Structural relationship between negative thermal expansion and quartic anharmonicity of cubic ScF_3
Supplemental Material

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Phonon densities of states (DOS) of ScF_3 with the cubic DO_9 structure were obtained from inelastic neutron scattering experiments, and from first-principles density functional theory calculations. The overall agreement between experiment and computation was good, so we present here some additional observations of calculated phonons.

The radial distribution functions (Fig. 1) calculated by first-principles MD show a large broadening of the second peak (nearest F-F distance) compared to the first peak (nearest Sc-F distance) at higher temperatures. Similarly, the angular distribution function for the F-Sc-F bond angle (Fig. 2) shows a broad distribution with a FHWM of about 10 degrees. Both of these results are consistent with uncorrelated motions of fluorine atoms. This is also evident in the attached animation, in which relative motions of two nearby F atoms undergo frequent changes in phase and frequency. The geometry of the DO_9 structure offers little constraint on the transverse modes of F atom motion, also suggested by the first-principle MD calculations. Figure 3 shows the plane-projected atomic trajectories of Sc and F atoms. Fluorine atoms execute large excursions in the two directions

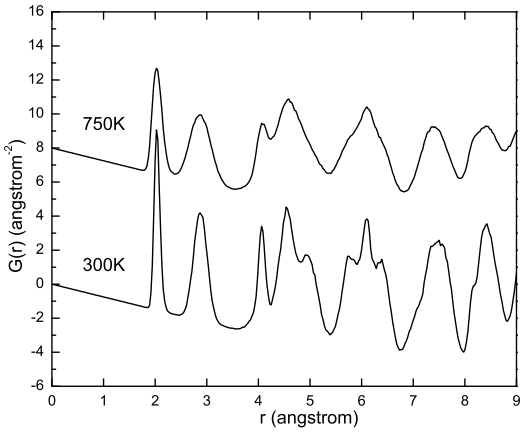

FIG. 1: Radial distribution functions from first-principle MD calculations.

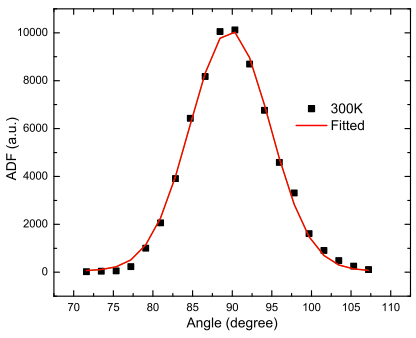

FIG. 2: The angular distribution function for F-Sc-F angle at 300K from first principle molecular dynamics and its Gaussian fit.

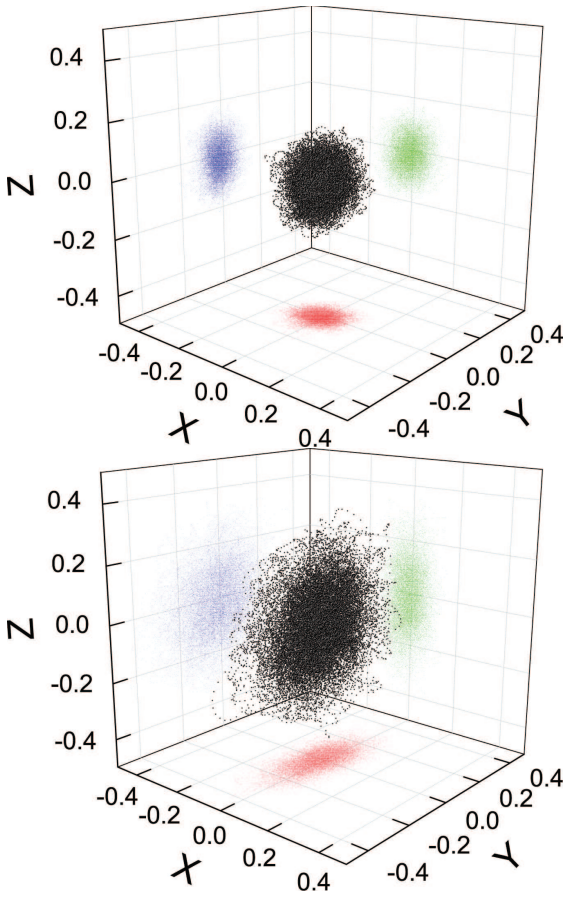

FIG. 3: First-principles MD trajectories and their projections onto x-y, y-z, and x-z planes for Sc (left) and F (right) at 300 K. Distances are in Å. The direction of Sc-F bond is $\hat{x}$.

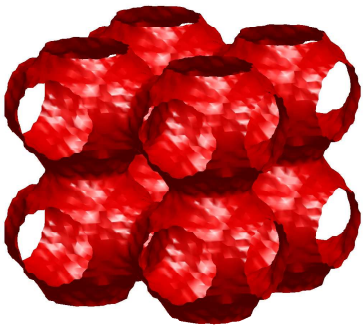

FIG. 4: Isosurface of Grüneisen parameter $\gamma = -5$ for phonon dispersion branch 4+. The Γ point is at the center of the plot and R points are at centers of the spheroids. Centers of neighboring spheroids are connected along M-R directions.

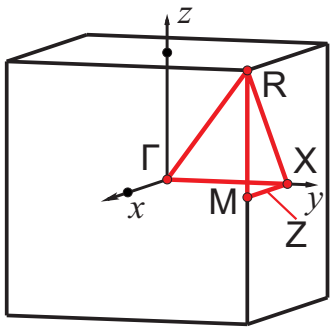

FIG. 5: The first Brillouin zone of ScF_3 and its high symmetry points.

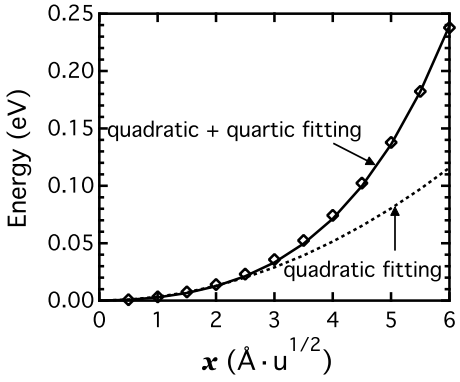

FIG. 6: The frozen phonon potential of mode R4+ at Z point and its quadratic and quadratic+quartic fit. x is the normal mode coordinate. u is the atomic mass unit. For this mode, F atoms vibrate at different magnitudes and the largest displacement is 0.15 Å for $x = 1.0$ Å·u$^{1/2}$.

transverse to the Sc-F bond.

Some of these modes with large F displacements were found by frozen phonon calculations to be purely quartic oscillators, or have large quartic contributions to their potentials. These quartic modes caused the quasiharmonic calculations to predict very large and negative Grüneisen parameters, and we mapped where this occurred in the Brillouin zone. The isosurface of Grüneisen parameter $\gamma = -5$ for phonon dispersion branch 4+ is shown in Fig. 4. The phonon modes inside the tubes of spheroids are the ones that have substantial quartic terms in their potentials and contribute most to the NTE. For example, the frozen phonon calculation for Z point (Fig. 5), which is the midpoint between the M point (purely quartic mode potential) and the X point (purely quadratic mode potential), is shown in Fig. 6. The frozen phonon potential at the Z point has a substantial quartic term.

Although the F atoms are confined to Sc neighbors by harmonic forces, by geometry the transverse modes are quartic oscillators that stiffen with increased thermal vibrational amplitude. Meanwhile, the increased longitudinal forces on the Sc atoms pull them together, causing NTE, and the increased length of the Sc-F bonds cause longitudinal vibrations to soften with temperature.

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