,^{7b} Ti, Zr, etc.¹⁵ Specifically, an isotropic ZTE with a larger temperature range $(0.23 \times 10^{-6}/K, 300-900 \text{ K})$ has been achieved in $(Sc_{0.85}Ga_{0.05}Fe_{0.1})F_3$ presumably because of a short-range structure distortion.^{7b} However, the local vibrational dynamics of Sc and substituted metal atoms is equally essential and critical to elucidating the ZTE mechanism.

Here we present an isotropic ZTE compound, $(Sc_{0.8}Fe_{0.2})F_3$ (Fe20), displaying an extremely low coefficient of thermal expansion (CTE) of -0.17×10^{-6} /K over a wide temperature range of 300–700 K. The direct experimental evidence for the ZTE mechanism is validated by a joint analysis of synchrotron Xray and neutron pair distribution functions (XPDF and NPDF), as well as extended X-ray absorption fine structure (EXAFS). In particular, a delicate balance is observed between the weakened PTE of the chemical bonds and also the suppressed thermal vibration of the Sc/Fe–F atoms, ultimately giving rise to ZTE. The present work not only broadens the scope of hightemperature isotropic ZTE materials but also provides a comprehensive understanding of the local vibrational dynamics leading to ZTE behavior.

Scandium fluoride (ScF₃) crystallizes in a cubic structure with the $Pm\overline{3}m$ space group (Figure 1a). It is comprised of cornershared ScF₆ octahedra. With increasing temperature, coupled vibrations occur in these fluorine-linked ScF₆ octahedra, which brings them closer together and results in an overall NTE in ScF₃ (Figure 1b).¹⁶

A series of $(Sc_{1-x}Fe_x)F_3$ solid solutions (x = 0, 0.05, 0.10, 0.15, and 0.20) were synthesized by a conventional solid-state reaction method.^{7b,c} Rietveld structure refinement on powder X-ray diffraction (XRD) shows that Fe occupies the Sc crystallographic site (0, 0, 0) and all of the $(Sc_{1-x}Fe_x)F_3$ solid solutions share the same cubic structure with ScF₃ (Figure S1). High-temperature

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Figure 1. (a) Cubic crystal structure of ScF_3 . (b) ScF_6 octahedral rotation with increasing temperature, as indicated by the red arrows, thus causing shrinkage of the lattice volume.

XRD data of $(Sc_{1-x}Fe_x)F_3$ solid solutions were collected to investigate the lattice thermal expansion. As depicted in Figure 2a, ScF₃ demonstrates a strong NTE. Its lattice constant



Figure 2. (a) Lattice constants of $(Sc_{1-x}Fe_x)F_3$ solid solutions (x = 0, 0.05, 0.10, 0.15 and 0.20; for clarity, they are denoted as ScF₃, Fe5, Fe10, Fe15, and Fe20, respectively). (b) Contour plots of the (100) peaks of ScF₃ and Fe20 as a function of the temperature. The color bar indicates the normalized intensity. Black and blue arrows demonstrate variation of the peak positions with increasing temperature.

decreases smoothly upon heating with a linear CTE of -3.46 $\times 10^{-6}$ /K (300–800 K).⁷ By the substitution of Sc with Fe, the strong NTE in pure ScF₃ is gradually weakened in $(Sc_{0.95}Fe_{0.05})F_3$ (Fe5), $(Sc_{0.9}Fe_{0.1})F_3$ (Fe10), and $(Sc_{0.85}Fe_{0.15})F_3$ (Fe15), with CTEs of -2.78, -1.79, and -0.99 (all $\times 10^{-6}$ /K, 300–800 K). Further, the lattice constant of Fe20 remains basically unchanged over a wide temperature range (300-700 K), exhibiting an obvious ZTE with a very small CTE value of $-0.17 \times 10^{-6}/K$ (Figure 2a). The obvious increase in the lattice constant above 700 K presumably comes from the PTE contribution of the chemical bonds. The atomic displacement parameters (APDs) of the F atoms of Fe20 also increase more slowly than those of ScF_{3} , implying a weakened transverse motion (Figure S3). Contour plots of the (100) peaks of pure ScF₃ and Fe20 are presented in Figure 2b. With rising temperature, the (100) peak position of ScF₃ shifts to higher 2θ angles. In sharp contrast, a small movement occurs in the (100) peak of Fe20 upon heating, visually confirming its isotropic ZTE property.

