Criticality, entropic elasticity, and negative thermal expansion of a Coulomb floppy network: ScF$_3$-inspired theory for a class of ionic solids.

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Floppy Networks (FNs) play a prominent role in soft condensed matter, from polymers and rubber to biomolecules, glasses, and granular materials. They provide valuable insight into the origin of anomalous mechanical and thermal properties of these systems. Here, we demonstrate how the very same concept of FN emerges in the context of a family of crystalline ceramic materials, an open framework ionic solids, which can be conceptualized as Coulomb floppy networks. One remarkable example is ScF$_3$ which exhibits a number of unusual properties, including quantum structural phase transition near ambient pressure and negative thermal expansion (NTE). Yet other examples are found among diverse families of topical materials, from pure silicon to superconducting cuprates and iron pnictides, whose anomalous vibrational and structural properties and still ill-understood. Our microscopic theory traces these effects to a FN-like crystalline architecture, which is stabilized by the net electrostatic repulsion that plays the role similar to an osmotic pressure in a polymeric gel. NTE in this type of inorganic solids has essentially the same origin as in gels and rubber. For ScF$_3$, our theory provides an accurate quantitative description of NTE, compressibility, and structural phase diagram, all in excellent agreement with multiple experiments. The entropic stabilization of criticality explains the observed phase behavior, while significant entropic contribution to elasticity accounts for the marked discrepancy between the experimentally observed compressibility and the \textit{ab initio} calculations. Our results explain a range of exotic properties of topical open framework solids and pave the way to engineering new classes of self-assembled metamaterials with tunable structural and thermomechanical properties based on the concept of Coulomb FNs.

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Theoretical understanding of condensed matter invariably rests on the concept of the hierarchy of energy scales associated with various intra- and inter-atomic interactions. Typically, the full microscopic Hamiltonian is reduced to an effective model, which describes the low-energy degrees of freedom, subject to the constraints imposed by the high-energy interactions. Floppy Networks (FNs) is a class of such models, in which constituent particles are bound by rigid links and where the total number of constraints imposed by these links is smaller than required for the global rigidity of the system, i.e. violating the Maxwell’s criterion of mechanical stability. A simple and intuitive physics of under-constrained FNs has been widely used in soft condensed matter, where it plays prominent role in explaining anomalous mechanical and thermal properties of polymers, rubber, fibers, glasses, and granular materials [1–8]. The defining feature of a FN is the existence of zero-energy deformations. These "floppy" modes lead to a number of unusual properties, including non-Gaussian fluctuations, entropic elasticity, negative thermal expansion (NTE), fragile behavior, and topological edge modes.

In contrast, FN-type models found a very limited use in the realm of traditional solid state physics. This is surprising, because interactions between the nearest atoms in many crystalline materials are significantly stronger and more rigid than all others, yet their number is often not sufficient for the global rigidity of the structure. This makes FN an excellent starting point for describing many complex crystalline solids. In this paper, we illustrate the potential of this approach by constructing a comprehensive microscopic theory of a particular family of open-framework ionic crystals, which recently gained prominence thanks to the observation of large and tunable isotropic NTE, crucial for many technological applications [9–22]. One remarkable representative of this family is ScF$_3$ [23–27], where NTE is observed in the vicinity of an underlying quantum phase transition: the cubic lattice becomes unstable under very modest external pressure, often less than 1 GPa. In the absence of controlled microscopic theory, the question of the physical origin of NTE in ScF$_3$ remained controversial. The two leading contenders are quartic phonon anharmonicity [26] and the correlated anion vibrations known as rigid unit modes (RUMs) [14]. In either case, ScF$_3$ with its simple, empty perovskite crystal structure [Fig. 1(a)] has been proposed as a perfect example of the respective mechanism. Here, we develop a microscopic theory which shows that neither of these mechanisms is crucial for the observed anomalous behaviors.

Our theory describes ScF$_3$ and other ionic compounds with FN architecture as Coulomb Floppy Networks. The theory explains both NTE and the underlying structural phase transition and provides an accurate quantitative account for the experimental observations [15–27]. Furthermore,
our FN-based description allows one to make a connection to other well known examples of NTE materials: the polymeric gels and rubber, usually considered to be completely unrelated to crystalline solids. While we focus at the specific case of cubic ScF$_3$ sketched in Fig. 1(a), most of our conclusions can be adapted to other crystalline materials featuring FN architecture. In fact, such is the situation in many systems of high topical interest, ranging from pure silicon, which shows NTE at low temperature, to superconducting cuprates and iron pnictides [28–30], where strong, highly covalent nearest-neighbor bonds form under-constrained FNs.

In constructing our theory, we capitalize on a clear separation of energy scales between those deformations of ScF$_3$ lattice that do change the lengths of stiff Sc-F bonds and those that do not. We formalize this idea by representing all the interactions between the nearest-neighbor Sc and F ions with a single potential, $V_b(r_{ScF})$. A convenient starting point is to assume that this potential is infinitely rigid, which corresponds to the FN limit where all Sc-F bonds have a fixed lengths, $r_b$. This assumption is later relaxed, leading to a controlled perturbation theory.

