SnTe was originally studied in the context of lattice vibrations in diatomic lattices [1]. There has been a recent resurgence of interest following its identification as a crystalline topological insulator, which is intimately related to its room temperature structure (the fcc rocksalt structure) [2–4]. Stoichiometric SnTe is expected to be semiconducting with the minimum gap in the band structure of approximately 0.1 eV at the L point in the Brillouin zone [5–7]. Perfectly stoichiometric SnTe has, however, never been grown. Instead the crystals are always Te rich [8,9], with the extra Te being accommodated in the lattice by Sn vacancies. The vacancies lead to a high free carrier concentration of holes, nh, that do not freeze out at low temperature. Moreover, the material undergoes a phase transition to a rhombohedral structure upon cooling. Such a structural transition would then strongly affect some of its topologically protected states [2], as has been reported in the Pb1−xSnxSe class of crystalline topological insulators [10].

The exact transition temperature, Tc, is dependent on the value of nh [11].

While the transition is predicted to be a displacive ferroelectric transition [12–15], no ferroelectric transition has previously been seen in bulk samples due to screening by the free carriers. However a ferroelectric-like response has been reported recently in ultrathin films [16]. Whether this response coexists with metallic conductivity is not clear. A shift of much of the electronic density of states (eDOS) within 2 eV below Ef was seen with ARPES [7], suggesting an electronic mechanism. It is unclear whether the polarization is the primary order parameter or a secondary order parameter as in some manganites [17]. For an insulator the divergence (or not) of the dielectric constant at Tc resolves this issue. For metallic SnTe direct evidence establishing that polarization is the primary order parameter is however missing.

The nonstoichiometry means that SnTe is not insulating but a degenerate semiconductor (with a finite resistivity at low temperature). Ferroelectricity and metallic conductivity are different macroscopic responses, with the former involving the separation of localized charges, while the latter is a property of delocalized electrons. Since local charges are strongly screened by conduction electrons, the two properties might be considered to be mutually exclusive. Theoretically, they may however coexist [18], and such a coexistence was found in recent experimental studies of BaTiO3 [19] and LiOsO3 [20]. Coexistence is possible for electron concentrations up to a critical value at which the Thomas-Fermi screening length falls below a critical correlation length for ferroelectricity [19].

Generally, ferroelectric displacive transitions are expected to be accompanied by changes in the dynamics of the lattice with the energy of a soft phonon mode at some high-symmetry q points (either at the zone center or edge) decreasing on cooling to a minimum at Tc, only reaching zero for a continuous transition and then rising [21,22]. A typical example is the first-order structural transition from cubic to a ferroelectric tetragonal phase in PbTiO3 [23–25], which is driven by a soft transverse optic mode at the Brillouin zone center. Empirically ferroelectric transitions are almost all first order. The reason for this is not clear although the long-range nature of the dipole-dipole interactions is sometimes credited [26]. The coupling between the polarization and strain further favors a first-order instability [27]. In contrast for SnTe we report that the phonon frequency approaches zero at the structural transition consistent with a continuous or very weakly first-order transition.

There are many examples of nearly continuous structural distortions in metals such as the cubic to tetragonal transition in V3Si and Nb3Si [28] driven by a soft acoustic mode towards the zone edge. However these martensitic transitions are not ferroelectric. Our identification that a zone center transverse optic phonon softens and recovers going through Tc in SnTe indicates its transition is a ferroelectric transition like that in PbTiO3.

Previous investigations of the phonon dispersion curves in SnTe carried out by Pawley et al. [1] and more recently Li et al. [29] using inelastic neutron scattering found significant softening of the transverse optic phonon energy towards the Brillouin zone center (Γ point). Similar softening has been
reported in the binary material Pb$_{1-x}$Sn$_x$Te [30]. Although the softening was strongly temperature dependent, phonon energies never softened close to zero even at the lowest measured temperatures. Therefore these authors suggested SnTe and Pb$_{1-x}$Sn$_x$Te approached ferroelectric transitions without ever passing through them. However indications of a structural distortion have been reported in other experiments such as powder x-ray diffraction where peak splitting was seen consistent with the cubic phase being distorted along (1,1,1) directions to a rhombohedral shear angle of $\delta\alpha \sim 0.115^\circ$ [31]. Other signatures of the transition are a change of Bragg reflection intensity in neutron scattering [32] consistent with a relative shift of the two fcc sublattices of $\sim 0.007$ (~4 pm), and changes in the Raman spectrum [33] and heat capacity [34]. A cusplike anomaly in the electrical resistivity at $T_c$ [35,36] has been attributed to the presence of a soft phonon mode. The samples previously studied with inelastic neutron scattering most likely had a value of $n_b$ that was sufficiently high for $T_c$ to have been suppressed. A clear proof that the observed structural transition is a ferroelectric displacement is then lacking. To determine whether SnTe is indeed ferroelectric, we performed inelastic x-ray measurements on a small, close to stoichiometric, single crystal.

