Entropic elasticity and negative thermal expansion in a simple cubic crystal

David Wendt1, Emil Bozin1, Joerg Neuefeind2, Katharine Page2, Wei Ku†4, Limin Wang†4, Brent Fultz3, Alexei V. Tkachenko4, Igor A. Zaliznyak1§

While most solids expand when heated, some materials show the opposite behavior: negative thermal expansion (NTE). In polymers and biomolecules, NTE originates from the entropic elasticity of an ideal, freely jointed chain. The origin of NTE in solids has been widely believed to be different. Our neutron scattering study of a simple cubic NTE material, ScF3, overturns this consensus. We observe that the correlation in the positions of the neighboring fluorine atoms rapidly fades on warming, indicating an uncourelated thermal motion constrained by the rigid Sc-F bonds. This leads us to a quantitative theory of NTE in terms of entropic elasticity of a floppy network crystal, which is in remarkable agreement with experimental results. We thus reveal the formidable universality of the NTE phenomenon in soft and hard matter.

INTRODUCTION
Near-zero or negative thermal expansion (NTE) is well known in metallic alloys of the invar (Fe0.64Ni0.36) family, where it is closely related to electronic magnetism (1). These alloys are widely used in applications requiring dimensional stability of metallic parts, e.g., in precision instruments, watches, and engines. Until recently, much less attention was paid to insulating NTE ceramics, which hold promise for numerous applications in electronics, optics, and medicine (2–5). Somewhat surprisingly, because of the specific crystal lattice geometry, NTE in these materials can have the same physical origin as a more common, positive thermal expansion (PTE): atomic thermal motion.

Interest in these systems was renewed with the observation of large isotropic NTE in zirconium tungstate, ZrW2O8, and then in the structurally related AM2O8, AM2O7, and A2M3O12 phases (A = Zr, Hf, Sc, Y, ... and M = W, V, Mo, P, ...) and their solid solutions (2, 6), which opened avenues for designing ceramic materials with tailored thermal expansion (2–5). These compounds have complex crystal structures, which can be viewed as three-dimensional (3D) networks of AX6 octahedra and MX4 tetrahedra (X = O) that share the corner X atoms and, most importantly, contain nearly straight, twofold-coordinated M-X-M and M-X-A linkages [the so-called open framework structures (2)].

NTE in such a structure can be explained by the transverse thermal motion of anion atoms, X, in the presence of the strong M-X bond, which has small or negligible thermal expansion: the so-called guitar string effect (2, 7, 8). As the amplitude of the anion transverse vibration increases with temperature, the metal atoms in M-X-M linkages are pulled closer together, thus causing the net contraction of the structure. While this simple picture does not consider the correlated motion of nearby X anions caused by their interactions in the lattice, in what follows, we show that it provides an adequate description of NTE in ScF3 (9).

An appealing model for including anion correlation considers vibrations that preserve the structure of the MXn polyhedra, which thus move as rigid bodies, without deforming the anion-anion bonds (2, 10–13). The relative importance of such rigid unit modes (RUMs) has been rationalized by arguing that vibrations distorting the high symmetry of the polyhedron must have a high energy cost and therefore contribute relatively little to NTE (5). A priori, such an ad hoc assumption is not required for the NTE effect, and its relevance has been a matter of debate (2, 5, 10–20). In a structure that is underconstrained, RUMs correspond to zero-energy floppy phonon modes (5, 10). In a fully constrained structure, such as a cubic network of corner-sharing octahedra in ScF3 (Fig. 1A), vibrations that do not distort polyhedra are present on special low-dimensional manifolds occupying zero volume fraction of the system’s phase space (5, 10). Nevertheless, it has been argued that phonons in the vicinity of these manifolds, quasi-RUM, which involve only small distortions of the polyhedra, have special importance for NTE. ScF3 was suggested to be a perfect example of an NTE system where the tension effect is enabled by RUM (Fig. 1B) (5).

RESULTS
Pair distribution function (PDF) analysis (20, 21) of neutron total scattering is a powerful and direct experimental method for studying average local atomic structures and their relevance for NTE (5, 21). The PDF, g(r), which is obtained from the measured scattering intensity, S(Q), gives the probability distribution of interatomic distances weighted by the scattering lengths of the constituent atoms and thus is uniquely sensitive to local structural patterns. Figure 1 (C to E) presents the PDF of ScF3 measured on NPDF (C and D) and NOMAD (E) neutron diffractometers at temperatures from 2 to 1099 K. These measurements are complementary and show good agreement in the temperature range where they overlap.