In the absence of other interactions between the ions, our system would be a true floppy network: with 12 degrees of freedom and 6 constraints per unit cell, there would be 6 zero energy modes that do not change the lengths of Sc-F bonds. These ”floppy” modes can be parameterized by displacements, $u_{n\nu}$, of F ions in the directions perpendicular to the corresponding primitive vectors of the cubic lattice, $a_\nu$ ($n$ indexes the sites of the cubic lattice and $\nu = x, y, z$ corresponds to the position of the F ion with respect to Sc in the unit cell). In the leading order, there is no displacement of F along the Sc-F bond, i.e., $a_\nu \cdot u_{n\nu} = 0$. If $r = a/2$ is half of the lattice constant, it must satisfy the following geometric constraint,

$$r^2 - r_b^2 + \langle u_{n\nu}^2 \rangle = 0.$$  (1)

The Coulomb energy of an ideal cubic ScF$_3$ lattice is expressed as $-3NM\tilde{e}^2/r$, where $N$ is number of Sc ions (unit cells), $M = 2.98$ is the Madelung constant, and effective static charges of Sc and F ions are $3\tilde{e}$ and $-\tilde{e}$, respectively. In an ideal ionic crystal, $\tilde{e} = e$ is electron charge; in real materials it is reduced by covalency. Since the electrostatic interactions between the nearest Sc and F ions are already included in $V_b$, we only need to account for the contributions from all other pairs of ions, which results in the electrostatic term, $3N(6 - M)e^2/r$, in the Hamiltonian. In order to incorporate the geometric constraint, Eq. (1), into our theory, we introduce the conjugated Lagrange multiplier field, $\kappa/4$. Exponentiating the constraint in a standard way, we obtain an
FIG. 1. Crystal structure and schematics of Coulomb floppy network model in ScF$_3$. (a) A simple, empty perovskite cubic structure of ScF$_3$. (b) The floppy network structure of ScF$_3$ is stabilized by net Coulomb repulsion. Thermal motion of F ions (green spheres) transverse to rigid Sc-F bonds pulls Sc ions closer together, leading to NTE. (c) In a polymer gel, a disordered floppy network is stabilized by internal osmotic pressure [1–4]. (d) Schematic representation of quasi-RUM eigenmodes, which can be viewed as “breathing rotations” of ScF$_6$ octahedra where the coordinated movement of F ions results in extension of inter-ionic bond lengths, in contrast to RUMs (circular arrows), which preserve rigid octahedra.

additional term, $\delta H = 3N \kappa (r^2 - r_b^2 + \langle u^2 \rangle)/2$, in the effective Hamiltonian of the system,

$$H_{eff} = K + 3N \left[ \frac{(6 - M) e^2}{r} + \frac{\kappa (r^2 - r_b^2)}{2} \right] + \frac{\kappa}{2} \sum_{n,\nu} u_{n\nu}^2 + 8N r^3 P + \frac{z^2 e^2}{2r^3} \sum_{n,\nu,\nu'} u_{n\nu} \hat{G}_{n\nu,\nu'} \cdot u_{n'\nu'}.$$

(2)

Here, $K$ is kinetic energy, $8N r^3 P = PV$ accounts for external pressure, and the last term describes the fluctuational corrections to the electrostatic energy associated with the transverse dis-
placements of F ions. Note, that the dynamic effective charge, $z\epsilon$, which relates ion displacement to the resulting dipole moment (known as Born effective charge) is in a general case different from the static charge, $\tilde{\epsilon}$, that enters the Madelung energy.

The electrostatic repulsion between non-nearest neighbor ions provides the tension force that stabilizes the structure and renders finite stiffness to the floppy modes. The equilibrium values of $\kappa$ and $r$ can be found by minimizing free energy, or, equivalently, $\langle H_{\text{eff}} \rangle$. Minimization with respect to $\kappa$ simply recovers the original geometric constraint, Eq. (1). On the other hand, minimization with respect to $r$ yields the Lagrange multiplier, $\kappa = (6 - M)\tilde{\epsilon}^2/r^3 - 8rP$. This parameter determines the tensile force applied to each Sc-F-Sc link, $f = \kappa r/2$, which balances the negative internal pressure due to the net electrostatic repulsion. Its effect can be compared to the osmotic pressure in a polymer gel, which results in stretching of an otherwise floppy polymer network, making it rigid, as illustrated in Fig. 1(b)-(c). The (positive) external pressure reduces the tension on Sc-F bonds and therefore shifts the system back towards the floppy network regime.

After switching to Fourier representation, $u_{q\nu} = \frac{1}{\sqrt{N}} \sum_n u_{n\nu} e^{-i q \cdot r_n}$, and diagonalization of the dipole tensor $\hat{G}_{q,\nu\nu'}$, the canonical Hamiltonian of an uncoupled oscillators is obtained,

$$H_{\perp} = \sum_{q,\sigma} \left[ \frac{|p_q^{(\sigma)}|^2}{2m_F} + \frac{\tilde{\epsilon}^2}{2r^3} \left( 6 - M - P/P_0 + \gamma_q^{(\sigma)} \right) |u_q^{(\sigma)}|^2 \right].$$ (3)

Here, $P_0 = \tilde{\epsilon}^2/8r^4 \approx 14.6$ GPa (assuming $\tilde{\epsilon} = 0.9\epsilon$ [27]). The frequencies of F phonons obtained from this Hamiltonian are,

$$\hbar \omega = \hbar \omega_0 \sqrt{6 - M + \gamma_q^{(\sigma)} - P/P_0},$$ (4)

where $\hbar \omega_0 = \hbar \tilde{\epsilon}/\sqrt{r^3m_F} \approx 18$ meV.

Adopting the point-charge approximation, i.e. neglecting electronic polarizability of the ions and the difference between static and dynamic effective charge, $z\epsilon = \tilde{\epsilon}$, we obtain the dispersion curves shown by dashed lines in Fig. 2(a). The energy gap, $\hbar \omega_{\text{min}} = \hbar \omega_0 \sqrt{\epsilon_0 - P/P_0}$, is controlled by parameter $\epsilon_0 = (6 - M + \gamma_{\text{min}})$, where $\gamma_{\text{min}} = \min\{\gamma_q^{(\sigma)}\}$. In a qualitative agreement with the experiment [23, 24], application of an external pressure reduces the soft mode gap, leading to structural instability. Within the point-charge approximation, however, $\gamma_{\text{min}} = \gamma_{\text{min}}^{(0)} \approx -2.71$ and $\epsilon_0 \approx 0.31$, which results in a large gap, $\approx 10$ meV at $P = 0$, and critical pressure $P_c = \epsilon_0 P_0 \approx 4.5$ GPa, both of which are significantly higher than the experimental values.
Going beyond the point-charge approximation, one needs to account for electronic polarizabilities of F and Sc ions, $\alpha_F$ and $\alpha_{\text{Sc}}$, respectively, and allow for a difference between the static and dynamic effective charges [27, 31]. These effects lead to the renormalization of the gap parameter,

$$\epsilon_0 = 6 - M + \gamma_{\text{min}} = 6 - M + \gamma_{\text{min}}^{(0)} \left( \frac{z e}{\tilde{e}} - \frac{\gamma_0 \alpha_F}{r^3} \right)^2 \left( \frac{1 + \gamma_0 \alpha_F/r^3}{1 + (\gamma_{\text{min}}^{(0)} + \gamma_0) \alpha_F/r^3} \right),$$  