The single crystal was grown from equal molar weights of high-purity elements Sn (99.9999%) and Te (99.9999%) wrapped in Mo foil (99.95%), sealed in an evacuated silica ampoule and heated to 850°C, well above the melting temperature [8]. The mixture was slowly cooled to 760°C and the ampoule then quenched into water at room temperature. The structural transition at $T_c = 75$ K was identified in the extracted crystal from a clear change in the slope of the electrical resistivity (see Supplemental Material [48]). A value of $n_b = 3.23 \pm 0.05 \times 10^{20}$ cm$^{-3}$ was deduced from a measurement of the Hall resistivity at 2 K (see Supplemental Material [48]). The value of $T_c = 75$ K is in good agreement with previous measurements for similar $n_b$ [11].

Following an initial examination with diffuse scattering (Supplemental Material [48]), the single crystal was studied by inelastic x-ray scattering with the ID28 instrument at the ESRF (Grenoble). A backscattered silicon (9,9,9) monochromator was used. The scattered photons were analyzed with 9 single-crystalline spherical silicon analyzers mounted in a pseudo-Rowland-circle geometry. Energy scans were performed at constant Q-vector by varying the temperature of the monochromator covering the range $-19.82$ meV to $19.82$ meV in 0.68 meV steps centered at the analyzer energy of 17.794 keV. The penetration depth of the incident x rays was 45 $\mu$m, ensuring reported results are bulk properties. The energy resolution had a Lorentzian line shape with a 3 meV FWHM. Measurements were made over different zones to distinguish the different phonons. The experimental spectra are well described by the instrument resolution convolved with antisymmetrized pairs of Lorentzians for each mode, respecting detailed balance [37], plus a narrow fixed width Lorentzian at the elastic position [see Fig. 2(b) for an example].

Electronic structure calculations were performed for the stoichiometric compound, using scalar-relativistic density functional theory (DFT) as implemented in the vasp package, [38–40], a plane wave basis with cutoff energy $E_c = 200$ eV, and $k$-point sampling with a linear density of 30/Å$^{-1}$ [grid size (8,8,8)]. The energy difference between the cubic and rhombohedral structures converged to within 0.05 meV/formula. We found the ground state energy for the rhombohedral structure to be about 0.2 meV/formula lower than for the cubic structure, with an optimum rhombohedral angular distortion of $\delta\alpha \approx 0.2^\circ$ and a ferroelectric displacement of $\tau \approx 0.009$. Ground state phonon dispersion calculations used the finite displacement method [41] in 128-atom supercells and confirmed the dynamical stability of the rhombohedral phase and the instability of the cubic phase (Supplemental Material [48]). The self-consistent ab initio lattice dynamics method (SCAILD) was then used to obtain phonon dispersion curves at finite temperatures for the cubic phase [42]. The calculated phonon dispersion for the two structures (rhombohedral at $T = 0$ and cubic at $T = 300$ K) are very similar over most of the Brillouin zone. The main differences are close to the zone center where there is a sharp reduction of the energy of the LO phonon [see Fig. 1] is larger than this, supporting the hypothesis that

![FIG. 1. The phonon dispersion for SnTe at 300 K in the reduced Brillouin zone of the conventional cubic cell. The markers are measured experimental points from the phonon annihilation energy transfer while the lines are calculated phonon dispersion curves for fcc SnTe at 300 K.](image-url)
the Thomas-Fermi-screening length exceeds the ferroelectric correlation length. However, the LO dispersion measured with neutrons by Pawley [1] is indistinguishable from our measurements, although a larger range for the dip, reflecting a shorter Thomas-Fermi-screening length, might have been expected from the absence of ferroelectric order in their crystal. This is reconciled by noting that the polarization may provide the dominant screening mechanism, explaining the dip in the LO mode [44].

