Landau theory and giant room-temperature barocaloric effect in MF$_3$ metal trifluorides

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The structural phase transitions of MF$_3$ (M=Al, Cr, V, Fe, Ti, Sc) metal trifluorides are studied within a simple Landau theory consisting of tilts of rigid MF$_6$ octahedra associated with soft antiferrodistortive optic modes that are coupled to long-wavelength strain generating acoustic phonons. We calculate the temperature and pressure dependence of several quantities such as the spontaneous distortions, volume expansion and shear strains as well as $T-P$ phase diagrams. By contrasting our model to experiments we quantify the deviations from mean-field behavior and found that the tilt fluctuations of the MF$_6$ octahedra increase with metal cation size. We apply our model to predict giant barocaloric effects in Sc substituted TiF$_3$ of up to about 15 JK$^{-1}$kg$^{-1}$ for modest hydrostatic compressions of 0.2 GPa. The effect extends over a wide temperature range of over 140 K (including room temperature) due to a large predicted rate $dT_r/dP = 723$ K GPa$^{-1}$, which exceeds those of typical barocaloric materials. Our results suggest that open lattice frameworks such as the trifluorides are an attractive platform to search for giant barocaloric effects.

I. INTRODUCTION

Metal trifluorides (or simply trifluorides) are a class of materials with chemical formula MF$_3$ (M=Al, Cr, V, Fe, Ti, Sc) and with an open lattice framework in which the trivalent metal ion M is surrounded by an octahedron of corner-shared fluorine atoms.$^{1,2}$ They are isostructural to ReO$_3$ a well-known ABO$_3$ perovskite in which the A site is vacant.$^3$ They can exhibit large thermal expansion (TE) which can be reversibly tuned from positive (PTE) to negative (NTE) by temperature, pressure, cation substitution, or redox intercalation.$^4$–$^8$ This makes the trifluorides attractive for designing materials that are dimensionally stable and resistant to thermal shocks.$^1$

At ambient pressure, most trifluorides exhibit antiferrodistortive structural transitions with cubic-to-rhombohedral ($c-r$) transformations in which the MF$_6$ octahedron tilts around the ($111$) axis. The tilting angles are large, e.g., about $14^\circ$ in AlF$_3$ at room temperature (RT)$^{12}$ and are accompanied by spontaneous shear and volume strains.$^{13}$ Such lattice instability is the result from the condensation of a three-fold zone-boundary $R^+_3$ phonon mode of the cubic phase located at the wavevector $(1,1,1)(\pi/a)$.14 Below the transition, the $R^+_3$ mode splits into a low energy $E_g$ doublet and a high energy $A_{1g}$ singlet.$^{15}$

Density functional theory,$^1$ molecular dynamics (MD) simulations,$^{16}$ and electrostatic energy considerations$^{17}$ have shown that the driving force of the lattice instability in the trifluoride is dipolar origin. When the M-F M bond bends, fluorine displaces transverse to the bond length generating an electric dipole with a negative end at the F$^-$ anion and a positive end at its cubic lattice site. This distortion concomitantly induces a polarization in the fluorine electron cloud that is opposite to the displacive dipole. While there is an energy penalty for creating such induced dipoles, the resulting interactions between the induced-dipoles and between the induced-dipoles with the ionic charges lower the total energy to favor the $r$ phase over the parent $c$-structure preferred by the purely ionic Madelung energy.

A trifluoride of special recent interest is ScF$_3$, an ionic insulator with a wide indirect energy band gap of about $8-10$ eV.$^{18}$ It does not have a structural transition to a $r$ phase at ambient pressure but rather exhibits incipient behavior in which a nearly flat M-R phonon branch
softens without condensing, as it has been observed by inelastic x-ray scattering experiments (IXS)\textsuperscript{19} and found in ab-initio calculations.\textsuperscript{20} It exhibits strong negative TE (-34 ppm K$^{-1}$ near RT) from 10 – 1100 K\textsuperscript{21} and are very strong lattice anharmonicities (its soft $R_4^4$ mode is described by a quartic potential energy in the tilts).\textsuperscript{22} Its incipient behavior and proximity to a r-phase induced by, e.g., cation substitution\textsuperscript{4,5,7} suggest that ScF\textsubscript{3} is one of the few known stoichiometric materials near a quantum structural phase transition.\textsuperscript{19}

With hydrostatic compression, the r phase can be induced at higher temperatures. For example, at about 0.6 GPa, a c – r transition is observed near RT in the incipient ScF\textsubscript{3}.\textsuperscript{21,23,24} X-ray diffraction experiments have determined the temperature-pressure phase diagrams for Sc substituted AlF\textsubscript{3} (Sc\textsubscript{1–x}Al\textsubscript{x}F\textsubscript{3}).\textsuperscript{7} Very significantly, they have observed linearly increasing transition temperatures with pressure with large rates ($dT_c/dP \approx 400 – 500$ K GPa$^{-1}$) that vary little with Sc concentration and pressure.\textsuperscript{7,21} Additional pressure-induced transitions have been reported at higher pressures.\textsuperscript{23,24}

While microscopic models for the trifluoride are available,\textsuperscript{14,16,17} there is currently no macroscopic approach based on the simple Landau phenomenology. The purpose of this work is thus to construct such a theory. Our model consists of rigid tilts of the MF\textsubscript{6} octahedra associated with the soft $R_4^4$ optic mode coupled to long-wavelength strain generating acoustic phonons. The model is similar to those used to describe the widely studied antiferrodistortive transitions of SrTiO\textsubscript{3} and LaAlO\textsubscript{3},\textsuperscript{25,26} but with the important distinctions that in the trifluorides the phase transition can be discontinuous and that there are large excess volume strains. By comparing our model to experiments on several trifluorides we quantify the deviations from mean-field behavior and found trends with the metal cation size.