(5)

where $\gamma_0 = -\sum_{\sigma} \gamma_{q}^{(\sigma)}/6 \approx 0.90$ is obtained within point-charge approximation [27, 31]. In principle, both effective charges and electronic polarizabilities can be obtained from first principle calculations [32, 33], or from experiment [34]. However, in order to reliably determine parameter $\epsilon_0$ and thus the critical pressure they need to be known with an exceptional precision. According to Eq. (5), if we assume the polarizability $\alpha_F = 1.0 \text{Å}^3$ the spectral gap becomes zero at $ze/\tilde{e} \approx 0.994$, while a change to $\alpha_F = 1.3 \text{Å}^3$ [27, 34] could be offset by a $< 2\%$ adjustment in effective charge ratio, to $ze/\tilde{e} \approx 0.976$. This sensitivity provides the explanation for a wide variation of critical pressure and temperature between various compounds chemically similar to ScF$_3$.

Using the experimental value of $P_c \approx 0.075$ GPa [23] for ScF$_3$ at 0 K, we obtain $\epsilon_0 \approx 0.005$. Note that determining this value with such an accuracy would require computation of the effective charges with a better than 0.5% precision. Solid lines in Fig.2(a) show the corresponding phonon dispersion curves. They are in excellent agreement with the experimentally measured dispersion of the low energy branch [24], as well as the phonon spectra numerically computed in [26]. The major difference is the absence of acoustic branches and hard optical phonons associated with longitudinal F oscillations, both of which are artificially ”switched off” in the rigid bond limit.

The most peculiar feature of the obtained phonon spectra are the ultra-soft phonon modes at the edges of the Brillouin zone (BZ). They have a nearly flat dispersion along the M-R line, which reaches its global minimum at a vertex, $q^* = (\pm \pi/a, \pm \pi/a, \pm \pi/a)$. These ultra-soft modes are commonly interpreted as RUMs, i.e. a coordinated rotations of the rigid octahedra formed by Sc together with six surrounding F ions with all inter-ionic distances fixed. However, the fixed distance between nearest F ions suggested by RUM picture is not supported neither by numerical simulations [26], nor by recent experiments [27].

In fact, the geometry of the ultra-soft “quasi-RUM” modes is fully determined by symmetry. For wave vectors at the edge of the Brillouin zone, which are invariant under symmetry transformations of the crystal that involve only $\mu$ and $\nu$ coordinates ($q^\mu = q^\nu = \pi/a$), the normal modes
FIG. 2. **Transverse phonons of Coulomb floppy network in ScF₃.** Curves are results of our theory, Eqs. (4), (5), and symbols are the experimental data points for ScF₃ from Ref. [24]. (a) The spectrum of the six transverse F phonon modes at $T = 0$, $P = 0$, calculated using point charge approximation ($\epsilon = 0.3$, dashed lines) and with the account for the ionic charge distribution ($\epsilon = 0.005$, solid lines). (b) The phonon spectrum at room temperature ($T = 300$ K, $P = 0$, $\epsilon = 0.05$, solid line), and at a critical point ($P = P_c(T)$, $\epsilon = 0$, dashed line). (c) The phonon density of states (DOS) for the six modes in (b), calculated for $\alpha_F = 1.0$ and $\alpha_F = 1.3$. Dashed line shows linear interpolation.
are either symmetric, or anti-symmetric with respect to a symmetry group of a square,

\[ u^{(\nu \mu)}_{q \pm} = (u^\nu_{q, \pm} \pm u^\mu_{q, \pm}) / \sqrt{2}. \]  

(6)

The low energy branch corresponds to the minus sign, with F ions moving in the mid-plane between two Sc ions, and it indeed resembles RUM-like rotations of F ions about Sc in \( \nu \mu \) plane. However, these are “breathing” rotations (Fig. [1](#fig:1)d). For a finite, even very large bond rigidity, the Sc-F and F-F distances do change, albeit quadratically in \( u \). Since Sc-F bond is under tension, its energy changes linearly with deformation, i.e. also \( \sim u^2 \). Note, that Sc-F bond rigidity only contributes to the next order terms in \( H_\perp \), giving rise to quartic anharmonicity [26]. These quasi-RUMs provide the strongest reduction of the repulsive electrostatic energy between F ions, which offsets, at least partially, the energy penalty associated with tension of Sc-F bonds. Thanks to the cancelation of these two energy contributions, there is almost no restoring force associated with the F displacement for such a coordinated motion. Hence, quasi-RUMS are in fact the least rigid of all the transverse modes for F ions. For \( P = \epsilon_0 P_0 \), the effects of Sc-F bond tension and F-F repulsion completely cancel each other, signalling an onset of a structural instability. Since the instability occurs at a vertex of the Brillouin zone, \( q^* \), it involves simultaneous quasi-RUM rotations in all three planes and results in a transformation from cubic to rhombohedral crystal structure.

