A real-space experimental model for negative thermal expansion in scandium trifluoride

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Negative thermal expansion (NTE) – the phenomenon where some materials shrink rather than expand when heated – is an intriguing and useful phenomenon, but it remains poorly understood. Current understanding hinges on the role of specific vibrational modes, but in fact thermal expansion is a weighted sum of contributions from every possible mode. Here we overcome this difficulty by deriving a real-space model of atomic motion in the prototypical NTE material scandium trifluoride, ScF$_3$, from total neutron scattering data. We show that NTE in this material depends not only on rigid unit modes – the vibrations in which the scandium coordination octahedra remain undistorted – but also on modes that distort these octahedra. Furthermore, in contrast with previous predictions, we show that the quasiharmonic approximation coupled with renormalisation through anharmonic interactions describes this behaviour well. Our results point the way towards a new understanding of how NTE is manifested in real materials.

I. INTRODUCTION

Almost all materials expand when heated, but some shrink instead. This phenomenon of negative thermal expansion (NTE) is of fundamental interest from a structural and thermodynamic point of view, and also commercially important for instance in preparing substrates resistant to thermal shock. It is among the most widely studied of the anomalous negative thermodynamic properties, others including auxetics with negative Poisson’s ratio and materials which soften under pressure (negative derivative of the bulk modulus with pressure).

The ‘tension effect’ provides our best understanding of the most common type of NTE, namely that arising from vibrational rather than magnetic or electronic reasons. Consider a linear chain of atoms of mass $m$ connected by stiff bonds. A transverse displacement of one atom will pull its neighbours inwards rather than stretching the bond. Describing these transverse motions as phonons of angular frequency $\omega$ and atomic displacement $u$, classical harmonic phonon theory gives $\langle u^2 \rangle = k_B T / m \omega^2$, where $T$ is the temperature. By geometry, if the bonds do not change their length, the thermal motion reduces the lattice parameter $a$ from a value $a_0$ at low temperature to $a \approx a_0 (1 - \langle u^2 \rangle / \omega^2) = a_0 (1 + a T)$, giving a negative value of the coefficient of linear thermal expansion, $a = a^{-1} \partial a / \partial T = -k_B / m a_0^2 \omega^2$. There are two ways in which this simple picture is far from a complete explanation. First, it represents thermal expansion in terms of a single type of vibration, but in reality the coefficient of thermal expansion is a weighted sum over every vibrational mode, many of which (typically including the bond stretching vibration) will contribute towards positive thermal expansion. Thus the phonons that give the tension effect may be too small a fraction of the total number of vibrations, and we need to understand the physical reasons why they will be sufficiently significant to give overall NTE. In this regard, there is currently no physical understanding of why our subject material, ScF$_3$, shows NTE, whereas almost every cubic perovskite material has positive thermal expansion, even though they all have the same basic network structure.

Second, the fragment of a structure shown in isolation when we visualise the tension effect, like the chain we discussed above, is in reality part of a nearly-infinite crystal structure. The connections to the rest of the structure give constraints that can significantly reduce the flexibility of the fragment and hence reduce the contribution of the tension effect to thermal expansion. Simply isolating a small part of the structure and hoping this gives an explanation for NTE is naive at best. Thus there is an urgent need for a more holistic understanding of NTE systems, and simply calculating whether a material has NTE on the basis of the behaviour of phonon modes does not constitute an explanation.

We present here an experimentally-derived atomistic...
model for NTE in the prototypical material ScF₃, obtained from a total scattering experiment analysed using the Reverse Monte Carlo (RMC) method. Whilst there have been a few reports of total scattering measurements of NTE materials, including ScF₃ itself, they have not been used to generate an atomic model of the fluctuations associated with NTE which could provide a consistent demonstration of the tension effect. The atomic configurations generated by the RMC method are consistent with both the local and long-range structure of the material, and contain the contribution from every vibrational mode. Our analysis of the configurations, and their variation with temperature, builds a lot of new detail onto the traditional understanding of the tension effect. In addition to seeing the expected thermal expansion of the Sc–F bond even as the Sc···Sc distance decreases, we have shown that the fluctuations associated with the tension effect are a mix of whole-body rotations and bond-bending distortions of ScF₆ octahedra.