Isotropic ZTE materials are best for applications requiring strict thermal stability. Otherwise, a large temperature variation would cause stress concentration and thus material fatigue or even failure. So far, some chemically modified isotropic ZTE materials have been reported like $Fe[Co(CN)_6]$ (-1.47 × 10⁻⁶/ K, 4.2–300 K),¹⁰ Zr_{1-x}Sn_xMo₂O₈ (-0.06 × 10⁻⁶/K, 12–600

K),¹¹ nano Mn₃Cu_{0.5}Ge_{0.5}N (0.12 × 10⁻⁶/K, 12–230 K),¹² TaO₂F (0.29 × 10⁻⁶/K, 300–773 K),¹³ Zn₄B₆O₁₃ (0.28 × 10⁻⁶/K, 13–110 K),¹⁴ and (Sc_{0.85}Ga_{0.05}Fe_{0.15})F₃ (0.23 × 10⁻⁶/K, 300–900 K).^{7b} Similar to the above compounds, Fe20 shows a relatively small CTE value (-0.17×10^{-6} /K) in a wide temperature range up to 700 K. It is difficult to achieve such a steady isotropic ZTE value because the lower-energy phonon modes are generally overwhelmed by the high-energy counterparts.

Partial substitution of Sc with heterogeneous atoms like Ga/ Fe,^{7b} Ti, or Zr¹⁵ is demonstrated to suppress the NTE of ScF₃. Here our motivation is to unveil the physical picture captured from a local structural perspective. Temperature-dependent synchrotron XPDF and NPDF were analyzed on Fe20. The G(r)functions of Fe20 XPDF are presented in Figure 3a. The blue and



Figure 3. (a) G(r) functions of Fe20 with increasing temperature (blue, room temperature; red, high temperature). Atomic peaks are marked by dashed lines. (b) M–F and M–M atomic peaks (M represents Sc and Fe). Red and black arrows indicate peak shifts with increasing temperature. Distance changes in (c) Sc–F and M–F and (d) Sc–Sc and M–M. Black squares indicate atomic pairs of ScF₃. Red circles and blue diamonds demonstrate M–F and M–M in Fe20 from XPDF and NPDF.

red G(r) functions indicate room and high temperatures, respectively. Atomic peaks at 2, 4.5, and 5.7 Å correspond to the nearest, second-nearest, and distinct M-F neighbor interatomic distances (here M indicates Sc and Fe). The atomic peak located at around 2.6-3.1 Å, marked by the black box, demonstrates the F–F atomic pair, and the peak at 4 Å indicates the M-M atomic interactions. For clarity, the temperature dependence of the G(r) functions of M-F and M-M are enlarged and are presented in Figure 3b. The M-F peak shifts to a higher distance region marked by the red arrow, while the M-M distance barely changes, as shown by the black arrow. Quantitatively, the M-F distance in Fe20 slowly expands with increasing temperature, accompanying a weak CTE of $4.36 \times$ 10^{-6} /K (300–700 K), as demonstrated by the XPDF (red circles) and NPDF (blue diamonds) results. This implies that the PTE contribution is significantly suppressed. Note that there is a considerable PTE of Sc-F (black squares) in ScF₃ (CTE of 13.85 \times 10⁻⁶/K, 300-700 K;¹⁶ Figure 3c). The M-M interatomic distances in Fe20 remain almost the same during the whole temperature range, revealing a ZTE behavior in accordance with its macroscopic lattice ZTE.

The magnitudes of the Fourier transforms of Sc and Fe K-edge EXAFS signals, $k^2\chi(k)$, are presented in Figure 4a as a function of



Figure 4. (a) Fourier transforms of Sc and Fe K-edge EXAFS signals. Isolated thermal (b) MSRD_{||}, (c) MSRD_⊥, and (d) γ = MSRD_⊥/MSRD_{||} of Sc-F in ScF₃ (black squares), Sc-F (red circles), and Fe-F (blue squares) of Fe20. Solid lines are the best fits based on the Einstein model.

the temperature. Local vibration dynamics of Sc-F and Fe-F in Fe20 were analyzed separately by solely considering the first coordination shell. The parallel mean-square relative displacement (MSRD_{II}) values of Sc-F and Fe-F in Fe20 and Sc-F in pure ScF₃ show comparable temperature response (Figure 4b), which implies the similar stretching bond force constants of Sc/ Fe-F and Sc-F. The perpendicular MSRD₁ value of Sc-F in ScF_3 is strongly sensitive to the temperature. However, an apparent discrepancy between the MSRD | values of Sc/Fe-F in Fe20 and Sc-F in ScF₃ is observed. The former ones reveal a highly suppressed temperature dependence (Figure 4c), which demonstrates that Sc-F in ScF₃ bends more flexibly than Sc/ Fe–F in Fe20. The value of $\gamma = MSRD_{\perp}/MSRD_{\parallel}$ represents the degree of anisotropy of relative thermal vibration. The γ value of Sc-F in ScF₃ reaches a higher value of \sim 19 at high temperatures, 16 close to that of high NTE compounds, such as 22 in Ag₂O, 17 24.2 in CuScO₂, 18 and 26 in ZrW₂O₈. 19 It is interesting to note that the anisotropy of Sc-F in Fe20 decreases approximately by a factor of 2 ($\gamma = 11.4$) and that of Fe-F remains as 8.8, similar to 6 and 11 in extremely weak NTE compounds of Ge and CuCl, respectively.²⁰ The reduced γ values of Sc/Fe-F in Fe20 depict a clear physical scenario in which the Sc/Fe-F bond is much stiffer with respect to the bending of Sc-F in ScF₃. This anisotropy of relative thermal vibration, related closely to the low frequency phonon modes and responsible for NTE, is highly suppressed in $(Sc_{1-x}Fe_x)F_3$ solid solutions, in contrast to the highly vibrating Sc-F atomic correlation found in ScF₃.