Near the critical point, the floppy network behavior that was previously suppressed by tension is recovered. At a finite temperature, however, thermal fluctuations provide another, entropic elasticity mechanism for FN stabilization. Such entropic stabilization is aided by a steric constraint on displacement, \( u_{n \nu \mu} \), which was originally omitted in the effective Hamiltonian, Eq. (2). Namely, the effect of core repulsion of the nearest F ions becomes significant when the fluctuations increase in amplitude on the way to become unstable according to the harmonic analysis. This can be accounted for by imposing a constraint, \( u_{n \nu \mu}^2 < u_0^2 \), on each component, \( \mu \), of the displacement field, \( u_{n \nu \mu} \), where \( u_0 \sim 1 \text{Å} \) is a model parameter that determines the effective steric confinement of F ions. In the mean field approximation, this constraint can be represented as an additional rigidity, \( \kappa_T = 2k_BT/u_0^2 \), adding \( \delta H_T = \sum_{n, \nu} \kappa_T u_{n \nu \mu}^2 / 2 \) to the quasi-harmonic Hamiltonian of the system, \( H_\perp \) [31]. Combining the effects of temperature and pressure, we obtain the following expression for the gap parameter that controls the criticality,

\[ \epsilon(T, P) = \epsilon_0 + (\chi T - P)/P_0, \]  

(7)
where $\chi = k_B/(4ru_0^3)$. According to this result, there is a linear dependence of the critical temperature on pressure. It also predicts that the square of the floppy phonon’s energy increases linearly with temperature, $(\hbar \omega(T))^2 = (\hbar \omega_0)^2 (\epsilon_0 + \chi T/P_0)$, in perfect agreement with experiment [24]. By setting $u_0 = 1.00\text{Å}$, we obtain a close match between the coefficient of proportionality, $(\hbar \omega_0)^2 \chi / P_0 = 2k_B\hbar^2 / (m_F u_0^2) \approx 0.038$ meV$^2$/K, and its experimental value $0.0376(5)$ meV$^2$/K [24]. This, in turn, allows us to evaluate the slope of the $P_c(T)$ curve, $dT_c/dP = \chi^{-1} \approx 580$ K/GPa, which compares favorably with the experimental value, $\approx 525$ K/GPa [23, 24]. The resulting phase diagram, $P_c(T)$, is presented in the insert to Fig. 3(a). Fig. 3(a) shows the variation of critical temperature for Sc$_{1-x}$Ti$_x$F$_3$ and Sc$_{1-x}$Al$_x$F$_3$ series, which (aside from pure AlF$_3$) is quite accurately described by the $r$-dependence of $\epsilon_0$ given by Eq. (5).

NTE emerges as a natural property of a floppy network: the constraint, Eq. (1), relates an increase in transverse fluctuations of F ions to the overall contraction of the crystal, $(r - r_b)/r_0 \approx -\langle u_{nm}^2 \rangle/2r_0^2$. In order to calculate $\langle u_{nm}^2 \rangle$, we first determine the density of states (DOS) from our theory. The resulting DOS features three peaks, at energies $\hbar \omega_1 \approx 1.1\hbar \omega_0 \approx 20$ meV, $\hbar \omega_2 \approx 1.5\hbar \omega_0 \approx 27$ meV, and $\hbar \omega_3 \approx 2\hbar \omega_0 \approx 36$ meV (Fig. 2(c)), in agreement with both numerical and experimental data [26]. The low energy quasi-RUM part of DOS is well described by a linear function. This is a reflection of the fact quasi-RUMs have very weak dispersion along the MR line. Their dispersion perpendicular to the MR line is thus equivalent to that of 2D phonons, which explains the linear DOS behavior.

We calculate NTE analytically by adopting a simple, approximate expression for DOS, $g_{\omega} \approx 2 \omega \Theta (\omega - \omega_-) \Theta (\omega_+ - \omega)$, obtained by extrapolating the linear quasi-RUM behavior all the way up to the high frequency cut-off, $\omega_+ = \omega_0 \sqrt{\epsilon + \lambda_+}$. The opening of a gap for finite $\epsilon$ results in a low energy cut-off of the spectrum, at $\hbar \omega_- = \hbar \omega_0 \sqrt{\epsilon + \lambda_-}$. Parameter $\lambda_-$ accounts for the effect of small, but finite dispersion of quasi-RUMs along the MR line, which makes the average energy along this line slightly higher than the gap, $\hbar \omega_0 \sqrt{\epsilon}$. By performing the integration, $\langle u_{nm}^2 \rangle = \hbar/2m_F \int d\omega n_{\omega} g_{\omega}/\omega$, we obtain,

$$\Delta = \frac{r - r_b}{r_0} = \frac{2r_0 k_B T}{e^2 \lambda_+} \ln \left( \frac{1 - e^{-\hbar \omega_+ / k_B T}}{1 - e^{-\hbar \omega_- / T}} \right).$$

In the classical regime, $k_B T \gtrsim \hbar \omega_+$, the logarithm in this expression can be replaced with $\ln(\omega_+ / \omega_-) = \ln(\lambda_+ / (\epsilon + \lambda_-))$. The upper and lower cut-off parameters are obtained by matching this classical result with the one calculated for the exact DOS shown in Fig. 2(c). This gives $\lambda_+ \approx 4.3$ ($\hbar \omega_+ \approx 37$ meV, $\hbar \omega_+ / k_B \approx 430$ K), and $\lambda_- \approx 0.005$. As shown in Fig. 2(c), the result-
ing slope of $g_\omega$ is in excellent agreement with the linear portion of the exact DOS. The prefactor in front of the logarithm in Eq. (8) is very close to the result obtained within a much simper, Einstein model of F vibration, which neglects any dispersion, replacing $\gamma^{(\sigma)}_q$ in Eq. (4) with its average value [27]. Hence, the non-trivial dispersion and ultrasoft quasi-RUMs are not essential for NTE and only give rise to a logarithmic correction factor ($\approx 2$ at 300 K) to Einstein approximation.