An inspection of g(r) curves reveals several remarkable features, of which the most important is the distinct behavior of Sc-F and F-F pair distributions. NTE of the average crystal structure is manifested by the systematic negative shift to smaller r of PDF peaks from atomic pairs with large separation, r, with increasing temperature. It is most clearly seen in Fig. 1D. The nearest F-F (∼2.8 Å) peak shows similar NTE behavior. On the other hand, the nearest-neighbor Sc-F (∼2 Å) peak shifts on heating to slightly larger r, consistent with the conventional PTE (7, 22). This peak broadens only moderately with temperature, by about

1 Condensed Matter Physics and Materials Science Division, Brookhaven National Laboratory, Upton, NY 11973, USA. 2 Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. 3 Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA 91125, USA. 4 CFN, Brookhaven National Laboratory, Upton, NY 11973, USA. 5 Present address: Stanford University, Stanford, CA 94305, USA. 6 Present address: Tsung-Dao Lee Institute & School of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, China. 7 Corresponding author. Email: zaliznyak@bnl.gov
distance distributions of particular atomic pairs, to Gaussian distributions, which are well resolved and can be uniquely associated for additional discussion.

Fig. 2 (D to F). While the Sc-F bond shows PTE of _g_r(max) at 500 K. (D) The color map representation of the temperature evolution of _g_r emphasizes the negative shift of peaks with increasing temperature, which is most evident at large r. (E) PDF measured on the same sample on NOMAD diffractometer for temperatures from 2 to 1100 K (bottom to top). Here, each curve is an average of _g_r obtained using the wave vector ranges with _Q_max varying from 23 to 32 Å⁻¹ by increments of 1 Å⁻¹. For visibility, data at each temperature above 2 K are shifted upward by 1. The vertical lines in (C) and (E) mark nominal distances corresponding to Sc-F (dash-dotted), F-F (dashed), and Sc-Sc (overlapping with lattice repeats; solid) atom pairs in the ScF₃ structure.

20% at 450 K (this accounts for the decrease of peak maximum in Fig. 1), indicating a very stiff Sc-F bond. In contrast, the width of the nearest F-F peak increases markedly, revealing rapid loss of F-F correlation with increasing thermal motion. Even more marked is the behavior of further-neighbors F-F distributions. The corresponding peaks [marked by dashed lines in Fig. 1 (C and E)] are only present at T ≤ 300 K and entirely disappear at higher temperatures, suggesting complete loss of positional correlation between further-neighbors F atoms. Such a liquid-like F-F PDF pattern indicates randomly phased transverse local motion of F atoms and is inconsistent with the RUM model where a large number of F-F distances are constrained by the rigid unit geometry (5, 18, 19). Also see the Supplementary Materials for additional discussion.

We quantify the observed behaviors by fitting the first several PDF peaks, which are well resolved and can be uniquely associated with distance distributions of particular atomic pairs, to Gaussian distributions (Fig. 2, A to C). The results of this analysis are summarized in Fig. 2 (D to F). While the Sc-F bond shows PTE of ≈5% parts per million (ppm) at 1000 K, both Sc-Sc, _r_{Sc-Sc} = a [lattice repeat distance (LRD)], and the nearest F-F, _r_{F-F}, distances exhibit NTE above twice larger in magnitude (Fig. 2D). The large error bars on _r_{F-F} reflect marked broadening of the F-F peak with temperature. While the full width at half maximum (FWHM) of Sc-F and Sc-Sc (LRD) peaks increases by less than 50% at 1000 K, the width of the nearest F-F distribution shows nearly an order-of-magnitude larger change, increasing to nearly 1 Å (Fig. 2E). This indicates an uncertainty of the nearest F-F distance that is comparable to the _r_{F-F} distance itself, invalidating the RUM model assumption of quasi-rigid ScF₆ octahedra.

