Colossal Pressure-Induced Softening in Scandium Fluoride

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The counterintuitive phenomenon of pressure-induced softening in materials is likely to be caused by the same dynamical behavior that produces negative thermal expansion. Through a combination of molecular dynamics simulation on an idealized model and neutron diffraction at variable temperature and pressure, we show the existence of extraordinary and unprecedented pressure-induced softening in the negative thermal expansion material scandium fluoride ScF_3. The pressure derivative of the bulk modulus B, $B' = (\partial B/\partial P)_{P=0}$, reaches values as low as -220 ± 30 at 50 K, and is constant at -50 between 150 and 250 K.

Just over 20 years ago a seminal paper on negative thermal expansion in ZrW_2O_8 [1] marked the beginning of a new area in materials chemistry and physics that has led to the discovery of many materials whose phonon behavior gives rise to highly anomalous physical properties. Since then we have seen not only many more materials showing negative thermal expansion, but also increases in the size of expansivities [2–4]. For example, around ten years ago, record positive *and* negative expansivities were reported in the network material $Ag_3Co(CN)_6$ [5]. Other counterintuitive properties related to atomic structure include negative linear compressibility [6] and negative Poisson's ratio [7]. More recently we have identified a new negative structural property, *pressure-induced softening*, in which the material becomes softer (less stiff) under pressure [8–11]. In this Letter we report a new instance of this property with an extremely large, indeed unprecedented, negative size of the associated coefficient.

Negative thermal expansion (NTE) is counterintuitive because any individual chemical bond always shows *positive* thermal expansion: it is harder to push two atoms together from the equilibrium distance than it is to pull them apart. Experimentally, positive thermal expansion of individual bonds has been directly observed in a number of materials, including the title material ScF_3 [12–18]. The asymmetry in the distance dependence of the bond potential

means that at high temperature the vibration of the bond involves the bond stretching more than compressing, leading to an increase in the average separation, as illustrated in Fig. 1(a). This positive thermal expansion of the chemical bond usually leads to positive thermal expansion of the whole crystal. One common reason for negative thermal expansion of a crystal is called the "tension effect," which is illustrated in Fig. 1(b). Transverse motion of an atom strongly bonded to two neighbors on opposite sides will pull their mean positions inward, thereby reducing the average separation. This effect increases with temperature, leading to a negative expansivity, even with positive expansivities of the bonds. For a material such as the subject of this Letter, ScF_3, the transverse atomic motions associated with the tension effect are seen in the atomic displacement parameters, as shown in Fig. 1(c). We recently quantified this using neutron scattering methods [18].

Pressure-induced softening is also counterintuitive, for similar reasons. The asymmetry of the potential energy of the chemical bond means that the more a bond is compressed, the harder it is to compress further, and the more the bond is stretched, the easier it is to stretch it further. Thus we expect any material to become stiffer as it is compressed. An familiar example is the snowball: it is soft when first formed, but then compression in the hand turns it into a hard sphere. However, in 1998 it was observed that amorphous silica shows the opposite behavior over the pressure range 0–1.5 GPa [19]. It is as if the snowball gets softer the more we squash it. Resistance to compression is quantified by the bulk modulus, $B = -V\partial P/\partial V$; its pressure dependence, $B' = \partial B/\partial P$, is our quantity of interest here. A negative value of B' indicates pressure-induced softening [8–11]. We previously reproduced the
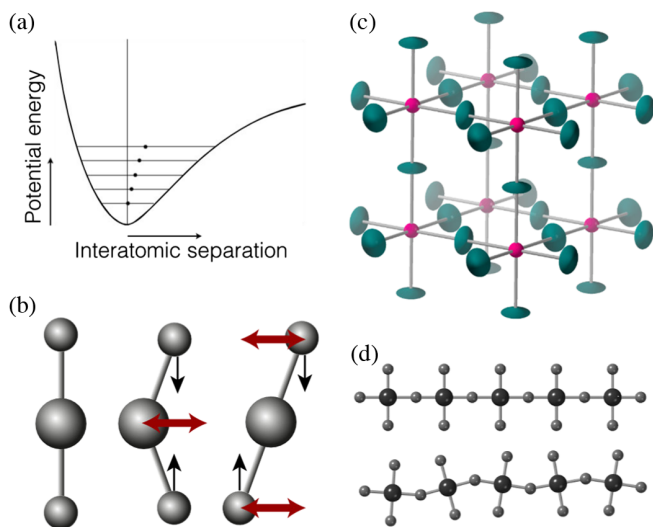
(a)