Another important property of floppy networks is entropic elasticity. A well-known example is elastic response of polymers and rubber to stretching, suppressing the chain entropy [1–3]. In the case of a Coulomb FN solid, such as ScF$_3$, the overall compressibility remains finite even for infinitely rigid bonds thanks to thermal (and quantum) fluctuations. According to Eq. (3), applied pressure reduces the stability of the network, increasing fluctuations and, therefore, entropy. The associated entropic contribution to bulk modulus can be calculated using Eqs. (7) and (8),

$$B_u = -\frac{1}{3} \left( \frac{\partial \Delta}{\partial P} \right)^{-1} = \frac{1}{3} \lambda_+ P_0 e^2 (\epsilon + \lambda_-) / r_0 k_B T.$$ Thanks to near-proportionality of $\epsilon$ to temperature, for finite $T$ it quickly reaches a constant asymptotic value, $B_u \approx 2 (r_0 / u_0)^2 \lambda_+ P_0 / 3 \approx 185$ GPa.

We can now relax the approximation of fixed bond length, $r_b$, by including the bond potential, which we expand up to the second order in deformation, $V_b(r_b) = V_b^{(0)} + f_0(r_b - r_0) + \kappa_b (r_b - r_0)^2 / 2$, in the effective Hamiltonian, Eq. (2). The constraint, Eq. (1), dictates that the two contributions to the compressibility, $B_b^{-1} = 12 r / (\kappa_b + \kappa)$ due to bond rigidity and $B_u^{-1}$ associated with fluctuations are additive, $B^{-1} = B_b^{-1} + B_u^{-1}$. This result explains the pronounced disagreement between the DFT result for bulk modulus, $\approx 89$ GPa [32, 33], and a much lower experimental value, $B \approx 60$ GPa, measured in ScF$_3$ at 300 K [17, 23]. Using the value $B_b = 89$ GPa from DFT and accounting for the fluctuational contribution to compressibility, we obtain $B = 1 / \left( B_b^{-1} + B_u^{-1} \right) \approx 60$ GPa, in excellent agreement with both experiments and molecular dynamics simulations [35].

Our result for NTE, Eq. (8), can be connected to the conventional quasi-harmonic theory for thermal expansion of solids, where,

$$\frac{r - r_0}{r_0} = \frac{1}{3V B} \sum_i \Gamma_i E_i.$$ (9)

Here, $E_i$ are energies of individual phonon modes and $\Gamma_i$ are known as Grüneisen parameters, which express the ratio between contribution to internal pressure and energy density for each mode, $\Gamma_i = -\partial \ln \omega_i / \partial \ln V$. Typically, for crystalline solids Grüneisen parameters are determined by the non-linearity of interatomic bond potentials and are of the order of 1. In the case of Coulomb FN in ScF$_3$, however, the dominant contribution, $\Gamma(\omega) \approx -B / 2P_0 (\omega_0 / \omega)^2$, comes from the explicit pressure dependence of the Hamiltonian, $H_\perp$. Since $B \gg P_0$, this parameter
is anomalously large and negative. After substituting it into Eq. (9), however, the bulk modulus cancels and the final result is indeed equivalent to Eq. (8).

In our theory, we can employ Eq. (9) to describe the positive thermal expansion (PTE) of Sc-F bonds. In addition to the dominant contribution coming from the pressure dependence of phonon frequencies, there is a sub-dominant term $1/2$ in Grünisen parameter, $\Gamma_i$, resulting from the $\sim 1/r^3$ scaling of potential energy in Eq. (3). One can show that it is this term that describes the phonon pressure responsible for PTE of Sc-F bond; the compressibility $B^{-1}$ in Eq. (9) in this case has to be replaced with $B_{b}^{-1}$ [31]. Thus, the very same floppy phonons that give rise to a pronounced NTE also lead to PTE of Sc-F bonds.

We complete the description by recalling that there are 6 more phonon branches in the system, 3 acoustic phonons and 3 hard optical modes associated primarily with longitudinal displacements of Sc and F ions, which were neglected in the rigid bond picture. We account for these modes within Einstein approximation, by representing the deformation of 6 Sc-F bonds in response to the displacement of a Sc ion with a simple harmonic potential with spring constant $2V''_b + 4V'_b/r_0 = 2(\kappa_b + \kappa) = 24Br_0$. The corresponding phonon energy is $\hbar\omega_{Sc} = \hbar\sqrt{24Br_0/m_{Sc}} \approx 50$ meV. The spring constant for longitudinal F oscillations, without account for electrostatic corrections, is $2\kappa_b = 2(12B - 8P_0(6 - M))r_0$, which gives the energy of hard optical phonon, $\hbar\omega_\parallel = \hbar\sqrt{24(B - 2P_0)r_0/m_F} \approx 63$ meV. Both energies are very close to the peaks in phonon DOS observed experimentally, as well as to numerical results [26]. We account for the contribution of these modes to thermal expansion by assigning them a single energy, $\hbar\omega_{hard} = \hbar(\omega_{Sc} + \omega_\parallel)/2 \approx 56$ meV and an effective Grünisen parameter, $\Gamma$. Combining the contributions from soft floppy phonons and hard longitudinal modes we obtain,

$$\Delta_b = \frac{r_b - r_0}{r_0} \approx \frac{kT}{3NB_b\nu_0} \left[ \frac{1}{2} D_2 \left( \frac{\hbar\omega_+}{k_B T} \right) + \Gamma \Phi \left( \frac{\hbar\omega_{hard}}{k_B T} \right) \right].$$

Here, $\Phi(x) = x/(\exp(x) - 1)$ is the Bose-Einstein correction function to the equipartition theorem (Bernoulli function) and $D_2(x) = 2/x^2 \int_0^x x'^2(\exp(x') - 1)^{-1}dx'$ is a 2D Debye function. The overall NTE effect is given by the sum of the earlier result obtained within rigid bond approximation, Eq. (8), and Sc-F bond extension associated with internal phonon pressure given by Eq. (9), $(r - r_0)/r_0 = \Delta + \Delta_b B_0/B$ [31]. As shown in Fig 3(b), our results for NTE and for PTE of Sc-F bonds are in excellent agreement with experimental data in ScF$_3$. By using $\Gamma$ as the only adjustable parameter, we obtained $\Gamma = 1$, well within the expected range.