We also apply our model to predict the barocaloric effect (BCE) in the trifluorides. BCEs are reversible thermal changes in a substance in response to changes in hydrostatic pressure and are currently of enormous interest for their potential in developing clean and efficient solid-state cooling technologies.\textsuperscript{27} It is expected that materials with strong TE such as the trifluorides should give rise to large barocaloric responses, as their entropy rate ($\partial S/\partial P)_T = -(\partial V/\partial T)_P$, according to the Maxwell's relations.\textsuperscript{27} Indeed, we show that the isothermal changes entropy in the trifluorides are comparable to those of other classes of materials exhibiting so-called giant BCEs,\textsuperscript{28–30} and that it can extend over a broad temperature range which includes RT for modest changes in pressure as a result of their large barocaloric coefficients $dT_c/dP$. So far, the BCE in the trifluoride has not been studied neither experimentally nor theoretically.

This paper is organized as follows: In Sec. II we present our Landau theory to describe the structural transitions; in Sec. III we show our results and discussion including a comparison to the isostructural compounds ReO\textsubscript{3} and WO\textsubscript{3}; and in Sec. IV we present our conclusions.

\section{II. LANDAU THEORY}

\subsection{A. Free energy}

We choose the order parameter as the linear displacement $Q = (Q_1, Q_2, Q_3)$ which represents, in first order, an antiferrodistortive rotation of the MF\textsubscript{6} octahedra through angles $\phi_i$ and $-\phi_i$, ($i = 1, 2, 3$) about axes parallel to a cube edge. We normalize the $Q$'s in such a way that they are numerically equal to the linear fluorine displacements. They are related to $\phi_i$ by $\tan \phi_i = 2Q_i/a$, where $a$ is the lattice constant, see Fig. 1. In addition to the antiferrodistortive distortion, we introduce elastic strains $\eta_{\alpha}$ as a secondary order parameter. We write the components of the strain tensor in the usual Voigt notation: $\eta_{\alpha} = \epsilon_{\alpha\alpha} = \partial u_\alpha/\partial x_\alpha \ (\alpha = 1, 2, 3)$, $\eta_4 = 2\epsilon_{yz} = 2(\partial u_y/\partial z + \partial u_z/\partial y)$, $\eta_5 = 2\epsilon_{zx} = 2(\partial u_x/\partial z + \partial u_z/\partial x)$, and $\eta_6 = 2\epsilon_{xy} = 2(\partial u_x/\partial y + \partial u_y/\partial x)$. We do not consider fluctuations in $Q$ and $\eta_{\alpha}$.

Our Landau free energy density is given as follows:

$$G_Q + G_\eta + P \sum_{\alpha=1}^{3} \eta_{\alpha},$$

where $G_Q$ is a strain-free free energy,

$$G_Q = G_0 + A_0 \left(Q_1^2 + Q_2^2 + Q_3^2\right) + \frac{u}{2} \left(Q_1^2 + Q_2^2 + Q_3^2\right)^2 + \frac{3v}{2} \left(Q_1^2 Q_2^2 + Q_1^2 Q_3^2 + Q_2^2 Q_3^2\right) + \frac{w_1}{6} \left(Q_1^2 + Q_2^2 + Q_3^2\right)^3,$$

where $A_0 = A_0(T - T_0)$ and $T_0$ is the supercooling temperature that limits of stability of the parent c-phase. $G_Q$ is an energy density with elastic couplings,

$$G_\eta = a_0 \left(\eta_1 + \eta_2 + \eta_3\right) \left(Q_1^2 + Q_2^2 + Q_3^2\right) - \epsilon_t \left[\eta_1 \left(2Q_1^2 - Q_2^2 - Q_3^2\right) + \eta_2 \left(2Q_2^2 - Q_1^2 - Q_3^2\right) + \eta_3 \left(2Q_3^2 - Q_1^2 - Q_2^2\right)\right] + \frac{1}{2} \sum_{\alpha\beta} C_{\alpha\beta}^0 \eta_\alpha \eta_\beta.$$

$A_0, u, v, w, a_0, \epsilon_t,$ and $\epsilon_t$ are model parameters independent of temperature and pressure and $C_{\alpha\beta}^0$ are the usual elastic constants of the parent phase in the Voigt notation. The third term in the free energy (1) is a hydrostatic compression where $P$ is measured from atmospheric pressure.
In writing the free energy (1), we have not considered any polar degrees of freedom associated with phonon modes that break inversion symmetry as there is no evidence that such lattice modes are unstable in the trifluorides, e.g., the zone-center TO phonon modes do not condense and remain fairly energetic such as in ScF₃ (4 − 5 THz) and other trifluorides. Moreover, Clausius-Mossotti theory predicts that the ground state exhibits antipolar order from the MF₃ tilts with null polarization. We have also ignored sixth-order cubic anisotropies. Our results will show that this is justified as long as we are describing the r-phase. In Appendix B, we show, however, that they are essential to describe other pressure-induced phases. We have also neglected any polar degrees of freedom associated with phonon modes that would break inversion symmetry, as there is no evidence that such lattice modes are unstable in the trifluorides.