(c)

(b)

(d)

FIG. 1.   (a) Representation of the potential energy of a bond between two atoms as a function of separation r: the mean separation increases with temperature. (b) Illustration of the tension effect: transverse motions of an atom connected to two other atoms will pull the neighboring atoms together if the motions do not stretch the bonds. (c) Crystal structure of ScF_3 showing transverse motions of the F atoms by representing the atoms as ellipsoids whose major axes reflect the thermal motion. (d) Top: A perfect alignment of atomic octahedra as in ScF_3. In this arrangement compression (stretching) along the horizontal axis involves compression (stretching) of the bonds. Bottom: An elevated-temperature configuration where the thermal motion has rotated the octahedra. Compression or stretching now involves rotations of the bonds.

experimental negative value of B' in amorphous silica [19] using molecular dynamics simulations [20], and showed that the effect is strongly correlated with the same sort of structural fluctuations that give rise to negative thermal expansion.

Perhaps the best-known example of pressure-induced softening—which has attracted continued scientific interest precisely because of its rarity—is the minimum in the bulk modulus of cerium metal coinciding with the "volume collapse" at the transition from the γ to the α phase [21–25]. This phase transition is driven by the electronic rather than the phonon structure, although the exact mechanism is still debated. The associated pressure-induced softening is characteristic of "pseudocritical" behavior above a structural phase transition [26]. In theory, such behavior can be described in terms of the specific heat critical exponent α, with $B \sim (P_c - P)^\alpha$ and therefore $B' \sim -\alpha B/(P_c - P)$, diverging to negative infinity at the critical pressure P_c. In practice, however, this cannot be used to achieve arbitrarily low B': typically, a first-order phase transition occurs at a spinodal point well before this pressure [26]. Furthermore, B' values typically increase rapidly away from the critical point. At the critical point of Ce, where the bulk modulus indeed drops to zero, $B' \approx -58$, but this

increases rapidly as the temperature and pressure are changed, and in particular approaches zero at ambient pressure [25].

A simple explanation for a vibrational, rather than electronic, origin of pressure-induced softening is presented in Fig. 1(d), which shows two linear arrangements of octahedra. In the case of perfect alignment, compression or stretching of the system involves compressing or stretching the bonds between atoms. If these bonds are strong—which they usually are—the elastic modulus is large. At a raised temperature, thermal atomic motion involves crumpling of the arrangement. In this case, compression is made easier because it can now be achieved by further rotations of the bonds, requiring much less force in general than compressing bonds. This point has been discussed elsewhere in the context of the rigid unit mode model [27,28], a set of ideas related to how the flexibility of the network of corner-shared structural polyhedra (such as SiO_4 tetrahedra in silicates, TiO_6 octahedra in perovskites, and ScF_6 octahedra in the title material) impacts the nature of the lattice vibrations and thence on behavior such as phase transitions [28,29] and negative thermal expansion [30]. With large rotations, the projection of the longitudinal compressional force resolves more onto causing octahedral rotations than onto compression of individual bonds. Larger external pressure then causes even larger rotations, and the material becomes even softer. This is pressure-induced softening. Equivalently, we can consider stretching the crumpled chain: expansion first reduces the degree of rotation, until it reaches the point where further stretching of the system can only be accommodated by stretching the bonds, so that the system becomes elastically stiffer on stretching.

Pressure-induced softening has been observed in two materials that show negative thermal expansion, ZrW_2O_8 [31] and $Zn(CN)_2$ [32]. We previously simulated pressure-induced softening in $Zn(CN)_2$ by the molecular dynamics method [8], reproducing the experimental result. We also predicted a particular temperature dependence of B', which we subsequently confirmed experimentally [9]. Using an analytical model we showed that pressure-induced softening may be *inevitable*—rather than merely *possible*—in materials that show negative thermal expansion [10], and in a simulation of several zeolites we showed that this prediction is reasonable [11].