In conclusion, we extended the concept of FN, which is ubiquitous in polymers, disordered and
FIG. 3. Phase diagram and negative thermal expansion in ScF$_3$. (a) Dependence of the critical temperature, $T_c$, on half lattice spacing, $r$. Solid lines are theoretical results, Eq. (5), for two values of $\alpha_F$ with $ze/\tilde{e}$ used as fitting parameter. Dashed lines include correction for the reduction of confinement parameter with $r$, assuming $\Delta u_0 = \Delta r$. Symbols represent experimental data for Sc$_{1-x}$Ti$_x$F$_3$ (circles) and Sc$_{1-x}$Al$_x$F$_3$ (squares) from Refs. [16, 17]. Insert shows theoretical $P_c(T)$ phase diagram, Eq. (7), with data points representing experimental results for ScF$_3$ from Ref. [23]. (b) Solid lines show theoretical dependencies of the lattice NTE (blue), and Sc-F bond length (green). Symbols represent experimental data from Refs. [23, 27]. Dashed line is the result for infinitely rigid Sc-F bond, Eq. (8).

soft matter [1–8], to open framework ionic solids. By doing so, we constructed a theory that treats these materials as Coulomb floppy networks (CFNs) stabilized by the net electrostatic repulsion and provides a very accurate description of their thermal properties and structural phase diagram. We presented our approach by considering the specific example of ScF$_3$, which demonstrates the physics of CFNs unobscured by structural complexities [23–27]. The tension in Sc-F-Sc bonds resulting from the net Coulomb repulsion leads to finite stiffness of transverse fluctuations and endows FN with structural stability. External pressure reduces bond tension and, combined with the electrostatic energy gain due to coordinated quasi-RUM motion, leads to an instability of cubic
structure. Thermal fluctuations under steric constraint, on the other hand, provide mechanism for entropic stabilization, leading to the increase of spectral gap and critical pressure with temperature. NTE effect emerges as a natural consequence of the underlying floppy network behavior. In contrast with the common belief in the field, NTE does not rely neither on (quasi-)RUMs, which give only logarithmic corrections to a more naive Einstein model for transverse F modes \[27\], nor on quartic anharmonicity of the ultra-soft phonons. Instead, the anharmonicity is geometric in origin, leading to a theory that is essentially quasi-harmonic, yet starkly distinct from classical Grüneisen-type theories where thermal expansion is driven by anharmonic inter-atomic potentials. The theory describes phonon spectra, phase diagram, NTE, and entropic elasticity of CFNs and is in excellent agreement with experimental data in ScF\(_3\). It can be applied to explain anomalous vibrational and structural properties in a range of topical materials, from pure silicon to cuprates and iron pnictides \[27–30\], and opens new avenues for the predictive modeling of these effects in solids and metamaterials \[36, 37\], which currently are beyond the reach of \textit{ab initio} methods.

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SUPPLEMENTARY INFORMATION

Criticality, entropic elasticity, and negative thermal expansion of a Coulomb floppy network solid

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A. Electrostatic coupling within point charge approximation

Within the point charge approximation, the electrostatic contribution to Hamiltonian, $H_{\perp}$, in terms of "floppy" mode displacements, $u_{n\nu}$, can be written as follows,

$$V_{el} = \frac{\tilde{e}^2}{2r^3} \sum_{n,n',\nu,\nu'} u_{n\nu} \cdot \hat{G}_{nn',\nu\nu'} \cdot u_{n'\nu'} = \frac{\tilde{e}^2}{2r^3} \sum_{n,\nu} \left[ -\gamma_0 |u_{n\nu}|^2 + \sum_{(n',\nu') \neq (n,\nu)} u_{n\nu} \cdot \hat{T}_{nn',\nu\nu'} \cdot u_{n'\nu'} \right].$$  \hspace{1cm} (S1)

Here, $a = 2r$ is the lattice constant,

$$T_{nn',\nu\nu'}^{\mu\mu'} = -r^3 \frac{\partial^2 R^{-1}}{\partial R^\mu \partial R^{\mu'}} = r^3 \left( \frac{\delta_{\mu\mu'}}{R^3} - \frac{3R^\mu R^{\mu'}}{R^5} \right), \quad R = r_{n\nu} - r_{n'\nu'},$$  \hspace{1cm} (S2)

where $\mu, \mu' = x, y, z$ and the diagonal force constant, $\gamma_0$, is given by,

$$\gamma_0 = -\frac{1}{2} \sum_{n',\nu'(non-NN)} z_{\nu'} T_{nn',\nu\nu'}^{\nu\nu'} \approx 0.90, \quad \nu = x, y, z, \nu' = 0, x, y, z.$$  \hspace{1cm} (S3)

Note, that here the summation over $\nu'$ includes the terms coming from interactions with Sc ions (to which $\nu' = 0$ is assigned), with the exception of the nearest Sc neighbors of a given F. Accordingly, $z_{\nu'} = +3$ for $\nu' = 0$, and $z_{\nu'} = -1$ for $\nu' = x, y, z$.

After switching to the Fourier variables defined in the main text, $u_{q\nu} = \sum_n u_{n\nu} \exp \left( -i\mathbf{q} \cdot \mathbf{r}_{n\nu} \right)$, the non-local part of the electrostatic potential can be re-written in the following form,

$$\sum_{(n',\nu') \neq (n,\nu)} u_{n\nu} \cdot \hat{T}_{nn',\nu\nu'} \cdot u_{n'\nu'} = \sum_{q,\nu,\nu'} u_{q\nu} \cdot \hat{G}_{q,\nu\nu'} \cdot u_{-q\nu'},$$  \hspace{1cm} (S4)

$$G_{q,\nu\nu'}^{\mu\mu'} = \frac{3a^3}{8} \left( \frac{\partial^2}{\partial q^\mu \partial q^{\mu'}} - \frac{\delta_{\mu\mu'}}{3} \frac{\partial^2}{\partial q \cdot \partial q} \right) \sum_{R_{\nu\nu'}} \exp \left( i\mathbf{q} \cdot \mathbf{R}_{\nu\nu'} \right).$$  \hspace{1cm} (S5)

Here, $\mathbf{R}_{\nu\nu'} = (a_{\nu'} - a_{\nu})/2 + k\mathbf{a}_x + l\mathbf{a}_y + m\mathbf{a}_z$, and $k, l, m \in Z$. 