Minimizing Eq. (1) with respect to the strains gives,

\[
\eta_1 = -\frac{e_a}{3C_a} \left( Q_1^2 + Q_2^2 + Q_3^2 \right) + \frac{e_t}{2C_t} \left( 2Q_1^2 - Q_2^2 - Q_3^2 \right) - \frac{P}{3C_a},
\]

\[
\eta_2 = -\frac{e_a}{3C_a} \left( Q_1^2 + Q_2^2 + Q_3^2 \right) + \frac{e_t}{2C_t} \left( 2Q_2^2 - Q_1^2 - Q_3^2 \right) - \frac{P}{3C_a},
\]

\[
\eta_3 = -\frac{e_a}{3C_a} \left( Q_1^2 + Q_2^2 + Q_3^2 \right) + \frac{e_t}{2C_t} \left( 2Q_3^2 - Q_1^2 - Q_2^2 \right) - \frac{P}{3C_a},
\]

\[
\eta_4 = \frac{e_r}{C_r} Q_2 Q_3,
\]

\[
\eta_5 = \frac{e_r}{C_r} Q_1 Q_3,
\]

\[
\eta_6 = \frac{e_r}{C_r} Q_1 Q_2,
\]

where \( C_a = (1/3) \left( C_{11}^0 + 2C_{12}^0 \right) \) is the bulk modulus, \( C_t = (1/2) \left( C_{11}^0 - C_{12}^0 \right) \), and \( C_r = C_{44}^0 \) are the shear tetragonal and rhombohedral moduli, respectively.

When the spontaneous strains of Eq. (4) are substituted back into Eq. (1), we obtain, as expected, that the free energy has the same form as that of Eq. (2) for the strain-free case except with renormalized quadratic \((u \text{ and } v)\) and quartic coefficients \((\tilde{u} \text{ and } \tilde{v})\) and a uniform energy shift due to pressure,

\[
\tilde{G}(T, P) = G_0 + \frac{1}{2} \tilde{A} \left( Q_1^2 + Q_2^2 + Q_3^2 \right)
\]

\[
+ \frac{\tilde{u}}{2} \left( Q_1^2 + Q_2^2 + Q_3^2 \right)^2
\]

\[
+ \frac{3 \tilde{v}}{2} \left( Q_1^2 Q_2^2 + Q_1^2 Q_3^2 + Q_2^2 Q_3^2 \right)
\]

\[
+ \frac{w_1}{6} \left( Q_1^2 + Q_2^2 + Q_3^2 \right)^3
\]

\[
- \frac{1}{2} \frac{P^2}{C_a},
\]

where,

\[
\tilde{A} = A - \frac{2e_a P}{C_a},
\]

and,

\[
\tilde{u} = u - \left( \frac{5e_a^2}{C_a} + \frac{3e_t^2}{C_t} \right),
\]

\[
\tilde{v} = v + \left( \frac{3e_t^2}{C_t} - \frac{1}{3} \frac{e_t^2}{C_r} \right).
\]

We conclude the presentation of the free energy here. In the next section we apply our model to describe the \(c \rightarrow r\) transition of the trifluorides.

**B. \(c \rightarrow r\) transition**

The symmetry of the ground state and order of the phase transition is determined by the choice of \(\tilde{u}\) and \(\tilde{v}\). For a \(c \rightarrow r\) discontinuous (continuous) transition, we must have \(\tilde{v} < 0\) and \(\tilde{u} + \tilde{v} < 0\) \((\tilde{u} + \tilde{v} > 0)\).

To describe the r-phase, we take \(Q = (Q_s/\sqrt{3})(1, 1, 1)\), where \(Q_s\) is determined by minimization of the free energy (5),

\[
Q_s(T, P) = \pm \left\{ \sqrt{\left( \frac{\tilde{u} + \tilde{v}}{w_1} \right)^2 - \frac{\tilde{A}}{w_1} - \left( \frac{\tilde{u} + \tilde{v}}{w_1} \right)^2} \right\}^{1/2}.
\]

Substitution of the order parameter (8) into Eq. (4) gives, respectively, the following the spontaneous volume and shear strains,

\[
\eta_a = \eta_1 + \eta_2 + \eta_3 = -\frac{e_a}{C_a} Q_s^2 - P/C_a,
\]

\[
\eta_r = \eta_4 + \eta_5 + \eta_6 = \frac{e_r}{3C_r} Q_s^2 = \cos \alpha_C,
\]

where \(\alpha_C\) as the angle between any two axes of the c unit cell.