Phonon dispersion curves at $T_c = 75$ K are shown in the Supplemental Material [48]. There is no measurable change of the experimentally determined elastic constants between 300 K and 75 K consistent with previous measurements [14,45]. The only observable temperature dependence is for the TO mode approaching $\Gamma$ and we focus on this in the following.

The measured energies of the transverse optic (TO) phonon at 300 K and at $T_c = 75$ K are shown in Fig. 2(a). A softening of the phonon energy towards the Brillouin zone center, $\Gamma$, at low temperature is clearly seen. Measured spectra at $Q = (3,3,0.2)$ are shown in Fig. 2(b) at 300 K and 75 K; the 3 peaks correspond to phonon creation (negative energy), phonon annihilation (positive energy), and a small elastic contribution at zero energy. The resolution function makes very low energy phonons difficult to distinguish from the elastic line close to the zone center where the Bragg condition is met. Thus, in Fig. 2(a) the 75 K data are missing a point at $Q = (3,3,0.95)$. Further temperature points were measured for the TO phonon along the $(1,1,0)$ direction. This confirms the softening on cooling to $T_c$ [Fig. 2(c)], while Fig. 2(d) shows that on further cooling below $T_c$ to 50 K and then to 25 K the phonon energy recovers. Individual scans at $Q = (0.1,0.1,1.5)$ are shown in Figs. 3(a)–3(c), along with calculated fits. Unconvoluted scans at $Q = (1.8,1.8,4.2)$, the closest point to $\Gamma$ that could be measured accurately, showing that this mode does not change with temperature.

The values of phonon energies at $\Gamma$ were determined by linearly extrapolating the phonon energy squared $E(q)^2$ plotted against $q^2$ to $q^2 \to 0$ (Supplemental Material [48]), where $q$ is the reduced momentum. Figure 4(a) shows that $[E_{TO}(\Gamma)]^2$ decreases linearly with temperature to almost zero at $T_c$ and increases again above $T_c$. In the Landau theory of ferroelectrics the ratio of the slopes $d([E_{TO}(\Gamma)]^2)/dT$ below $T_c$ to above $T_c$ should be $-2$. The electrical resistivity was previously found to be adequately described with a simple model calculation based on this ratio for a temperature range $0.35 < (T - T_c)/T_c < 1.4$ [35]. The solid line in the figure is a fit assuming the Landau theory ratio and including a saturation of $E(q)^2$ towards a fixed value at high temperature reflecting the much larger temperature range $0.35 < (T - T_c)/T_c < 4$ spanned by our measurements.

The continuous “second-order” nature of the transition, previously suggested by heat capacity measurements [34], is
The temperature dependence of the TA phonon linewidth at
of anharmonicity described in the text is shown by the solid line.

The TO linewidth is enhanced at the zone center above
\( T_c \) and this enhancement is suppressed below
\( T_c \). Figure 4(c) shows the linewidth of the TA phonon at
\( Q = (1.8, 1.8, 4.2) \). The TA width is smaller than the TO width and
has no significant temperature dependence.

We now discuss the linewidth of the TO phonon. The
linewidth as a function of
\( \mathbf{q} \) below \( T_c \) (Supplemental Material [48]). Figure 4(b) shows the linewidth as a function of
temperature at \( Q = (0.1, 0.1, 1.5) \) and \( Q = (0.125, 0.125, 5) \). The linewidth is seen to be large above
\( T_c \), but is suppressed below \( T_c \). The calculation for a simple model of
anharmonicity described in the text is shown by the solid line.

We find that the damping of the TO phonons close to the zone center can be explained by
a conventional coupling of displacement and strain. Such a coupling acts to make the transition first order. The continuous
(or only weakly first order) nature of the transition then
requires that the dipole mode-mode coupling term in a Landau
expansion of the free energy (the fourth-order term in powers of the polarization) is large in the absence of strain. The
marked difference of the measured LO phonon energy from
that calculated with DFT suggests that a strong many-body
dipole-dipole screening may be present in the parent insulating
material. Identical LO phonon energies across samples where
the structural transition is present or absent also suggest that
\( T_c \) is not suppressed by screening of the dipole-dipole interaction
through added charge carriers. Another mechanism for the
suppression is provided in Ref. [11] where it is suggested
that it is due to the removal of valence electrons rather than
screening from conduction electrons. Our results support such
a diminished role for the conduction electrons and indicate
that their contribution to characteristics such as the soft-mode
phonon linewidth is minor.

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