The loss of F-F pair correlation is further revealed by the temperature dependence of the intensity of the LRD (≈4 Å peak) (Fig. 2F). It contains partial contributions from both nearest-neighbor Sc-Sc and next-nearest-neighbor F-F pairs, in proportion _σ_{Sc} : _σ_{F} ≈ 1.6, where _σ_{Sc} and _σ_{F} are coherent scattering cross sections of Sc and F, respectively. A PDF peak presents the probability distribution of interatomic distance; therefore, its integral intensity must be temperature independent. This roughly holds for Sc-F peak. A small systematic drift of its intensity, which is likely caused by T-dependent background, is within the error bar of the average value. In contrast, the LRD peak rapidly loses a substantial part of its intensity above ≈300 K, where F-F correlations disappear. The decrease is consistent with the loss of the entire ≈40% partial contribution of F-F pairs, which, above ≈300 K, contribute to broad background rather than to the narrow LRD peak described by the fit.

Motivated by these observations, we use a simple model for the probability distribution of the nearest F-F distance, which is presented in Fig. 3. It assumes uncorrelated thermal motion of individual F atoms, which is subject to a single constraint of the rigid Sc-F bond. If Sc atoms were fixed at the nodes of ScF₆ lattice, then the constraint would result in F atoms following ring trajectories with the Sc-F bond sweeping a cone. The resulting _r_{F-F} probability distribution would be that of a distance between two points randomly positioned on the two nearest rings. This model has no adjustable parameters because the radius of the rings, _r_{1} (the average transverse deviation of F), and _r_{Sc-Sc} = a are obtained from the Rietveld refinement of the coherent Bragg scattering contained in our data (Fig. 4, B and C).

The model can also be set up using Sc-F and Sc-Sc distances obtained from PDF peaks in Fig. 2, although the accuracy of this refinement is lower. While larger systematic error in this approach affects some of the analysis below ≈200 K where changes are weak, above this temperature, this analysis gives results in close agreement with Figs. 3A and 4A.

Unexpectedly, when broadened by convolution with the Gaussian of the same width as Sc-F peak at 2 K to account for experimental resolution (truncation), our oversimplified model provides adequate description of the measured F-F distribution for all temperatures where NTE is observed (dashed lines in Figs. 3A and 4A). In this model, the peak maximum follows lattice NTE, in agreement with Fig. 2D. The model can be further improved if, instead of rings [or conventional Gaussian thermal displacement (TD) ellipsoids; Fig. 3B], F atoms are randomly positioned on a torus-shaped Gaussian distribution peaked at the same major diameter, _2r_{a}, and with the minor diameter representing the F part of the Sc-F peak FWHM (Fig. 3C). This improved model conjectured by Sleight (2) provides slightly better agreement with the data (Fig. 3A), as quantified by the reduced mean square deviation, _χ^2_, presented in Fig. 4A. The _χ^2_ analysis is a standard way to evaluate the goodness of fit: Where _χ^2 ≈ 1, the data are indistinguishable from the model. With _N ≈ 11 effectively independent data points used in our comparison, _χ^2 < 3 places the model within 3σ interval or above 99.5% likelihood level. The model begins to fail above ≈700 K, where _χ^2 increases to ~10, but NTE also fades. Below ≈200 K, the broadening of the F-F peak is small and _χ^2 < 1,
which means that within the experimental error, our model cannot be distinguished from other models, such as RUM.

DISCUSSION

The essential implication of our analysis is that thermal motion of even the nearest F atoms is uncorrelated rather than in RUM (Fig. 3, D and E). The spread of the F-F PDF peak with temperature follows from the increase in size of the manifold (circle or torus) populated by each F atom in the course of its thermal motion. Underlying this model is the phenomenon of energy scale separation, where two very different energies govern longitudinal and transverse motion of the F ion.

Then, in some temperature range, transverse modes can be thermally excited and the corresponding degrees of freedom can be equipartitioned, while longitudinal vibrations are still frozen out. In this case, Sc-F bonds are rigid, while F transverse vibrations are uncorrelated. In-}

titioned, while longitudinal vibrations are still frozen out. In this case, energies govern longitudinal and transverse motion of the F ion.

The phenomenon of energy scale separation, where two very different energies govern longitudinal and transverse motion of the F ion.