Experiments usually report the ratio between the lattice constants \(c_H\) and \(a_H\) of a hexagonal unit cell,

\[
\frac{c_H}{a_H} = \sqrt{\frac{3}{2} \frac{1 + 2 \cos \alpha_R}{1 - \cos \alpha_R}}.
\]
where $\alpha_R$ is the angle between any two vectors of a r-unit cell. $\alpha_R$ and $\alpha_C$ are related as follows:

$$\cos \alpha_R = \frac{1}{2} \frac{1 + 3 \cos \alpha_C}{1 + \cos \alpha_C}.$$  \hspace{1cm} (11)

We now derive expressions for the relevant temperature scales. From $Q_s$ of Eq. (8), we find that the stability of the $r$ phase ends at the superheating temperature,

$$T^*(P) = T^*(0) + \left( \frac{2 \epsilon_a}{A_0 C_a} \right) P,$$  \hspace{1cm} (12)

where $T^*(0) = T_0 + \frac{w_1}{A_0} \left( \frac{\tilde{u} + \tilde{v}}{w_1} \right)^2$ is the superheating temperature at ambient pressure. In the next sections, we calculate the heat capacity per unit volume, the entropy per unit volume, and the latent heat per unit volume of the transition at $T > T_c$.

The CTE is given as

$$\kappa(T) = \frac{\partial^2 \tilde{G}}{\partial T \partial P},$$

$$= \left\{ \begin{array}{ll}
\left( \frac{\partial V_0}{\partial T} \right) = \kappa_0, & T > T_c \\
\kappa_0 + \frac{2 \epsilon_a}{C_a} \frac{A_0}{\sqrt{(\tilde{u} + \tilde{v})^2 - \tilde{u}^2}} & T < T_c.
\end{array} \right.$$  \hspace{1cm} (15)

We calculate the entropy per unit volume from the free energy of Eq. (5),

$$S(T, P) = -\frac{\partial G}{\partial T} = \left\{ \begin{array}{ll}
S_0, & T > T_c \\
S_0 - \frac{A_0}{2} Q_s^2(T_c, 0), & T < T_c.
\end{array} \right.$$  \hspace{1cm} (16)

The latent heat per unit volume of the transition at $P = 0$ is then given as follows,

$$T_c \Delta S(T_c, 0) = T_c \times \frac{A_0}{2} Q_s^2(T_c, 0),$$  \hspace{1cm} (17)

where $\Delta S(T_c, 0)$ is the entropy jump at the $c \rightarrow r$ transition.

We now calculate the heat capacity per unit volume,

$$C_P = T \frac{\partial S(T, P)}{\partial T},$$

$$= \left\{ \begin{array}{ll}
C_0^0, & T > T_c \\
C_0^0 + T \frac{A_0}{4} \frac{A_0}{\sqrt{(\tilde{u} + \tilde{v})^2 - \tilde{u}^2}} & T < T_c.
\end{array} \right.$$  \hspace{1cm} (18)

where $C_0^0 = T \frac{\partial S_0}{\partial T}$ is a reference heat capacity in the high temperature phase.

From Eq. (16), we calculate the isotropic changes in entropy,

$$\Delta S(T, P) = \left\{ \begin{array}{ll}
0, & T > T_c \\
-\frac{A_0}{2} (Q_s^2(T, P) - Q_s^2(T_c, 0)) & T < T_c.
\end{array} \right.$$  \hspace{1cm} (19)

We conclude the presentation of our model here. In the next section we apply it to several trifluorides.

### III. RESULTS AND DISCUSSION

#### A. Fits and comparison to experiments

We now discuss our fits to several trifluoride compounds. For pure TiF$_3$ and AlF$_3$, we fit our model to their observed $c_H/a_H$, M-F-M bond angle, volume expansion, CTE and latent heat of the transition, see Fig. 2. For Sc$_{1-x}$Al$_x$F$_3$ with $x < 1$, we do a slightly different fit since their latent heats are unknown: we fix the ratio $dT_c/dP = 2e_a/(A_0 C_a)$ to that of the pure compound AlF$_3$. This is justified by the observed linear $T - P$ phase diagram of Sc$_{1-x}$Al$_x$F$_3$ with a slope that varies little with composition $x$. We do a similar fit for Sc$_{1-x}$Ti$_x$F$_3$. The resulting parameters together with the calculated supercooling and superheating temperatures are given in Table 1.

Overall, we find that that there is good agreement between our model and experiments. The discrepancies between the observed and calculated M-F-M bond angles above $T_c$ shown in Figs. 2 (g) and (h), are due to local lattice distortions from the average c-structure, which we have not considered in our model. More importantly, the deviations from mean-field behavior are most noticeable in the volume expansions of ScF$_3$ and AlF$_3$, (see Figs. 2 (c) and (d)), which correspond to the extreme cases of large and small metal ion radius considered in this work ($r_{Sc} = 0.745$ Å, $r_{Al} = 0.535$ Å). This suggests a trend with M-cation size. In ScF$_3$, NTE is the result of cooperative tilt fluctuations of the rigid ScF$_6$ octahedra which reduce the average Sc-Sc distance while keeping the Sc-F distance fixed. Such fluctuations can only give rise to NTE; therefore the PTE in AlF$_3$ must originate from non rigid modes such as Al-F bond stretching, which we have not considered in our model.
Sc\textsubscript{1-x}Ti\textsubscript{x}F\textsubscript{3} with \( x = 0.7 \) has a mean B site radius in between these two extremes (0.69 Å) and the deviations from our model and its observed volume expansion are tiny, which indicates that the fluctuations of both rigid and non-rigid modes are unimportant. A picture therefore emerges in which rigid octahedra fluctuations dominate the TE for large metal ions and decrease with their size, while non rigid vibrational modes dominate the TE for small metal ions and decrease with increasing radius.