ScF_3 has attracted a lot of interest for its negative thermal expansion [16,18,33–40]. The crystal structure is shown in Fig. 1(c): it is so irreducibly simple that it is effectively one of the few possible three-dimensional generalizations of the standard one-dimensional diatomic chain [41]. The cubic structure of ScF_3 is exceptionally stable. In particular, unlike other 3d transition metal trifluorides, at ambient pressure there is no sign of a phase transition to a rhombohedral structure down to 0.4 K [42], suggesting
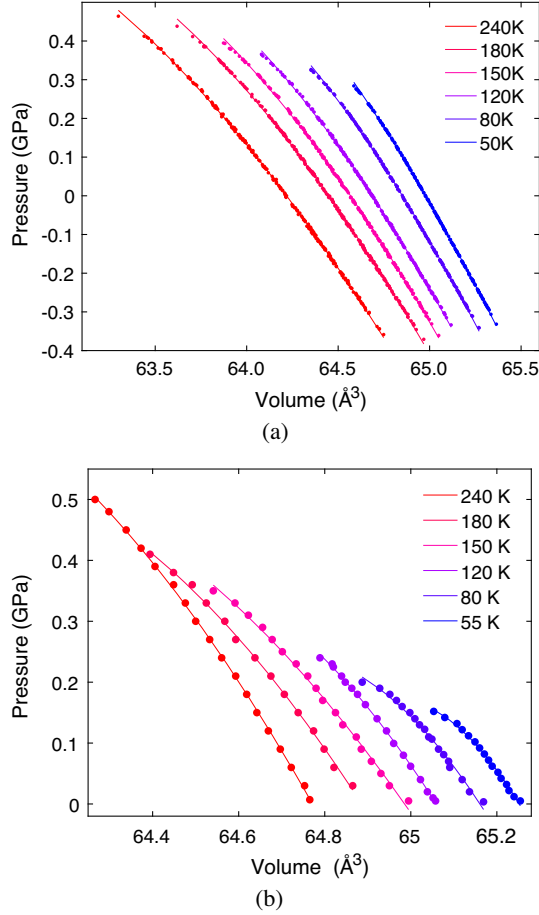
(a)

(b)

FIG. 2. $P(V)$ curves showing data from molecular dynamics simulation (a) and diffraction experiment (b) shown as filled circles, with the fitted third-order Birch-Murnaghan equation of state [Eq. (1)] shown as curves.

(a)

(b)

FIG. 3.   Temperature dependence of B_0 (a) and B' (b) obtained from fitting the third-order Birch-Murnaghan equation of state to crystal volume obtained from molecular dynamics simulation of our idealized model for ScF_3. The actual fitting is shown in Fig. 2(a).

that the system is near a quantum phase transition [43]. On the other hand, the rhombohedral phase can be stabilized by an applied pressure of 0.7 GPa at ambient temperature [44]. Because of both the anomalous thermal expansion and the proximity to a pressure-induced phase transition, one might expect this material to be a strong candidate for pressure-induced softening.

To explore the dynamics of the ScF_3 structure, we developed a deliberately very simple atomistic model, with only a single bond-stretching interaction (Sc–F) and two bond-bending interactions (Sc–F–Sc and F–Sc–F); full details are given in the Supplemental Material [45]. The parameters were tuned by comparing the predictions with the results of *ab initio* calculations [35]. Molecular dynamics simulations using this model showed negative thermal expansion, as expected (Fig. S1 in the Supplemental Material [45]).

We analyzed the pressure dependence of the atomic structure in the simulation over a wide range of temperatures, analyzing the results using the standard third-order Birch-Murnaghan equation of state:
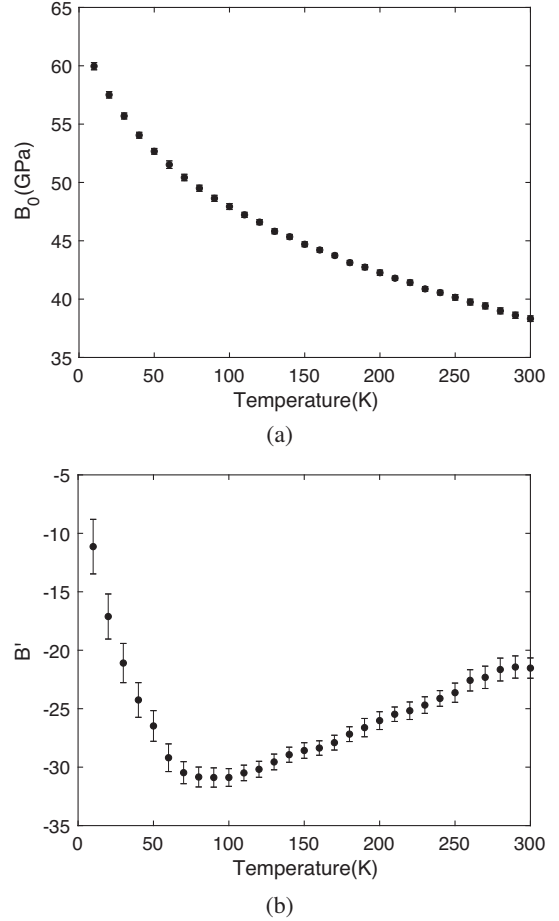
$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right]$$
$$\times \left\{ 1 + \frac{3}{4}(B' - 4) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}, \quad (1)$$