Then, in some temperature range, transverse modes can be thermally excited and the corresponding degrees of freedom can be equipartitioned, while longitudinal vibrations are still frozen out. In this case, Sc-F bonds are rigid, while F transverse vibrations are uncorrelated. Inspection of the vibrational spectra measured in ScF3 (17, 18, 22) reveals two major phonon groups, which rise to maxima in the density of states below $\omega_0 \approx 22$ meV and above $\omega_0 \approx 62$ meV. These correspond to transverse and longitudinal vibrations, respectively. This separation of energy scales implies that transverse degrees of freedom are thermally excited and equipartitioned at $T > \omega_0/k_B \approx 260$ K ($k_B$ is Boltzmann constant), while the longitudinal rigidity of the Sc-F bond persists up to at least $T \approx \omega_0/k_B \approx 710$ K. This is exactly the temperature range where NTE is observed and where our model provides very good description of the PDF data (Fig. 4).

The exceptional longitudinal rigidity of the Sc-F bond, which underlies the NTE mechanism in ScF3, is rooted in covalence, where the hybridization of Sc and F electronic orbitals that lie deep inside the valence band is responsible for the large energy cost of changing the Sc-F distance (23–26). Also see the Supplementary Materials for additional discussion. This Lewis-type dative bonding, where paired electrons delocalize between ions to lower their kinetic energy, has recently been described as a “charge transfer bond” (24). Although it has long been known that ScF3 is anomalous among supposedly ionic metal trifluorides, MF3 (M = Al, Sc, Fe, In, ...) (27), only relatively recently has the exceptional strength of the Sc-F bond been traced to the covalent nature of the valence molecular orbitals (MOs). The comparative analysis of the x-ray photoemission spectra and the density functional theory (DFT) electronic structure calculations (25) for the (ScF3)$_3$ cluster have indicated a large contribution to the Sc-F bonding energy of a specific $(5a_1)$ d $\rightarrow p$ MO at $\approx -5$ eV. A modest hybridization $(|5a_1| \approx 0.83 \mid |p_F| + 0.16 \mid |Sc3d|)$ does not lead to sizeable charge transfer such that Sc$^{3+}$ and F$^{-}$ appear to be close to their nominal ionic oxidation states. We performed DFT electronic structure calculations in ScF3, which further support these findings, indicating slightly hybrid valence bands below $\approx -4$ eV and strong anisotropy of the effective potential of F ions (26). Also see the Supplementary Materials for additional discussion.
These observations immediately suggest a simple theoretical description of the NTE effect, where each Sc-F bond is treated as a rigid monomer link and the entire ScF$_3$ crystal structure is treated as a floppy network of such freely jointed monomers, a direct 3D analog of the celebrated model of polymer chains (Fig. 3, B and D) (28, 29). Without electrostatic interactions, the network is underconstrained (floppy): The number of constraints imposed by rigid Sc-F links is six per unit cell, while the number of degrees of freedom is 12. In particular, the motion of the Sc ion is constrained by rigid bonds in all three directions, while each of the F ions has two zero-energy displacement modes corresponding to motion orthogonal to the Sc-F bond. In the absence of external tension, the system has no rigidity and would collapse. In ScF$_3$, net Coulomb repulsion between charged ions provides tension (negative pressure), which stabilizes the system and balances its entropic elastic (see the Supplementary Materials for additional discussion).

We thus separate interactions in the system into a sum of the nearest-neighbor pair potentials, which include the cumulative effect of electrostatic Coulomb attraction, core repulsion, and covalent bonding and, in the simplest approximation, are treated as rigid links and the remaining Coulomb potential of non-nearest-neighbor ions. The resulting effective Hamiltonian for the fluoride transverse motion is (see the Supplementary Materials for additional discussion)

$$H = K + \frac{3N(6-M)e^2}{4\pi\varepsilon_0 r} - \sum_i \frac{\gamma e^2}{4\pi\varepsilon_0 r_i^3} u_i^2$$