In the final part we separately analyse the effects of anharmonicity in ScF₃, through an evaluation of the variation of the distribution of atomic displacements with temperature. Anharmonicity has the effect of reducing NTE at high temperatures, and it has been suggested that one important phonon in ScF₃ has a large anharmonic energy. Here we demonstrate that anharmonicity in the form of quartic terms involving individual modes does not significantly affect the distribution of atomic displacements, suggesting that NTE can be understood within the context of the traditional quasiharmonic approximation when taking account of quartic anharmonicities through phonon renormalisation, rather than through the effect on the intrinsic energy of certain individual phonon modes.

II. BACKGROUND: RECIPROCAL-SPACE MODEL OF NEGATIVE THERMAL EXPANSION IN ScF₃

Scandium trifluoride, ScF₃, has the rhenium trioxide structure, equivalent to the perovskite structure with a vacant A site (Figure 1). It displays isotropic negative thermal expansion over the range 0 K to 1100 K, with a linear coefficient of thermal expansion of $\alpha = -10 \text{MK}^{-1}$ at 200 K. This can be rationalised in terms of the tension effect: since the Sc–F bond is relatively stiff, the F atom will mostly vibrate in a direction perpendicular to the Sc–F–Sc line, as indeed we see from the experimental atomic displacement parameters represented in Figure 1. These transverse motions of the F atom will pull its two neighbouring Sc atoms closer together and, since all F atoms will have similar motion, this will lead to an overall reduction in the dimensions of the crystal consistent with the simple picture of the chain of atoms discussed above.

Accurate calculations of the phonon dispersion curves of ScF₃ show that the lowest-energy phonons with transverse motions of the F atoms involve whole-body rotations of the ScF₆ octahedra. These modes are known as the Rigid Unit Modes (RUMs), and their existence provides a natural mechanism for the tension effect in NTE materials since they have the necessary low energy. However, in the case of ScF₃ RUMs only exist for wave vectors along the lines symmetrically related to $(\frac{1}{2}, \frac{1}{2}, 0)$ for $-\frac{1}{2} < \xi < \frac{1}{2}$, where the points $\xi = 0$ and $\xi = \pm \frac{1}{2}$ are labelled $M$ and $R$ respectively. Thus the line of wave vectors of RUMs in ScF₃ occupies a tiny – effectively infinitesimal – fraction of reciprocal space, and necessarily virtually all phonons must involve distortions of the ScF₆ octahedra. These include the phonons whose wave vectors are close to, but not exactly on, the line $M$–$R$; these too have been shown from ab initio calculations to contribute to NTE. Even if the pure RUM motions have the highest contribution to NTE of any phonon, the tiny weighting of this set of phonons in reciprocal space means that the tension effect model will necessarily involve distortions of the ScF₆ octahedra. One of the purposes of this paper is to quantify this properly, by transforming back into real space where localised motions can be described as a superposition of all phonon modes. This will give us a new perspective of the role of RUMs in the tension effect that will be applicable to many NTE materials, and will enable us to understand, for the first time, why NTE can exist in some materials but not in other materials with close structural similarity.
mean bond length, and indeed as expected the Sc–F bond shows normal positive thermal expansion (expansion coefficient $\alpha = +15 \text{ MK}^{-1}$) whereas $a/2$ decreases on heating defining the negative thermal expansion. This result is consistent with a recent x-ray study.\(^\text{14}\) Figure 2 also shows the temperature dependence of the mean distance between neighbouring Sc atoms. One might expect, given the locations of the Sc atoms, for this distance to reflect exactly the lattice parameter. However, although slight, we see a difference between these two quantities that grows on heating, with the Sc···Sc distance showing a slightly weaker dependence on temperature than for the linear dimensions of the crystal, and a change to positive expansivity at a lower temperature. A similar effect was seen in Zn(CN)$_2$, where the (negative) expansivity of the Zn···Zn distance is less negative than the linear expansivity of the crystal.\(^\text{16}\) In that case the difference is due to the fact that the primary mechanism for NTE is from the acoustic modes.\(^\text{27}\) This is of course different to ScF$_3$, where the main NTE modes are rotational modes of optic character that lie along the edges of the Brillouin zone. However, by symmetry these modes transform into transverse acoustic modes as the wave vectors changes from the $M$–$R$ line to zero, as seen in the dispersion curves reported in references 15 and 28. We propose that the behaviour of the Sc···Sc distance is associated with this feature.