Fig. 3 shows the predicted spontaneous shear strains, order parameter, and specific heats for Sc\textsubscript{1-x}Al\textsubscript{x}F\textsubscript{3} and Sc\textsubscript{1-x}Ti\textsubscript{x}F\textsubscript{3} using our parametrization. Our prediction for the shear strains in AlF\textsubscript{3} compares well with experiments.\textsuperscript{13}

Figures 4 (a) and (b) show the \( T - P \) phase diagrams of Sc\textsubscript{1-x}Ti\textsubscript{x}F\textsubscript{3} and Sc\textsubscript{1-x}Al\textsubscript{x}F\textsubscript{3} calculated from Eq. (13). The linear dependence between \( T \) and \( P \) of our model agrees with the observed phase diagram for Sc\textsubscript{1-x}Al\textsubscript{x}F\textsubscript{3}. Using Eq. (13) and the parameters from Table I, we find that \( dT_a/dP \approx 0.4 \times 10^3 \) K GPa\(^{-1}\) which is in excellent agreement with experiments.\textsuperscript{7,21} For Sc\textsubscript{1-x}Ti\textsubscript{x}F\textsubscript{3}, we predict that \( dT_a/dP \approx 0.7 \times 10^3 \) K GPa\(^{-1}\). There are no reports on the calculated or measured \( T - P \) phase diagram for Sc\textsubscript{1-x}Ti\textsubscript{x}F\textsubscript{3} in the literature.

In Appendix A, we derive expressions for the temperature dependence of the soft mode frequencies. In the parent \( c \) phase, we find the usual mean field behavior for the \( R_a^+ \) mode, \( \omega_{R_a^+} \propto \sqrt{A_0(T - T_0)} \), which is in agreement with IXS.\textsuperscript{19} In addition, our values for \( A_0 \) given in Table I are about what is expected from the observed soft mode ( \( A_0 \approx 3 \times 10^{-3} \) meV K\(^{-1}\) Å\(^{-5}\)) for ScF\textsubscript{3}.\textsuperscript{19} The temperature dependence of the A\textsubscript{1g} and E\textsubscript{g} phonon frequencies in the \( r \) phase has been measured by Raman scattering experiments for AlF\textsubscript{3}.\textsuperscript{3} However, we cannot compare to our model as the shear moduli \( C_i \) and

### Table I. Model parameters for Sc\textsubscript{1-x}Al\textsubscript{x}F\textsubscript{3} and Sc\textsubscript{1-x}Ti\textsubscript{x}F\textsubscript{3} and predicted supercooling (\( T_0 \)) and superheating (\( T' \)) temperatures at ambient pressure. Transition temperatures (\( T_c \)) taken from Refs. [5, 7, and 12]

|                | \( x = 1.0 \) | \( x = 0.4 \) | \( x = 1.0 \) | \( x = 0.7 \) |
|----------------|---------------|---------------|---------------|---------------|
| \( \kappa_0 \) [10\(^{-6}\) K\(^{-1}\)] | 10            | 10            | 0             | 0             |
| \( \tilde{v} + \tilde{u} \) [meV Å\(^{-1}\)] | 0.78          | 0.05          | -0.81         | -0.27         |
| \( A_0 \) [10\(^{-3}\) meV K\(^{-1}\) Å\(^{-5}\)] | 3.7           | 5.8           | 2.9           | 3.1           |
| \( \gamma \) [meV Å\(^{-2}\)] | 12            | 48            | 13            | 17            |
| \( \epsilon_a/C_a \) [Å\(^{-2}\)] | 0.13          | 0.20          | 0.17          | 0.17          |
| \( \epsilon_r/C_r \) [Å\(^{-2}\)] | 0.14          | 0.27          | 0.28          | 0.30          |
| \( T_0 \) [K] | 753           | 493           | 327           | 227           |
| \( T' \) [K]  | 718           | 493           | 344           | 228           |
| \( T_c \) [K] | 713           | 493           | 340           | 228           |
C. Comparison to ReO$_3$