with respect to both $r$ and $r_0$, yields the equilibrium values $r = r(T)$ and $r_0 = r_0(T)$. We thus obtain the relation $\gamma e^2 / \beta r_0^3 = \alpha T$, which means that the net entropic effect is split between PTE of the Sc-F bond and NTE of the lattice. It further yields the relation $\gamma e^2 / \beta r_0^3 = -\beta / \alpha T$, where $\beta \approx 0.36$, which determines the relative split between the two effects. $\gamma e^2 / \beta r_0^3 = 1.0 \cdot 10^{-6}T \approx 2.7 \cdot 10^{-6}T$ and $\gamma e^2 / \beta r_0^3 = 0.18 / (1 + T)$ $T \approx -7.4 \cdot 10^{-6}T$ (see the Supplementary Materials for additional discussion). These predictions are shown by dashed lines in Figs. 2D and 4C, which demonstrate remarkable agreement of our simple theory with experiment. We note that in our estimates, we neglected the covalent reduction of the ionic charge on F and Sc ions, which would increase the predicted NTE effect by $\approx 20\%$. This provides a ballpark estimate for the accuracy of our predictions. The leading effect of the presence of defects, such as F vacancies, or dipolar defects, which consists of a proportional change of the negative electrostatic pressure and, correspondingly,
In ZrW_2O_8, the RUM model was challenged by x-ray absorption measurements, indicating that its entropic origin is adequately captured by our model.

In ScF_3, RUM was observed at 2 K, where conventional, positive expansion dominates, and NTE is observed at >739 K, where deformation of the cubic crystal structure, such as ReO_3, where NTE is observed at ≈720 K (32), and AlF_3, where NTE is not observed because it only adopts the cubic structure above 739 K, where conventional, positive expansion dominates (32).

The general design rule for inorganic NTE materials is thus the presence of a floppy network formed by nearly straight C-A-C linkages, where an underconstrained light anion, A, such as oxygen or fluoride, in a sterically open position, is strongly bound to nearby cations, C (2). This floppy network architecture does not imply any specific geometry of the crystal structure, such as corner-sharing octahedra network in ScF_3. This is exemplified by ZrW_2O_8 and related materials, where, when looking at a crystal structure obscured by the coordination polyhedra, one can easily identify a network of nearly straight O-O-Zr and O-W linkages with an underconstrained and sterically open oxygen position. While the geometry of the resulting network and ionic positions is complex (although not as complex as in polymers), NTE in this structure can still be described using our approach, albeit requiring more cumbersome calculations of electrostatics.

On the basis of our experimental observations, we developed a simple theoretical description of the NTE effect in ScF_3, which is rooted in entropic elasticity of an underconstrained floppy network, similar in spirit to the celebrated Flory–de Gennes theory of polymer elasticity (28, 29). Our approach presents a paradigm shift, where instead of focusing on peculiar energetics of low-energy lattice vibrations, such as RUM (2–5, 7, 9–11, 30, 33–35), these vibrations are approximated by Einstein local phonon modes, and the focus is on their entropic contribution to free energy. Our results provide not only a clear understanding of the entropic elasticity origin of the NTE effect in the practically important class of materials and temperature range, including at and above room temperature, but also an accurate, quantitative, textbook description of NTE, thus opening new avenues for predictive modeling of this effect in solids.

**MATERIALS AND METHODS**

Neutron scattering measurements for temperatures from 2 to 1266 K were carried out with NOMAD, a time-of-flight total scattering diffractometer at the Spallation Neutron Source, Oak Ridge National Laboratory, using the polychromatic neutron beam. Additional measurements for temperatures from 15 to 450 K were performed using a similar setup with an NPDF total scattering diffractometer at the Manuel Lujan Neutron Scattering Center, Los Alamos National Laboratory. For these measurements, finely pulverized polycrystalline sample (grain size, <50 μm) of cubic ScF_3 crystals (99.999% purity) was loaded into extruded vanadium containers with outer diameter of 1 cm and height of 4 cm. The same sample was used in (17).

For NOMAD measurements, the setup used an Orange cryostat for measurements between 2 and 300 K and an ILL furnace for measurements between 300 and 1266 K. For the NPDF experiment, the
sample was placed in a closed-cycle cryofurnace. The data at each temperature were collected for 15 to 30 min (NOMAD) and 120 min (NPDF) after the temperature equilibration. The Rietveld analysis of Bragg scattering in the obtained neutron powder diffraction data provided accurate information about the average atomic positions and the thermal mean square displacements of atoms in the crystal lattice (Fig. 4).