where P and V are the pressure and volume respectively, and V_0 and B_0 are the values of V and B at zero pressure. As an expansion of the second-order Birch-Murnaghan equation of state, the third-order equation reduces to the second-order form when $B' = +4$, and many experimental systems actually have values of B' of roughly this size. Data for the functions $V(P)$ showing the fitted equation of state are shown in Fig. 2(a), and the fitted results for B_0 and B' are shown in Fig. 3. The temperature dependence of B' is very similar to that seen in $Zn(CN)_2$ and zeolites [9,11,57], with a rapid change in the value of B' on heating from zero temperature, until reaching a minimum value (the most negative value) and then a slow change to less negative values on further heating [57]. What is astonishing is that our model for ScF_3 predicts values of B' as extreme as -30.
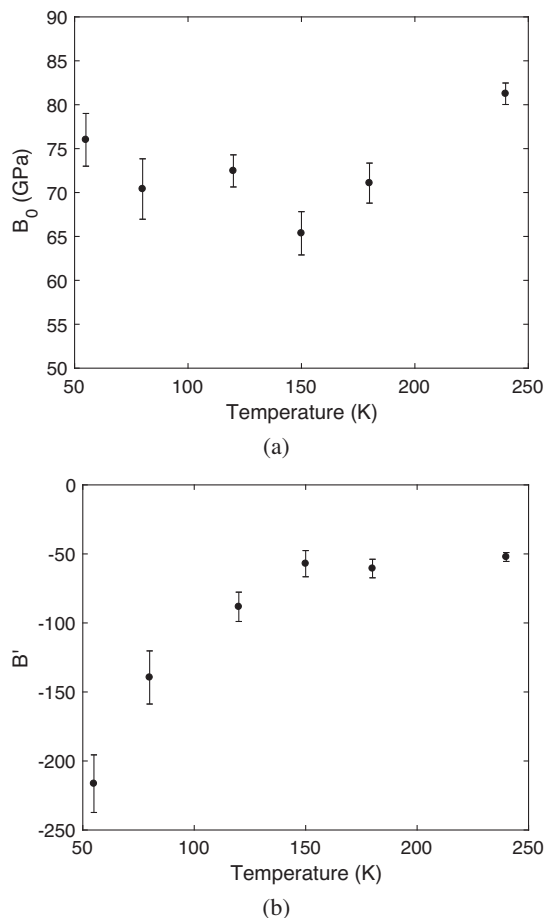
(a)

(b)

FIG. 4. Temperature dependence of B_0 (a) and B' (b) obtained from fitting the third-order Birch-Murnaghan equation of state to experimental data for the crystal volume as obtained from Rietveld analysis of diffraction data. The fitting is shown in Fig. 2(b).

FIG. 5. Mean-squared transverse displacement of the F atoms obtained from refinement of the crystal structure.

As we noted above, negative values of B' are very rare; such a large negative value due to a phonon mechanism is unprecedented, and a comparable value is achieved by Ce only close to its critical point.

To follow up this prediction we performed neutron powder diffraction measurements of ScF_3 under pressure for different temperatures on the GEM diffractometer at the ISIS spallation neutron facility. The diffraction patterns were fitted using the Rietveld method to obtain the lattice parameters and the atomic displacement parameters (all other aspects of the crystal structure are established by symmetry). All details of the experimental and analysis methods are given in the Supplemental Material, with a representative fit to the data shown in Fig. S2 [45].