In order to simplify the diagonalization of tensor $\hat{G}$, we first regroup the displacements, $u_{q,\nu}$, into three 2D vectors, $u'_{q,\nu} = (u'_{q,\nu}, u''_{q,\nu})$. Here, the triad of indices, $(\nu, \mu, \mu')$, is an even ($\epsilon_{\nu \mu \mu'} = 1$) permutation of $(x, y, z)$. In this representation, each matrix element, $\hat{G}_{\nu \nu'}$, is a $2 \times 2$ matrix,

$$
\hat{G}_{\nu \nu'} = \frac{3}{8} \sum_{k,l,m\in \mathbb{Z}} \left( \frac{L^2}{3} - m^2 \right) \frac{\partial^2}{\partial \phi \partial \phi'} \frac{\partial^2}{\partial \phi \partial \phi'} L^5 \cos(k \phi) \cos(m \phi') \cos(l \phi') \cos((k + 1/2) \phi) \cos((m + 1/2) \phi') \cos(l \phi') \frac{L^5}{L^5}, \tag{S6}
$$

$$
\hat{G}_{\nu \mu} = \frac{3}{8} \sum_{k,l,m\in \mathbb{Z}} \left( \frac{L^2}{3} - l^2 \right) \frac{\partial^2}{\partial \phi \partial \phi'} \frac{\partial^2}{\partial \phi \partial \phi'} L^5 \cos((k + 1/2) \phi) \cos((m + 1/2) \phi') \cos(l \phi') \cos((k + 1/2) \phi) \cos((m + 1/2) \phi') \cos(l \phi') \frac{L^5}{L^5}, \tag{S7}
$$

where $\phi = a q$, $L = \sqrt{k^2 + m^2 + l^2}$, and $L' = \sqrt{(k + 1/2)^2 + (m + 1/2)^2 + l^2}$.

Diagonalization of $\hat{G}_{q,\nu \nu'}$ for a given wave vector, $q$, yields six normal modes with the corresponding eigenvalues, $\gamma_{q}^{(\sigma)} = \gamma_{q}^{(\sigma)} + \gamma_0$.

**B. Corrections to the point-charge approximation**

In order to improve the above point-charge model, we will now include two additional effects discussed in the main text: finites electronic polarizabilities of ions, $\alpha_F$ and $\alpha_{Se}$, and difference between static and dynamic effective charges. Within the point charge approximation, displacement of a single F ion, $u_{\nu \nu}$, results in a local dipole moment, $d_{\nu \nu} = -e u_{\nu \nu}$. However, in a general case this result has to be corrected for non-trivial distribution and redistribution of ionic charges. In the spirit of our theory, which separates effects of the nearest-neighbor and the longer-range Coulomb interactions, we will distinguish between the corresponding two contributions to the dipole moment, $d_{\nu \nu} = -e (1 - \delta) u_{\nu \nu} + d_{\nu \nu}^*$, where $d_{\nu \nu}^*$ is an induced dipole due to a local electric field from non-nearest neighbors. According to Eq. (S1), for a specific case when only one F ion is displaced this electric field is related to the displacement as $E = -\varepsilon \gamma_0 u_{\nu \nu}/r^3$. Therefore, $d_{\nu \nu} = -e \varepsilon u_{\nu \nu}$, where $\varepsilon = e (1 - \delta + \alpha \gamma_0 / r^3)$ is known as Born effective charge, which, in principle, can be determined numerically, e.g. by DFT calculations.

For the case when multiple ions are displaced, the individual induced dipoles, $d_{\nu \nu}^*$, can be determined by minimization of a Hamiltonian that includes the electrostatic interactions, Eq. (S1), and the energy cost associated with electronic polarization, $H_\alpha = \sum_{n,\nu} d_{\nu \nu}^2 / 2 \alpha_F$. We can account for both of these effects by modifying the electrostatic part of $H_{\perp}$, $h_{q,\sigma} = \gamma_{q}^{(\sigma)} \left| u_{q}^{(\sigma)} \right|^2$, in Eq. (5),

$$
h_{q,\sigma} = -\gamma_0 (1 - \delta) u_{q}^{(\sigma)} \left( u_{q}^{(\sigma)} + 2 v_{q}^{(\sigma)} \right) + \gamma_{q}^{(\sigma)} (1 - \delta)^2 \left| u_{q}^{(\sigma)} + v_{q}^{(\sigma)} \right|^2 + \frac{\gamma_0 \alpha_F}{2} \left| v_{q}^{(\sigma)} \right|^2. \tag{S8}
$$
Here, $v_q^{(σ)}$ is related to $d_{nν/ε}$ through the same linear transformation as $u_q^{(σ)}$ to $u_{nν}$. By minimizing this energy with respect to $v_q^{(σ)}$, we find that $γ_q^{(σ)}$ in Eq. (3) has to be renormalized as follows,

$$γ_q^{(*)} = γ_q^{(σ)} \left( \frac{2e}{\tilde{e}} - \frac{γ_0α_F}{r^3} \right)^2 \left( \frac{1 + \gamma_0α_F/r^3}{1 + (γ_q^{(σ)})α_F/r^3} \right).$$

(S9)