It is interesting to compare ScF$_3$ with the isostructural compound ReO$_3$. At ambient pressure, ReO$_3$ exhibits a perovskite $c$ lattice structure from the lowest observed temperature up to its melting point despite its empty $A$ site and therefore low tolerance factor. The stability of the $c$ phase is a consequence of its metallicity: the Fermi pressure of delocalized Re 5$d$ electrons that occupy the $\pi^*$ conduction band keep the ReO$_6$ octahedra from tilting. On the other hand, such states are empty in the wide-gap insulator ScF$_3$. Its lattice structure remains cubic at all temperatures due to its purely ionic Madelung energy. Both compounds exhibit incipient lattice instabilities in their $c$-phases. In ScF$_3$, softening of the entire M-R phonon branch (with lowest point at $R$) has been observed by IXS from 300 to 8K at ambient pressure and also found by a first-principles calculation. The temperature dependence of the phonon energies is well-described by mean-field theory, as discussed above. Condensation of the $R_1^+$ mode and its associated $c-r$ transition can be induced by modest hydrostatic compression ($\sim 0.6$ GPa at RT) or cation substitution. It is unknown whether the transition is of first or second order. In ReO$_3$, inelastic neutron scattering experiments have observed softening from 280 to 2K without condensation of the M$_3^+$ phonon mode, which consists of in-phase rotations of rigid ReO$_6$ octahedra along a $[100]$ axis that passes through the metal cation. The supposedly observed linear temperature dependence of the mode energy is unusual as is shown by the blue dashed line in Fig. 6. However, we make the observation that the linear fit is hardly distinguishable from the standard mean-field behavior, $\omega_{M_3^+} \propto \sqrt{A_0(T - T_0)}$, with physically reasonable parameters ($A_0 \approx 2.5 \times 10^{-3}$ meV K$^{-1}$ Å$^{-5}$, and $T_0 \approx -296$K), see solid red line in Fig. 6. The mode can be condensed upon application of moderate pressures ($\sim 0.5$ GPa at RT) and a $P-T$ phase diagram has been established by neutron diffraction experiments in which the high-pressure phase has $c$ symmetry ($I\bar{m}3$) and the transition line is of second-order. Additional pressure-induced transitions have been reported in ScF$_3$ and ReO$_3$ at higher pressures.

Both ScF$_3$ and ReO$_3$ exhibit negative TE over a wide temperature range with a common origin: large quartic anharmonicities of their corresponding soft $R_1^+$ and M$_3^+$ modes consisting of rigid antiphase rotations of the ScF$_6$ and ReO$_6$ octahedra, respectively. The size of the effect, however, is an order of magnitude larger in...
TABLE II. Transition temperatures ($T_c$), isothermal entropy changes ($\Delta S$), isothermal heats ($Q = T_c \Delta S$), pressure changes ($\Delta P$), caloric strengths ($\Delta S/\Delta P$), refrigerant capacity (RC), and $T - P$ slope ($dT_c/dP$) of giant barocaloric materials.

| Compound            | $T_c$ [K] | $\Delta S$ [JK$^{-1}$kg$^{-1}$] | $Q$ [kJkg$^{-1}$] | $\Delta P$ [GPa] | $\Delta S/\Delta P$ [JK$^{-1}$kg$^{-1}$GPa$^{-1}$] | RC [Jkg$^{-1}$GPa$^{-1}$] | $dT_c/dP$ [K/MPa] | Ref. |
|---------------------|----------|-------------------------------|------------------|------------------|--------------------------------|--------------------------|------------------|------|
| Ni$_{49.26}$Mn$_{36.06}$In$_{14.66}$ | 293      | 24                            | 7.0              | 0.26             | 92                                           | 120                      | 18               | 28   |
| LaFe$_{11.33}$Co$_{0.47}$Si$_{1.2}$ | 237      | 8.7                           | 2.0              | 0.20             | 43.5                                         | 81                       | 73               | 29   |
| (NH$_4$)$_3$MoO$_4$F$_3$ | 297      | 55                            | 16.3             | 0.5              | 110                                          | 5200                     | 202              | 30   |
| Gd$_2$Si$_2$Ge$_2$ | 270      | 11                            | 2.9              | 0.20             | 55                                           | 180                      | 32               | 31   |
| Fe$_{49}$Rh$_{51}$ | 308      | 12.5                          | 3.8              | 0.11             | 114                                          | 105                      | 54               | 32   |
| Mn$_3$Ga$_3$ | 285      | 21.6                          | 6.2              | 0.09             | 240                                          | 125                      | 65               | 33   |
| (NH$_4$)$_2$SO$_4$ | 219      | 60                            | 13.2             | 0.10             | 600                                          | 276                      | 45               | 34   |
| BaTiO$_3$ | 400      | 1.6                           | 0.64             | 0.10             | 16                                           | 10                       | $\sim$58          | 35   |
| [TPrA] [Mn(dca)$_3$] | 330      | 35.1                          | 11.6             | 0.00689          | 5094                                         | 62                       | 231              | 36   |
| Sc$_{1-x}$Ti$_x$F$_3$ ($x = 0.85$) | 283.0    | 12                            | 3.4              | 0.10             | 120                                          | 406                      | 723              | This work |

FIG. 6. Temperature dependence of the $M^+_6$ phonon mode in ReO$_3$. Dashed-blue and solid-red lines correspond to purely linear and classical mean-field behavior, respectively. Data taken from Ref. [43].

