Comment on “Colossal Pressure-Induced Softening in Scandium Fluoride”

In a recent Letter [1], Wei *et al.* report neutron powder diffraction measurements at variable temperature and pressure of negative thermal expansion material, scandium fluoride ScF_3 [2]. The diffraction patterns were fitted using the Rietveld method to refine the lattice and the atomic displacement parameters, with other aspects of the crystal structure fixed by $Pm\bar{3}m$ cubic symmetry. From the structural refinement of the measured diffraction patterns, authors obtain the isothermal compressibility curves. These results thoroughly characterize the equation of state of this material in the low-pressure cubic phase (with increasing pressure, ScF_3 undergoes a structural transition to the rhombohedral structure).

The results reported by Wei *et al.* [1] are indeed very interesting and important because these results can be confronted with predictive, quantitative theories of negative thermal expansion (NTE) and pressure-induced softening and allow one to corroborate or invalidate certain approaches. Wei *et al.* discuss their observations in the context of model molecular dynamics simulations and simple one-dimensional models, which capture qualitative features of the observed phenomena, but do not provide a quantitative theory. On the other hand, a microscopic theory of vibrational and thermomechanical properties of empty perovskite crystals with ReO_3 structure (also rooted in neutron diffraction results [3]) has recently been proposed. This theory describes empty perovskite structures with strong nearest-neighbor bonds as Coulomb floppy networks (CFNs, floppy networks of rigid links stabilized by Coulomb interaction) and provides a very accurate quantitative description of NTE in ScF_3 [3,4].

Motivated to further corroborate the CFN theory, we compared its prediction for the mean-squared transverse displacement of the F atoms, $U_{\text{perp}} \equiv \langle u_{\text{perp}}^2 \rangle$, with that obtained by Wei *et al.* and observed a marked discrepancy. The experimental values are much smaller than those expected from theory (Fig. 1). In fact, the U_{perp} values of Wei *et al.* appear unphysically small, falling for $T \lesssim 150$ K well below the quantum limit for the Fluorine mean-squared transverse displacement due to zero-point motion at $T = 0$, $\langle u_0^2 \rangle = \hbar/m_F\omega_+ \approx 0.006 \text{ \AA}^2$ (dashed line in Fig. 1; $\hbar$ is Planck constant, m_F is mass of the F ion, and $\hbar\omega_+ \approx 37 \text{ meV}$ is the transverse F phonon bandwidth). We then compared these results with the previously published x-ray diffraction data of Greve *et al.* [2] and

FIG. 1. Mean-squared transverse displacement of the F atoms obtained from refinement of the crystal structure at $P \approx 0$. The triangles show the results of Rietveld refinement of neutron diffraction data measured on NPDF diffractometer at Los Alamos Neutron Science Center (down triangles) and NOMAD diffractometer at Spallation Neutron Source (up triangles) from Fig. 4(b) of Wendt *et al.* [3]. The circles and squares correspond to the x-ray data from Supplementary Material Fig. 1 of Greve *et al.* [2]. The (red) diamonds are the data of Wei *et al.* [1]. The solid line is theoretical prediction of Ref. [4]; the horizontal broken line shows the quantum limit for the Fluorine mean-squared transverse displacement due to zero-point motion at $T = 0$.

the neutron diffraction data of Wendt *et al.* [3]. We found the latter two datasets to be in good agreement with each other, as well as with the prediction of CFN theory (Fig. 1).

We thus observe that U_{perp} values reported in Fig. 5 of Ref. [1] are substantially incorrect. In our experience, such an underestimate of atomic displacement parameters can be caused by an incorrect accounting for the effects of beam absorption in the sample and sample environment (such as pressure cell in measurements of Wei *et al.*) in the Rietveld treatment of the diffraction data. This also explains unphysical negative atomic displacement parameters reported in Supplementary Material Figs. S7 and S8 of Ref. [1], where authors indeed write “the negative values are consistent with not including the effects of beam attenuation in the refinement process, which at this point could be taken into account by a positive constant shift of all values.” Whether the systematic error of U_{perp} in Fig. 5 of Ref. [1] can be accounted for by a simple shift is unclear.

An evaluation of large systematic errors present in Fig. 5 of Wei *et al.*, which is vitally important for comparison of those data with quantitative theories, is markedly missing in their Letter. Our Comment addresses this unfortunate omission and presents such an evaluation (Fig. 1), providing a reference for future such comparisons.

The purpose of this Comment is twofold: (i) to caution the researchers against using the U_{perp} data of Wei *et al.* [1] for direct quantitative comparisons with theory and (ii) to encourage the authors of Ref. [1] to reconsider their analysis and try to obtain reliable U_{perp} data by better accounting for the beam transmission and attenuation

effects. We believe that the data are of sufficient interest and importance to attempt an analysis [5], which would eliminate, or markedly reduce, the systematic error that is currently present in Fig. 5 of Ref. [1].

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