By the substitution of Sc with heterogeneous atoms, the nearest-neighbor M–F interactions exhibit weakened PTE, as determined by XPDF and NPDF, which results in a decreased PTE contribution to lattice expansion. On the other side, the

local thermal dynamics based on the EXAFS study elucidates that M-F bonds become stiffer with respect to bending, which gives rise to a highly reduced anisotropy of relative thermal vibration. The NTE contribution is simultaneously suppressed to macroscopic framework expansion. Consequently, a delicate balance is constructed between both repressed PTE, originating from atomic potential anharmonicity, and NTE components, attributed to the lower frequency modes. Ultimately, the isotropic ZTE is achieved in the composition of Fe20. The introduction of heterogeneous atoms into ScF₃ inevitably produces a certain degree of local distortion, which moves the F atoms away from its midpoint site.^{7b} This distortion ultimately impacts the thermal motions of F atoms in both the transverse and longitudinal directions, which correlates closely with the weakened transverse motion and suppressed chemical bond PTE in heterogeneous atom-doped ScF₃ solid solutions.

In summary, an isotropic ZTE was achieved in $(Sc_{1-x}Fe_x)F_3$ solid solutions. The CTE decreases to a small value of -0.17×10^{-6} /K. A joint analysis of PDF and EXAFS shows isotropic ZTE stemming from a balanced competition between the chemical bond PTE and local NTE contribution, both suppressed compared to ScF₃. The present work not only reports a new isotropic ZTE compound but also provides an unambiguous and comprehensive insight into the local thermal dynamics of the host and substituted atomic correlations, which could shed light on the thermal expansion of chemically engineered NTE framework solids.

ASSOCIATED CONTENT

S Supporting Information

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Experimental details, structure refinement, and EXAFS analysis (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Mohn, P. Materials science: A century of zero expansion. *Nature* **1999**, 400, 18–19.

(2) Takenaka, K.; Takagi, H. Giant negative thermal expansion in Gedoped anti-perovskite manganese nitrides. *Appl. Phys. Lett.* **2005**, *87*, 261902.

(3) Huang, R.; Liu, Y.; Fan, W.; Tan, J.; Xiao, F.; Qian, L.; Li, L. Giant negative thermal expansion in NaZn₁₃-type La(Fe,Si,Co)₁₃ compounds. *J. Am. Chem. Soc.* **2013**, *135*, 11469–11472.

(4) Azuma, M.; Chen, W. T.; Seki, H.; Czapski, M.; Olga, S.; Oka, K.; Mizumaki, M.; Watanuki, T.; Ishimatsu, N.; Kawamura, N.; Ishiwata, S.; Tucker, W. G.; Shimakawa, Y.; Attfield, J. P. Colossal negative thermal expansion in BiNiO₃ induced by intermetallic charge transfer. *Nat. Commun.* **2011**, *2*, 347.

(5) Chen, J.; Fan, L.; Ren, Y.; Pan, Z.; Deng, J.; Yu, R.; Xing, X. Unusual Transformation from Strong Negative to Positive Thermal Expansion in PbTiO₃–BiFeO₃ Perovskite. *Phys. Rev. Lett.* **2013**, *110*, 115901.

(6) Mary, T. A.; Evans, J. S. O.; Vogt, T.; Sleight, A. W. Negative thermal expansion from 0.3 to 1050 K in ZrW₂O₈. *Science* **1996**, *272*, 90.
(7) (a) Greve, B. K.; Martin, K. L.; Lee, P. L.; Chupas, P. J.; Chapman,

K. W.; Wilkinson, A. P. Pronounced negative thermal expansion from a simple structure: cubic ScF₃. J. Am. Chem. Soc. **2010**, 132, 15496–15498. (b) Hu, L.; Chen, J.; Fan, L.; Ren, Y.; Rong, Y.; Pan, Z.; Deng, J.; Yu, R.; Xing, X. Zero Thermal Expansion and Ferromagnetism in Cubic Sc_{1-x}M_xF₃ (M= Ga, Fe) over a Wide Temperature Range. J. Am. Chem. Soc. **2014**, 136, 13566–13569. (c) Hu, L.; Chen, J.; Fan, L. L.; Ren, Y.; Huang, Q. Z.; Sanson, A.; Jiang, Z.; Zhou, M.; Rong, Y. C.; Wang, Y.; Deng, J. X.; Xing, X. Adv. Mater. (Weinheim, Ger.) **2015**, 27, 4592.