The atomic PDF analysis based on total scattering approach yields local structural information on different length scales (21), allowing refinement of the mutual positions of nuclei in different atomic pairs. The reduced PDF, $G(r)$, is obtained from the measured total scattering structure factor, $S(Q)$, via a Fourier sine transform, $G(r) = 4\pi r^2 \rho(r) = \frac{2}{\pi} \int_0^\infty S(Q) \sin(Qr) dQ$. Here, $\rho_0$ is the scattering cross-section weighted atomic number density of the material and $\rho(r)$ is the atomic PDF, which we analyze. It is related to the radial distribution function (RDF), $R(r) = 4\pi r^2 \rho(r) = G(r) + 4\pi r^2 \rho_0$, which has the useful property that the quantity $R(r)dr$ gives the effective number of atoms in an annulus of thickness $dr$ at a distance $r$ from the given atom, and its integral counts the number of atoms. Both RDF and PDF were considered in this study. In our modeling, we analyzed the atomic PDF, $\rho(r) = R(r)/(4\pi r^2)$, which determines the probability for a pair of atoms to be at a distance $r$ (Figs. 1 to 3).

In practice, the $S(Q)$ total scattering data are measured only within a limited range of wave vectors, $Q$. The upper limit of integration in the Fourier transform determining the experimental $\rho(r)$ has to be chosen at some finite value, $Q_{\text{max}}$, which includes the data where the measurement accuracy is acceptable. Different $Q_{\text{max}}$ values lead to different weighting of the noisier data at large $Q$. The truncation of the Fourier transform also introduces systematic error in $\rho(r)$ in the form of the finite width of the PDF peaks and an oscillating "background" baseline ("truncation wiggles") (20, 21), which depend on $Q_{\text{max}}$. To evaluate these systematic errors, we analyzed data computed using different $Q_{\text{max}}$ values. The nominal $Q$ range covered in our study is [0.5, 35] Å$^{-1}$. The data were extrapolated to $Q = 0$ and Fourier-transformed using the wave vector ranges, $[0, Q_{\text{max}}]$, for $Q_{\text{max}}$ varied from 23 to 32 Å$^{-1}$ by increments of 1 Å$^{-1}$. The $g(r)$ data shown in the figures here, with the exception of Fig. 1 (C and D), were obtained by averaging the data from each $Q_{\text{max}}$ range. The error bars account both for the average statistical uncertainty and for the systematic truncation error. The latter is evaluated as the SD of the data obtained using different $Q_{\text{max}}$ values. The obtained $g(r)$ data were modeled using custom-made Python scripts.

The model for F-F pair probability distribution was constructed as follows. Considering the Sc-F longitudinal rigidity, the average transverse deviation, $r_{\text{t}}$, of the F atoms from the Sc-Sc bond axis and the lattice repeat parameter, $a$, were retrieved from Rietveld refinement of the Bragg diffraction contained in the corresponding dataset. These parameters can also be obtained from the analysis of PDF peaks; using the Pythagorean theorem, $r_{\text{t}}^2 = \frac{r_{\text{F}}^2}{2} - (a/2)^2$, where $r_{\text{Sc-Sc}}$ is the average Sc-F bond length and $a$ is the lattice repeat parameter measured as the fitted position of the Sc-F and Sc-Sc PDF peaks, respectively. This approach provides generally similar, albeit less accurate, model description because it is less accurate in determining both the lattice repeat and the transverse F displacement. We therefore opted for using the Rietveld refined parameters for our model. The data for 47 temperatures were used. The nearest-neighbor F-F distance distribution was modeled by placing evenly spaced points on perpendicular rings of radius $r_{\text{t}}$ and center separation $\frac{\pi}{4}$. The distances between each pair of points (not on the same ring) were calculated, and a histogram was created from the compiled set of distances. This histogram was then convoluted with a Gaussian distribution of SD equal to that of the Sc-F peak to account for truncation error and uncertainty in Sc atomic position. A second model was then created with rings replaced by Gaussian distributions peaked at these rings, which can be represented by tori of equal major diameter and separation to the rings and with the minor diameter, equal to the Gaussian FWHM, being equal to FWHM/√2 of the Sc-F peak, thus accounting for F atomic position uncertainty instead of convolution. The remaining procedure is identical to that of the first model.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/11/eaay2748/DC1

Supplementary Text

Table S1. Scandium ionization energies, $E_i$(Sc) (eV), and fluorine electron affinity, $E_f$ (eV), used in eq. S28.