### III. A REAL-SPACE ANALYSIS OF NEGATIVE THERMAL EXPANSION IN ScF$_3$

We collected total neutron scattering data from a powder sample of scandium trifluoride, measuring both the Bragg scattering – sensitive to the long-range order – and the diffuse scattering. From these data, we obtained the pair distribution function $D(r)$ (see Methods section), which is effectively a histogram of instantaneous interatomic distances. We then used the Reverse Monte Carlo (RMC) method\(^\text{29} - \text{28}\) to obtain a set of atomic configurations consistent with these data, each of which can be regarded as a plausible snapshot of the instantaneous atomic positions in this material.

The experimental lattice parameter is shown in Figure 2 plotted as $a/2$ (black circles, filled representing data from longer measurements and open from shorter measurements, with guide to the eye), half of the average instantaneous nearest-neighbour Sc···Sc distance obtained from analysis of the RMC configurations (red filled circles and guide to the eye), and the average instantaneous nearest-neighbour Sc–F distance also obtained from analysis of the RMC configurations (grey squares and guide to the eye). In each plot statistical error bars are smaller than the sizes of the data symbols.

In Figure 2 we show the details of an analysis performed using the GASP method, based on using geometric algebra to represent the rotations of polyhedral groups...
FIG. 3: (a) Comparison of the fluctuations of three angles associated with local motions taken from the RMC configurations. The red points show the departure of the Sc–F–Sc angle from its nominal value of 180°, the blue points show the variance of the F–Sc–F angle as it fluctuates from its nominal value of 90°, and the green points show the mean-square angle of rotation of the ScF₆ octahedra as a whole body. (b) Breakdown of the total motion (excluding displacements) of the atoms in the ScF₃ crystal from the GASP analysis of the RMC configurations, where the blue, magenta and red points and guides to the eye represent the fraction of the motion that is associated with whole-body rotations of the ScF₆ octahedra, deformations of the F–Sc–F right angles, and stretching of the Sc–F bonds respectively. In both plots statistical error bars are smaller than the sizes of the data symbols, and the lines/curves are given as guides to the eye.

TABLE I: The mismatch between different atomic configurations of a network of MX₆ octahedra and the ideal structure, decomposed by GASP into X–M–X bending, M–X stretching, and MX₆ rotation components. We compare ScF₃, a hypothetical perovskite structure in the limit as octahedra become infinitely deformable, and SrTiO₃ (reference 33). The hypothetical structure is an important comparison because, even if no rigidity constraints at all are applied to coordination octahedra, some fraction of their random distortion will always be mathematically attributable to a rigid-body rotation.

| Material    | Bend | Stretch | Rotation |
|-------------|------|---------|----------|
| ScF₃        | 70   | 10      | 20       |
| totally flexible | 75   | 5       | 20       |
| SrTiO₃      | 44   | 19      | 37       |

Comparing absolute values of ScF₃ and SrTiO₃ at a single temperature, say 300 K, we find that in SrTiO₃ the Ti–O–Ti angle fluctuates by an average of around 5° and the TiO₆ octahedra orientation fluctuates by around 2° while the corresponding sizes of the fluctuations in ScF₃ are around 14° and 7° respectively (Figure 3). On the other hand, the coefficient of thermal expansion of the Ti–O bond, 10 MK⁻¹ is comparable to that of ScF₃ cited above, with similar Sc–F and Ti–O bond lengths.