ScF$_3$ than in ReO$_3$. This can be understood from the distinct nature of their metal-nonmetal bonds. In ScF$_3$, there is little overlap between the charge densities that form the ionic bond between Sc$^{3+}$ and F$^{-}$, which favors large buckling fluctuations in the Sc-F-Sc chains. In ReO$_3$, the buckling fluctuations of the Re-O-Re bonds are reduced by the stiffer covalent bond formed by hybridized Re 5$d$ and O 2$p$ electrons.$^{42,50}$

D. Comparison to WO$_3$

Another interesting compound to compare with is tungsten bronze WO$_3$. Like ScF$_3$, WO$_3$ is an insulator but its high temperature phase is tetragonal ($t$) and it goes through several structural transitions upon cooling.$^{3}$ Its hypothetical c structure has an unstable $M^+_3$ mode consisting of opposite displacements of the cations and anions from unit cell to unit cell along the [110] directions,$^{51}$ which generate off-center displacements of W$^{6+}$ towards one of its nearest O$^{2-}$ with concomitant increase in their covalency.$^{52}$ Condensation of this mode leads to a t-structure of highly distorted WO$_6$ octahedra.$^{53}$ The energy gain due to the increase in covalency between W$^{6+}$ and O$^{2-}$ favors the t phase over the ionic c-structure.$^{52}$ The c phase can be stabilized in WO$_3$ by introducing electrons: when doped with Na, 3$s$ electrons begin to occupy the conduction band and, for sufficiently large concentrations, their Fermi pressure stabilizes the c phase.$^{50}$ Such a c phase displays PTE and mean-field softening with temperature of its M$_3^+$ phonon mode down to about 416 K where a structural transition to a t phase occurs.$^{54}$

IV. CONCLUSIONS

We have presented a Landau theory for trifluoride and have used it to calculate and predict the temperature and pressure dependence of several thermodynamic quantities. We have compared our results to existing experimental data on trifluorides and have quantified the deviations from mean-field theory. We have found that the fluctuations of their rigid MF$_6$ octahedra tend to increase with the metal cation size. We have used our model to predict a giant BCE in Sc$_{1-x}$Ti$_x$F$_3$ ($x = 0.85$) of up to 15 JK$^{-1}$kg$^{-1}$ for a pressure change of 0.2 GPa. This effect extends over a temperature range of over 140 K, which includes RT. Our results suggest that open lattice frameworks such as the trifluorides could be a promising platform to search for giant barocaloric effects.

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Appendix A: Soft Mode Frequencies

The soft mode frequencies are computed from the free energy (2) with the $\eta$’s constant,\textsuperscript{26}
\[ \varrho \omega_{ij}^2 \delta_{ij} = \frac{\partial^2 [G_{ij} + G_{ii}]}{\partial Q_i \partial Q_j}, \quad (i, j = 1, 2, 3) \tag{A1} \]
where $Q_i$ are principal-axis coordinates of the soft mode and $\varrho = 2m_F/\alpha^2$ is the mass density of fluorine atoms participating in each mode, where $m_F$ is the mass of the fluorine atom. The soft mode frequencies given in Eq. (A1) must be evaluated at the equilibrium points given in Eqs. (8) and (4). The free energy $G$ appearing in Eq. (A1) is that of Eq. (2) rather than that of Eq. (5) because the frequency of the acoustic modes associated with uniform strains vanishes in the long-wavelength limit.\textsuperscript{26}

In the c phase, the frequency of the $R_4^c$ mode is threefold degenerate since all strains vanish,
\[ \varrho \omega_{R_4^c}^2 = \tilde{A}. \tag{A2} \]
In the r phase, the mode splits into the $E_g$ doublet and the $A_{1g}$ singlet,
\[ \varrho \omega_{E_g}^2 = \tilde{A} + \left( 2\tilde{u} + 8\frac{e_a^2}{C_a} + 6\frac{e_t^2}{C_t} + \frac{1}{3} \frac{e_r^2}{C_r} + w_1 Q_s^2 \right) Q_s^2, \tag{A3a} \]
where $Q_s$ is given in Eq. (8).

\[ \varrho \omega_{A_{1g}}^2 = \tilde{A} + \left( 6[\tilde{v} + \tilde{w}] + 28\frac{e_a^2}{C_a} + \frac{4}{3} \frac{e_t^2}{C_t} + 5w_1 Q_s^2 \right) Q_s^2, \tag{A3b} \]

where $w_2$ and $w_3$ are parameters independent of temperature and pressure. We consider the following order parameters for the t-, o- and r-phases,
\[ t: (Q_1, Q_2, Q_3) = Q_s (0, 0, 1), \tag{B2a} \]
\[ o: (Q_1, Q_2, Q_3) = \frac{Q_s}{\sqrt{2}} (1, 1, 0), \tag{B2b} \]
\[ r: (Q_1, Q_2, Q_3) = \frac{Q_s}{\sqrt{3}} (1, 1, 1). \tag{B2c} \]

The contribution from the anisotropic terms of Eq. (B1) to the free energy is,
\[ \tilde{G}_{AN}(t) = 0, \tag{B2a} \]
\[ \tilde{G}_{AN}(o) = \left( \frac{3}{8} \tilde{v} + \frac{3}{16} w_2 Q_s^2 \right) Q_s^4, \tag{B2b} \]
\[ \tilde{G}_{AN}(r) = \left( \frac{1}{2} \tilde{v} + \frac{1}{6} (w_2 + w_3) Q_s^2 \right) Q_s^4. \tag{B2c} \]