Table S2. Parameters of an effective potential, $U(x) = \frac{1}{2} k_x x^2 + \frac{1}{4} k_x x^4$, for the longitudinal, $U_l(x)$, and transverse, $U_{\text{perp}}(x)$, with $k_x = 20$ Å$^{-4}$ fluorine displacement in ScF$_3$.

Table S3. Structural parameters of ScF$_3$ obtained from Rietveld refinements of NOMAD data showing the standard uncertainty for the lattice spacing, $a$ (measured in Å), and the atomic mean square displacement parameters (measured in 0.01 Å$^2$), isotropic for Sc ($U_{\text{iso-Sc}}$) and anisotropic for F ($U_{\text{aniso-Sc}}$ and $U_{\text{aniso-F}}$), both measured in 0.01 Å$^2$.

Table S5. Structural parameters of ScF$_3$ obtained from Rietveld refinements of NPDF data including parameters $R_{\text{wp}}$ and $R_q$ quantifying the goodness of the fit.

Fig. S5. Electronic band structure in ScF$_3$.

Fig. S2. Effective potential of the fluorine ion in ScF$_3$.

Fig. S3. Selected plots of Rietveld refinement of structural parameters in ScF$_3$.

**REFERENCES AND NOTES**

1. C. E. Guillaume, Recherches sur les aciers au nickel. Dilatations aux temperatures elevees; resistance electrique. C. R. Acad. Sci. 125, 235–238 (1897).

2. A. W. Sleight, Isotropic negative thermal expansion. Annu. Rev. Mater. Sci. 28, 29–43 (1998).

3. G. D. Barrera, J. A. O. Bruno, T. H. K. Barron, N. L. Allan, Negative thermal expansion. J. Phys. Condens. Matter 17, R217–R252 (2005).

4. C. Lind, Two decades of negative thermal expansion research: Where do we stand? Materials 5, 1125–1154 (2012).

5. M. T. Dove, H. Fang, Negative thermal expansion and associated anomalous physical properties: Review of the lattice dynamics theoretical foundations. Rep. Prog. Phys. 79, 066503 (2016).

6. T. A. Mary, J. S. O. Evans, T. Vogt, A. W. Sleight, Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW$_2$O$_8$. Science 272, 90–92 (1996).

7. L. Hu, J. Chen, A. Sanson, H. Wu, C. Gugliarri Rodrigues, L. Ollivi, Y. Ren, L. Fan, J. Deng, X. Xing, New insights into the negative thermal expansion: Direct experimental evidence for the “guitar-string” effect in cufc$_2$. J. Phys. Condens. Matter 138, 8320–8323 (2016).

8. G. Ernst, C. Bohrholm, G. R. Kowach, A. P. Ramirez, Phonon density of states and negative thermal expansion in ZrW$_2$O$_8$. Nature 396, 147–149 (1998).

9. B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas, K. W. Chapman, A. P. Wilkinson, Pronounced negative thermal expansion from a simple structure: Cubic ScF$_3$. J. Am. Chem. Soc. 132, 15496–15498 (2010).

10. A. K. A. Pryde, K. D. Hammonds, M. T. Dove, V. Heine, J. D. Gale, M. C. Warren, Origin of the negative thermal expansion in ZrW$_2$O$_8$ and Zr$_2$O$_7$. J. Phys. Condens. Matter 8, 10973–10982 (1996).

11. J. Z. Tao, A. W. Sleight, The role of rigid unit modes in negative thermal expansion. J. Solid State Chem. 173, 442–448 (2003).

12. M. G. Tucker, A. L. Goodwin, M. T. Dove, D. A. Keen, S. A. Wells, J. S. O. Evans, Negative thermal expansion in ZrW$_2$O$_8$ Mechanisms, rigid unit modes, and neutron total scattering. Phys. Rev. Lett. 95, 255501 (2005).

13. M. G. Tucker, D. A. Keen, J. S. O. Evans, M. T. Dove, Local structure in ZrW$_2$O$_8$ from neutron total scattering. J. Phys. Condens. Matter 19, 335215 (2007).