In particular, this correction leads to a significant change in spectral gap compared to the result of the point charge approximation,

$$ε_0 = 6 - M + γ_{\text{min}} = 6 - M + γ_0^{(0)} \left( \frac{2e}{\tilde{e}} - \frac{γ_0α_F}{r^3} \right)^2 \left( \frac{1 + \gamma_0α_F/r^3}{1 + (γ_0^{(0)})α_F/r^3} \right).$$

(S10)

C. Entropic stabilization of criticality

In the main text, we account for steric repulsion between F ions by imposing a constraint, $u_{nν}^2 < u_0^2$, on each component of the displacement field, $u_{nν}$, where $u_0 \sim 1\text{Å}$ is a model parameter. The resulting partition function has the following form:

$$Z = \text{Tr} \left( e^{-\frac{H_{\text{eff}}}{k_B T} \prod_{nνμ} Θ (u_0^2 - u_{nν}^2)} \right) = \text{Tr} \left( e^{-\frac{H_{\text{eff}}}{k_B T} \prod_{nνμ-∞} e^{k_{nν}^μ (u_0^2 - u_{nν}^2)} d{k_{nν}^μ}} \right).$$

(S11)

Here, we performed exponentiation of the step functions representing the steric constraints by introducing a set of fictitious fields, $κ_{nν}^μ$ (formally, this trick is analogous to a common method of exponentiating a delta-function). Within the mean field approximation, all individual parameters $κ_{nν}^μ$ can be replaced with a single value, $κ_T$. This results in the following addition to the effective Hamiltonian, $δH = k_B T \sum_{nνμ} [κ_T (u_{nν}^2 - u_0^2) + \ln κ_T]$. By minimizing its thermal average with respect to $κ_T$, we obtain the equilibrium value of this parameter, $κ_T = 1/(u_0^2 - \langle u_{nν}^2 \rangle) \approx 1/u_0^2$. We conclude that the effect of a steric constraint can be represented as an additional rigidity, $2k_B T κ_T = 2k_B T / u_0^2$, in the harmonic effective Hamiltonian of the system.

D. Thermal expansion of ScF bond and fluctuational correction to NTE result

Upon relaxing the approximation of infinitely rigid Sc-F bonds and expanding the bond potential $V_b$ in terms of $r_b - r_0$, the effective Hamiltonian takes the following form,

$$H_{\text{eff}} = 3N \left[ \frac{(6 - M)\tilde{c}^2}{r} + \frac{κ(r^2 - r_b^2)}{2} \right] + f_0(r_b - r_0) + \frac{κ_b}{2} (r_b - r_0)^2 + H_⊥ + H_∥. $$

(S12)
Here, \( f_0 = \frac{(6-M)e^2}{2r_0^2} \) and \( H_{\parallel} \) accounts for acoustic modes and optical phonons associated with displacements of F ions along Sc-F-Sc bonds. As before, the tension in Sc-F bond is balancing the negative electrostatic pressure, but it is now also related to the extension of the bond, \( f = f_0 + \kappa_b(r_b - r_0) \). At non-zero temperature and pressure, we once again perform minimization of \( \langle H_{\text{eff}} \rangle \), this time with respect to \( r_b \). In the leading order in \( \langle u_{\nu}^2 \rangle \) this gives,

\[
\Delta_b \equiv \frac{r_b - r_0}{r_0} = \frac{4r_0}{\kappa_b + \kappa} \left( \frac{1}{8r_0^3} \sum_{\mathbf{q},\sigma} \left\langle \frac{\bar{e}_b^2}{2r_0^3} (6 - M + \gamma_{\mathbf{q},\sigma}) \left| \bar{u}_{\mathbf{q},\sigma} \right|^2 \right\rangle - P \right) = \frac{\bar{P} - P}{3B_b} ,
\]

(S13)

Here, \( B_b = (\kappa_b + \kappa)/12r_0 \) is the contribution to the bulk modulus associated with bond rigidity and \( \bar{P} = \frac{1}{2} \langle \hat{H}_{\perp} \rangle / V \) has a meaning of phonon contribution to internal (negative) pressure. This result is an analogue of the classical Grüneisen formula, but for Sc-F bond expansion. The prefactor \( 1/2 \) has a meaning of effective Grüneisen parameter for our transverse F modes, coming from \( 1/r^3 \) scaling of their energies. As discussed in the main text, this is only a subdominant contribution to the total Grüneisen coefficient that determines the overall NTE effect,

\[
\Gamma_{\mathbf{q},\sigma}^{(\sigma)} = \frac{1}{2} \left( 1 - \frac{V}{\epsilon + \gamma_{\mathbf{q},\sigma}^{(\sigma)}} - \gamma_{\text{min}} \right) \frac{\partial P}{\partial \epsilon} = \frac{1}{2} - \frac{B}{2P_0} \frac{\omega_{\mathbf{q},\sigma}^2}{\omega_{\mathbf{q},\sigma}^{(\sigma)2}} .
\]

(S14)

Within our theory, in order to find the overall thermal expansion, \( (r - r_0)/r_0 \), we need to add the results for \( \Delta \) and \( \Delta_b \) given by Eqs. (8) and (10). However, prior to that, the value of \( \Delta \), which depends on pressure via \( \epsilon \), has to be adjusted due to internal phonon pressure, \( \bar{P} \):

\[
\frac{r - r_0}{r_0} = \Delta - \frac{\partial \Delta}{\partial \bar{P}} \bar{P} + \Delta_b = \Delta + \left( \frac{1}{B_u} + \frac{1}{B_b} \right) \frac{\bar{P}}{B} = \Delta + \frac{B_b}{B} \Delta_b
\]

(S15)

This result is now fully consistent with the traditional Grüneisen formula, Eq. (9), with \( \Gamma_{\mathbf{q},\sigma}^{(\sigma)} \) given by Eq. (S14). The effect of all other phonons can be included in Eqs. (S13), (S15) by adding their respective contributions to \( \bar{P} \). This yields Eq. (10) and the theoretical curves shown in Fig. 3(b).