We can also compare this analysis with the phonon
dispersion curves for ScF$_3$ calculated using ab initio method$^{45}$ and calculated for SrTiO$_3$ using a shell model fitted to inelastic scattering and infrared spectroscopy$^{34}$. We see that the octahedral cation–anion stretching frequencies are very similar (20 THz in ScF$_3$ and 22 THz in SrTiO$_3$), suggesting (given the similar masses of O and F) that the bonds in both ScF$_3$ and SrTiO$_3$ are of similar stiffness. In both ScF$_3$ and SrTiO$_3$ the octahedral rigid-body rotational phonons between the $R$ and $M$ wave vectors are of very low frequency compared to the stretching mode in both materials, namely between 0.6 to 1.2 THz in ScF$_3$ and between 1.3 to 2.5 THz in SrTiO$_3$ at a temperature of 200 K. However, the bending frequencies are different. If we take, for example, the transverse acoustic mode frequency at X, \((\frac{1}{2}, 0, 0)\), which is a shear mode that reflects bending distortions of the octahedra, we find that it is lower in frequency by around a factor of 2 in ScF$_3$ than in SrTiO$_3$, meaning the corresponding force constants are 4 times smaller. This is consistent with our finding that the ScF$_6$ octahedra are more rather more flexible than the TiO$_6$ octahedra.

V. ANHARMONICITY

There is a lot of current interest in the role of anharmonic phonon interactions in NTE. Typically the most important ones are those involving fourth-order interactions, which have the effect of changing phonon frequencies. Several recent papers have studied anharmonicity in ScF$_3$ in various ways.$^{15,19,35,36}$

In renormalised phonon theory$^{57}$ the temperature-dependence of a phonon angular frequency $\omega(k, j)$ (j labels the mode for any $k$) in the high-$T$ limit varies as$^{57,58}$

$$\omega^2(k, j) = \omega_0^2(k, j) + \frac{1}{2} k_B T \sum_{k', j'} \alpha_4(k, k', j, j') \frac{\omega_0^2(k', j')}{\omega_0^2(k, j)}$$

where $\omega_0^2$ is the square of the harmonic angular frequency, and the interactions characterised by the fourth-order anharmonic parameters $\alpha_4$ couple the phonon ($\pm k, j$) to all other phonons ($\pm k', j'$). This summation includes the case $(k, j) = (-k', j')$; when this case is taken alone, it represents the independent-mode approximation. It is this approximation only that is probed in a frozen-phonon calculation$^{19}$ and it will give just a small part of the overall picture. That is, the contributions from the modes $(k, j) \neq (k', j')$ are normally much more important than only the modes $(k, j) = (-k', j')$ in determining how phonon frequencies change with temperature. The DFT calculations of Li et al.$^{15}$ suggested that for the $R$-point mode the independent-mode anharmonic potential is quite large compared to the harmonic potential, but the summation over all modes may still mean that the primary anharmonic effects come instead from interactions across the Brillouin zone. Van Roekeghem et al.$^{28}$ recently studied the anharmonicity using both x-ray inelastic scattering and through calculations of the phonon frequencies via a renormalised phonon method. They showed, consistent with most perovskites, that the low frequency branch along the line $M$–$R$ and the three lowest-frequency optic modes at zero wave vector soften on cooling, consistent with renormalised phonon theory, whereas the higher-frequency modes harden on cooling. Similar results were obtained by Oba et al.$^{19}$ The softening on cooling arises from direct anharmonic interactions via renormalised phonon theory as described here, whereas the hardening of the high-frequency modes arises primarily from thermal expansion of the Sc–F bond. In this model, the renormalised phonons continue to look like phonons with well-defined frequencies, with lifetimes substantially larger than the phonon frequency (See Figure 3 of reference $^{36}$). Separately, in reference $^{18}$ we showed from simple considerations that anharmonic renormalisation of phonon frequencies will cause NTE to shift towards positive expansivity at higher temperatures; the same result is obtained by more detailed renormalised phonon theory calculations.$^{19,25}$