14. D. Cao, F. Bridges, G. R. Kowach, A. P. Ramirez, Frustrated soft modes and negative thermal expansion in ZrW$_2$O$_8$. Phys. Rev. Lett. 89, 215902 (2002).

15. J. N. Hancock, C. Turpen, Z. Schlesinger, G. R. Kowach, A. P. Ramirez, Unusual low-energy phonon dynamics in the negative thermal expansion compound ZrW$_2$O$_8$. Phys. Rev. Lett. 93, 225501 (2004).

Wendt et al., Sci. Adv. 2019;5:eaay2748 1 November 2019
16. Z. Schlesinger, J. A. Rosen, J. N. Hancock, A. P. Ramirez, Soft manifold dynamics behind negative thermal expansion. Phys. Rev. Lett. 101, 015501 (2008).
17. C. W. Li, X. TANG, J. A. Muñoz, J. B. Keith, S. J. Tracy, D. A. Abernathy, B. Fultz, Structural relationship between negative thermal expansion and quartic anharmonicity of cubic ScF₃. Phys. Rev. Lett. 107, 195504 (2011).
18. S. U. Handunkanda, E. B. Curry, V. Voronov, A. H. Said, G. G. Guzmán-Verri, R. T. Brierley, P. B. Littlewood, J. N. Hancock, Large isotropic negative thermal expansion above a structural quantum phase transition. Phys. Rev. B 92, 134101 (2015).
19. S. U. Handunkanda, C. A. Occhialini, A. H. Said, J. N. Hancock, Two-dimensional nanoscale correlations in the strong negative thermal expansion material ScF₃. Phys. Rev. B 94, 214102 (2016).
20. C. A. Young, A. L. Goodwin, Applications of pair distribution function methods to contemporary problems in materials chemistry. J. Mater. Chem. 21, 6464–6476 (2011).
21. T. Egami, S. Billinge, Underneath the Bragg Peaks: Structural Analysis of Complex Materials (Pergamon Press, Elsevier, ed. 2, 2012), vol. 37.
22. S. Piskunov, P. A. Zgurs, D. Bocharov, A. Kuzmin, J. Purans, A. Kalinko, R. A. Evarestov, S. E. Ali, F. Rocca, Interpretation of unexpected behavior of infrared absorption spectra of ScF₃ beyond the quasiharmonic approximation. Phys. Rev. B 93, 214101 (2016).
23. L. Pauling, The Nature of the Chemical Bond (Cornell Univ. Press, ed. 3, 1960).
24. S. Piskunov, P. A. Zgurs, D. Bocharov, A. Kuzmin, J. Purans, Electronic structure of cubic ScF₃ from first-principles calculations. Low Temp. Phys. 42, 556–560 (2016).
25. J. W. Kury, A. D. Paul, L. G. Hepler, R. E. Connick, The fluoride complexing of scandium(III) from first-principles calculations. Phys. Rev. B 78, 012105 (2008).
26. D. M. P. Mingos, The Chemical Bond II: 100 Years Old and Getting Stronger (Springer International Publishing, 2016), pp. 169–211.
27. Y. A. Teterin, A. Y. Teterin, Structure of x-ray photoelectron spectra of lanthanide compounds. Russ. Chem. Rev. 70, 347–381 (2002).
28. D. Bocharov, P. A. Zgurs, S. Piskunov, A. Kuzmin, J. Purans, Electronic structure of cubic ScF₃ from first-principles calculations. Low Temp. Phys. 42, 556–560 (2016).
29. D. Wendt, E. Bozin, J. Neuefeind, K. Page, W. Ku, L. Wang, B. Fultz, A. V. Tkachenko, I. A. Zaliznyak, Entropic elasticity and negative thermal expansion in a simple cubic crystal. Sci. Adv. 5, eaay2748 (2019).
Entropic elasticity and negative thermal expansion in a simple cubic crystal
David Wendt, Emil Bozin, Joerg Neuefeind, Katharine Page, Wei Ku, Limin Wang, Brent Fultz, Alexei V. Tkachenko and Igor A. Zaliznyak

Sci Adv 5 (11), eaay2748.
DOI: 10.1126/sciadv.aay2748