The resultant experimental $P(V)$ for different temperatures were fitted by the third-order Birch-Murnaghan equation of state and shown in Fig. 2(b). The fitted values of B_0 and B' are shown in Fig. 4. The astonishing result is that the extraordinarily large negative values of B' predicted by simulation are not only reproduced but are *exceeded* in
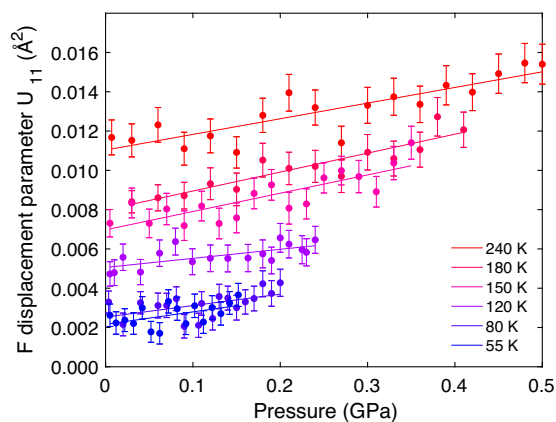
the experimental results, with a greatest negative value of $B' < -200$. We checked the robustness of this result by trimming the data range used in the fitting, and obtained results each time that are consistent within the estimated standard deviations. It might be argued that the third-order Birch-Murnaghan equation of state was not developed in anticipation of such large negative values of B', given that its derivation involves a Taylor expansion. However, the facts that the function fits the data to within the statistical accuracy, and that the fitting gives consistently large values of B' with relatively small estimated standard errors, are quantitative indications of the remarkable behavior seen here.

Figure 5 shows the fitted values of the fluorine transverse atomic displacement parameter—essentially the mean-square atomic displacement—as functions of pressure for different temperatures. This corresponds to the large transverse axis of the ellipsoids shown in the crystal structure, Fig. 1(c). At low pressure this quantity increases linearly with temperature as expected if the displacements are associated with thermal motions (Fig. S7 in the Supplemental Material [45]). Consistent with the ideas presented here, the data presented in Fig. 5 show that the mean-square amplitude of transverse motion of the fluorine atoms *increases* with pressure. On the other hand, in most materials the phonon frequencies increase under pressure due to force constants increasing, and higher frequencies lead to lower mean-square amplitudes of thermal motion. The behavior shown in Fig. 5 is consistent with enhanced rotations of the Sc–F bonds on increasing pressure. By contrast, the mean-square amplitudes of the other motions (isotropic motion of the Sc atom, longitudinal motion of the F atom) show no pressure dependence (Fig. S8 in the Supplemental Material [45]). These results are reproduced in the results of the molecular simulations on the simple model (Fig. S5 in the Supplemental Material [45]).

To explain why the pressure-induced softening of ScF_3 is so extreme, we consider our simple potential model. Recall that this has a stiff Sc–F bond, and two terms that control the flexing of the F–Sc–F right angle in the ScF_6

octahedron and of the linear Sc–F–Sc angle. Our recent total scattering study of ScF_6 [18] shows that there is considerable flexing of both these angles as compared with corresponding motions in other perovskites. The fact that NTE is largely absent in oxide perovskites suggests that this higher level of flexibility is essential for the mechanism of NTE, and by extension to the enhanced pressure-induced softening seen in ScF_3. To confirm this, in separate simulations we increased the parameters governing each angle term to increase the forces opposing bending. We found that increasing either of these parameters leads to a clear reduction in NTE, indeed turning the thermal expansion into positive expansivity. The effect is strongest from the F–Sc–F angle term, where increasing the value of the force constant by a factor of only 3.3 is sufficient to drive the thermal expansivity to a positive value [18]. Our simulations show further that the same changes in the model parameters will reduce the negative size of B'. This confirms that the enhanced pressure-induced softening in ScF_3 is associated with the high degree of angular flexibility found in this material.

Such large negative values of B' as seen in this study for ScF_3 are extraordinary: substantially greater than those for Ce metal, and greater still compared to other examples that arise from a vibrational rather than electronic mechanism. $Zn(CN)_2$, for example, only has B' down to values of -9.0 ± 0.7 [9]. The values of B' seen in this study (Fig. 4) are so far outside the norm that it seems appropriate to recognize this by calling the effect "colossal pressure-induced softening" [58].

Because of the link we have demonstrated between anomalous thermodynamic properties, the same crystal-engineering techniques used to design negative thermal expansion materials will be useful in discovering additional colossal pressure-induced softening materials. From a technological perspective, pressure-induced softening is particularly relevant to composite materials, where internal stress will be induced by differing thermal expansivities. By showing how extraordinarily large such effects can be, our results emphasize the importance of taking them into account when designing such composites. But we anticipate that colossal pressure-induced softening will also be a powerful tool that can be used to deliberately tune the thermodynamic behavior and physical properties of materials.

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[45] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.124.255502 for more details on the crystal structure of ScF_3; information about the molecular dynamics simulations with details of the method and implementation and some pertinent results not given in the main paper; and information about the neutron

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