We have analysed our RMC configurations to look for any effects of anharmonicity in the distributions of transverse displacements of fluorine atoms that might indicate that the independent mode model is more significant than the renormalised phonon model. This particular atomic displacement was chosen since it is active in the $R$-point RUM previously identified as having a dominant fourth-order term. Figure 4 shows the distribution of these displacements of F atoms away from the Sc····Sc line as a function of temperature. Two features of these data are noteworthy: first, the distributions are well fitted by Gaussian functions at all temperatures. Second, the fitted variance of these Gaussian distributions increases linearly with temperature, exactly as one would expect for a harmonic oscillator. We conclude that, to the extent to which anharmonicity is important in this material, it is completely described within the renormalised phonon approximation. In other words, although fourth-order interactions seen by individual phonon modes may limit their amplitude at high temperature, there is an insufficient number of such modes with near-zero harmonic terms to make an appreciable difference to the distribution of atomic positions. Thus overall the most important anharmonic interactions involve couplings between different phonons, as described by the renormalised phonon approximation rather than the independent mode approximation.

VI. DISCUSSION AND CONCLUSIONS

Our two key conclusions from the analysis of the RMC configurations discussed above are that that the vibrational modes active in this system involve appreciable distortion of the ScF$_6$ coordination octahedra, and that the transverse displacement of the F atoms, although as-
FIG. 4: (a) and (b) show histograms of the lateral displacements of the F atoms at the different temperatures (circles). At all temperatures the distributions are well described by Gaussian functions (thin lines). (c) shows the variance of the Gaussian fits as a function of temperature. The data follow a linear dependence on temperature throughout the range studied, as indicated by the fitted straight line, demonstrating that a renormalised phonon model is sufficient to describe the anharmonic effects in ScF₃.

associated with a quartic mode, can be well described by a Gaussian distribution whose width varies linearly with temperature, consistent with a renormalised harmonic phonon model. These results are closely related, since the RUMs are exactly the modes that will have small quadratic terms and in which the quartic terms are thus expected to be dominant. What they show is that the non-RUM vibrations make dominant contributions to the thermal expansion, and in particular to the NTE, of ScF₃.

We need to state clearly that the deformations of the ScF₆ octahedra do not in any way repudiate the importance of RUMs. It is a common misconception that the RUM model requires the octahedra to be very rigid, but in fact quite the opposite is true. The point is this. If we consider only the RUMs – which is the limiting case if the octahedra are incredibly stiff – the fact that they are restricted to wave vectors lying on lines in reciprocal space means that the RUMs are a vanishingly small fraction of the total number of phonon modes. Since many phonons have positive thermal expansion (see the data presented in reference [15]), they will dominate over the NTE contribution from the RUMs alone. Instead, to get overall NTE it is necessary that there is a sufficiently-large number of low-frequency RUM-like phonon modes close to the wave vectors of the RUMs. This is possible if the polyhedra (in this case the ScF₆ octahedra) have some flexibility. Thus we propose firstly that the existence of the RUMs gives a set of phonons with the necessary low frequencies and appropriate mode eigenvectors for the tension effect to give NTE, and secondly that the flexibility of the polyhedra allows the contribution from the RUMs to spread across a sufficiently large volume in reciprocal space to have enough thermodynamic weighting to give an overall NTE. This explains concisely why we have NTE in ScF₃ but only positive thermal expansion in other perovskites such as SrTiO₃; both materials have stiff cation–anion (Sc–F or Ti–O) bonds, but the TiO₆ octahedra are more resistant to bond-bending distortion than the ScF₆ octahedra.