(8) Hu, L.; Chen, J.; Xu, J.; Wang, N.; Han, F.; Ren, Y.; Pan, Z.; Rong, Y.; Huang, R.; Deng, J.; Li, L.; Xing, X. Atomic Linkage Flexibility Tuned Isotropic Negative, Zero, and Positive Thermal Expansion in MZrF₆ (M= Ca, Mn, Fe, Co, Ni, and Zn). *J. Am. Chem. Soc.* **2016**, *138*, 14530.
(9) (a) Chen, J.; Hu, L.; Deng, J. X.; Xing, X. R. Negative thermal

expansion in functional materials: controllable thermal expansion by chemical modifications. *Chem. Soc. Rev.* **2015**, 44, 3522–3567.

(10) Margadonna, S.; Prassides, K.; Fitch, A. N. Zero thermal expansion in a Prussian blue analogue. *J. Am. Chem. Soc.* **2004**, *126*, 15390–15391.

(11) Tallentire, S. E.; Child, F.; Fall, I.; Vella-Zarb, L.; Evans, I. R.; Tucker, M. G.; Keen, D. A.; Wilson, C.; Evans, J. S. Systematic and controllable negative, zero, and positive thermal expansion in cubic Zr_{1-x}Sn_xMo₂O₈. *J. Am. Chem. Soc.* **2013**, *135*, 12849–12856.

(12) Song, X.; Sun, Z.; Huang, Q.; Rettenmayr, M.; Liu, X.; Seyring, M.; Li, G.; Rao, G.; Yin, F. *Adv. Mater.* **2011**, *23*, 4690–4694.

(13) Tao, J. Z.; Sleight, A. W. Very low thermal expansion in TaO_2F . J. Solid State Chem. 2003, 173, 45–48.

(14) Jiang, X. X.; Molokeev, M. S.; Gong, P. F.; Yang, Y.; Wang, W.; Wang, S. H.; Wu, S. F.; Wang, Y. X.; Huang, R. J.; Li, L. F.; Wu, Y. C.; Xing, X. R.; Lin, Z. S. Near-Zero Thermal Expansion and High Ultraviolet Transparency in a Borate Crystal of $Zn_4B_6O_{13}$. *Adv. Mater.* **2016**, *28*, 7936–7940.

(15) (a) Morelock, C. R.; Gallington, L. C.; Wilkinson, A. P. Evolution of Negative Thermal Expansion and Phase Transitions in $Sc_{1x}Ti_xF_3$. *Chem. Mater.* **2014**, *26*, 1936–1940. (b) Wang, T.; Xu, J.; Hu, L.; Wang, W.; Huang, R.; Han, F.; Pan, Z.; Deng, J.; Ren, Y.; Li, L.; Chen, J.; Xing, X. Tunable thermal expansion and magnetism in Zr-doped ScF₃. *Appl. Phys. Lett.* **2016**, *109*, 181901.

(16) Hu, L.; Chen, J.; Sanson, A.; Wu, H.; Guglieri Rodriguez, C.; Olivi, L.; Ren, Y.; Fan, X. R.; Deng, J. X.; Xing, X. R. New Insights into the Negative Thermal Expansion: Direct Experimental Evidence for the "Guitar-String" Effect in Cubic ScF₃. J. Am. Chem. Soc. **2016**, *138*, 8320–8323.

(17) Vaccari, M.; Grisenti, R.; Fornasini, P.; Rocca, F.; Sanson, A. Negative thermal expansion in CuCl: An extended x-ray absorption fine structure study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 184307.

(18) Ahmed, S. I.; Dalba, G.; Fornasini, P.; Vaccari, M.; Rocca, F.; Sanson, A.; Li, J.; Sleight, A. W. Negative thermal expansion in crystals with the delafossite structure: An extended x-ray absorption fine Communication

structure study of CuScO₂ and CuLaO₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, 79, 104302.

(19) Sanson, A. Toward an Understanding of the Local Origin of Negative Thermal Expansion in ZrW_2O_8 : Limits and Inconsistencies of the Tent and Rigid Unit Mode Models. *Chem. Mater.* **2014**, *26*, 3716.

(20) Fornasini, P.; Sanson, A.; Vaccari, M.; Artioli, G.; Dapiaggi, M. Local lattice dynamics and negative thermal expansion in crystals. *Journal of Physics: Conference Series* **2007**, *92*, 012153.