Appendix B: Sixth-order c anisotropy

In this Appendix, we discuss the effects of sixth-order anisotropies in some of our previous results. We will show that such anisotropies allow us to describe a possible phase competition between pressure-induced phases. So far, the evidence for phase competition has been experimentally reported in ScF\textsubscript{3} \textsuperscript{23,24} where near about 3.0 GPa, the r phase destabilizes and a structural transition to an orthorhombic (o) phase occurs. In addition, a MD simulation of AlF\textsubscript{3} has found a metastable o-phase in the free energy at ambient pressure and below the c -- r transition temperature.\textsuperscript{16} No r -- o transition has been observed in TiF\textsubscript{3}, FeF\textsubscript{3}, and CrF\textsubscript{3}.\textsuperscript{55,56}

It is well known that the free energy (5) does not support a stable o phase.\textsuperscript{25} To include it, we must add sixth-order c anisotropies,
\[ \frac{3w_2}{4} (Q_1^2 Q_2^2 + Q_3^4) + \frac{3}{2} (Q_1^4 + Q_2^4) + \frac{9w_3}{2} Q_1^2 Q_2^2 Q_3^2. \tag{B1} \]

where $w_2$ and $w_3$ are parameters independent of temperature and pressure. We consider the following order parameters for the t-, o- and r-phases,
\[ t: (Q_1, Q_2, Q_3) = Q_s (0, 0, 1), \tag{B2a} \]
\[ o: (Q_1, Q_2, Q_3) = \frac{Q_s}{\sqrt{2}} (1, 1, 0), \tag{B2b} \]
\[ r: (Q_1, Q_2, Q_3) = \frac{Q_s}{\sqrt{3}} (1, 1, 1). \tag{B2c} \]

The contribution from the anisotropic terms of Eq. (B1) to the free energy is,
\[ \tilde{G}_{AN}(t) = 0, \tag{B2a} \]
\[ \tilde{G}_{AN}(o) = \left( \frac{3}{8} \tilde{v} + \frac{3}{16} w_2 Q_s^2 \right) Q_s^4, \tag{B2b} \]
\[ \tilde{G}_{AN}(r) = \left( \frac{1}{2} \tilde{v} + \frac{1}{6} (w_2 + w_3) Q_s^2 \right) Q_s^4. \tag{B2c} \]

FIG. 7. Schematic phase diagrams of the trifluoride (a) at ambient pressure and (b) with applied hydrostatic compression. All transition lines are of first-order. Here, $A_0 T_0/(w_1 a^4) = 1.0 \times 10^{-3}$, $\tilde{u}/(w_1 a^2) = 6.0 \times 10^{-2}$, and $\tilde{v}/(w_1 a^2) = -7.0 \times 10^{-2}$. $P$ is in units of $C_s A_0 T_0/(2e_a)$.

For simplicity, we take $w_2 = 0$. Then, for $\tilde{v} < 0$ and $w_1 + w_3 > 0$, we find that the r phase is the global minimum for small spontaneous distortions ($Q_s^2 < -(3/4)(\tilde{v}/w_3)$) while the o phase is a local minimum; and vice versa for large distortions ($Q_s^2 > -(3/4)(\tilde{v}/w_3)$). For $\tilde{v} < 0$ and $w_1 + w_3 \leq 0$, the energy has unphysical divergences implying that higher-order terms must be taken into account. The t phase is always metastable.

The order parameter of the o phase with $w_2 = 0$ is given as follows,
\[ Q_s(T, P) = \pm \left( \sqrt{\frac{\tilde{u} + 3\tilde{v}/4}{w_1}} - \frac{\tilde{A}}{w_1} - \frac{\tilde{u} + 3\tilde{v}/4}{w_1} \right)^{1/2}, \]
where $\tilde{\Delta}$ is given by Eq. (6). The order parameter of the r-phase with sixth-order anisotropies is obtained by replacing $w_1 \rightarrow w_1 + w_3$ in Eq. (8).

Figure 7(a) shows a generic $w_3 - T$ phase diagram at ambient pressure calculated by comparing the free energies of the $c$, $r$ and $o$ minima. For small anisotropies ($w_3/w_1 \leq 2.2$), we find there is only a $c - r$ phase transition; while for large anisotropies ($w_3/w_1 \geq 2.2$), an additional $r - o$ phase change occurs at low temperatures. Figure 7(b) shows the $w_3 - T$ phase diagram at an applied pressure. As expected, pressure favors ordering: as the $c - r$ and $r - o$ transitions are pushed to higher temperatures. The corresponding free energy changes $\Delta G = G - G_o + P^2/(2C_o)$ of the $r$ and $o$ phases for $w_3/w_1 = 2.0$ are shown in Fig. 8. The free energy of the metastable $t$ phase is not shown for clarity. At ambient pressure, the $r$ phase is a global minimum while the $o$ phase is metastable, which is in agreement with MD simulations. With large enough applied pressures, the situation reverses and the $r$-phase becomes a local minimum while the $o$ phase is the ground state. Metal trifluorides must then lie in the region of low anisotropy ($w_3/w_1 < 2.2$), as no transition to an $o$ phase has been observed at ambient pressure.

![Diagram](image-url)
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