In conclusion, our real-space analysis of ScF₃, based on using the Reverse Monte Carlo method with neutron total scattering data to generate configurations of atoms over a wide range of temperatures, has allowed us to establish a quantitative view of the structural fluctuations associated with NTE. Comparison with a similar study of SrTiO₃, together with comparisons of published phonon dispersion curves, shows the importance of RUMs in giving rise to NTE, but that is also to have some degree of polyhedral distortion to spread the contributions to NTE across a wider range of wave vectors than those associated with the RUMs. Fluorinated octahedra have bonds that are as stiff as in their oxygenated counterparts, but have more bond-bending flexibility. On this basis we suggest that in the search for materials with large negative coefficients of thermal expansion, fluorinated analogues of other oxides with NTE – one example being ZnF₂ as an analogue of the rutile phase of TiO₂ – might prove to be particularly fertile.

**METHODS**

Neutron total scattering and diffraction experiments were performed on the Polaris diffractometer at the UK ISIS spallation neutron facility. The sample was obtained commercially, and x-ray and neutron powder diffraction measurements showed that the sample is of single phase within the limits of detection. The sample was packed into a cylindrical vanadium can of radius 8 mm. Measurements for 750 μA h were obtained over the temperature range 10–1200 K, with shorter runs at intermediate temperatures performed for crystal structure analysis. Rietveld refinement was carried out using the GSAS.
The data sets used were the total scattering function after correction and subtraction of the self term, $i(Q)$, the pair distribution function (PDF) $D(r)$ obtained as Fourier transform of the function $Q_i(Q)$ (the corrections to form $i(Q)$ and conversion to the PDF $D(r)$ were performed using the GUDRUN package, and the Bragg scattering profile. Key equations and data are given in the Supplementary Information, showing the high quality of the fitting we were able to achieve.

DATA AVAILABILITY

To be added on acceptance of article.

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AUTHOR CONTRIBUTIONS

M.T.D. and A.E.P. designed the study. J.D. and M.T.D carried out the experiments, with support from D.A.K. and M.G.T.. J.D. performed the data reduction with support from M.T.D. and A.E.P. The manuscript was written by M.T.D. with revisions suggested by A.E.P. and D.A.K..

COMPETING INTERESTS

The authors declare no competing interests.

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In Figure 3(a) the sizes of the fluctuations of the ScF$_6$ orientations and F–Sc–F angles are similar, but in Figure 3(b) the GASP analysis suggest that the motions of the F atoms associated with bond bending are rather larger than from rotations of the octahedra. These results are actually consistent with each other: the contribution to $M$ from the octahedral rotation will come from three axes, but there are 12 bending angles associated with deformation of the octahedra.

We note that the research group of Angus Wilkinson has explored several fluorides with crystal structures analogous to ScF$_3$, including materials various levels of doping. Many examples display phase transitions involving octahedra rotations and which appear to be continuous (second-order). These phase transitions will be accompanied by the softening of the RUM phonons on cooling towards the transition temperature, through the types of anharmonic interactions discussed in this paper as described by equation 1. We have shown that such a variation of the renormalised phonon frequency with temperature will lead to a reduction, or even elimination, of NTE, as also demonstrated in recent calculations.

In common usage, the term *quasiharmonic* model considers the effect of changes in volume on the phonon frequencies through the consequent changes in harmonic force constants, giving new harmonic phonon frequencies as modified by the anharmonic coupling of force constants to volume. The term renormalised phonon model considers how a renormalised harmonic Hamiltonian can result from a mean-field treatment of the anharmonic interactions between phonons, typically focussing on the fourth-order interactions.