Ferroelectric order versus metallicity in \( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \) (\( x = 0.009 \))

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We report on a thermal-expansion study of the ferroelectric phase transition in insulating \( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \) (\( x = 0.009 \)) and its evolution upon increasing charge-carrier concentration up to \( n \simeq 60 \times 10^{19} \text{cm}^{-3} \). Although electric polarization is screened by mobile charge carriers, we find clear signatures of the ferroelectric phase transition in the thermal-expansion coefficient \( \alpha \) of the weakly doped metallic samples. Upon increasing \( n \), the transition temperature \( T_c(n) \) and the magnitude of the anomalies in \( \alpha \) rapidly decrease up to a threshold carrier density \( n^* \) above which broadened anomalies remain present. There is no indication for a sign change of \( \alpha \) as is expected for a pressure-dependent quantum phase transition with \( n \) as the control parameter. Thus, the ferroelectric-like transition is either continuously fading away or it transforms to another low-temperature phase above \( n^* \), but this change hardly affects the temperature-dependent \( \alpha(T) \) data.

I. INTRODUCTION

Perovskite titanates \( \text{ATiO}_3 \) with divalent \( A \)-site ions contain tetravalent titanium with an empty \( 3d \) shell, such that these materials typically form band insulators. Some members of this \( A^2+\text{Ti}^{4+}\text{O}_3 \) family are ferroelectric such as \( \text{BaTiO}_3 \), \( \text{PbTiO}_3 \), \( \text{CdTiO}_3 \),\(^1\) whereas others like \( \text{SrTiO}_3 \), \( \text{CaTiO}_3 \), and \( \text{EuTiO}_3 \) show quantum paraelectric behavior,\(^5,11\) i.e., a ferroelectric long-range order is suppressed by quantum fluctuations. Although a ferroelectric transition is absent in both \( \text{SrTiO}_3 \) and \( \text{CaTiO}_3 \),\(^6,12\) mixing Sr and Ca on the \( A \) site (\( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \)) induces ferroelectricity already for tiny calcium substitutions \( 0.0018 \leq x < 0.02 \) with increasing Curie temperature \( T_c(x) \). For larger \( x \), relaxor ferroelectric behavior is observed and finally the material becomes antiferroelectric above \( x \simeq 0.12 \).\(^11,13\)

The high-temperature structure of \( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \) is cubic (space group \( \text{Pm}3\text{m} \), No. 221), but upon cooling it changes to the tetragonal, centrosymmetric space group \( I\overline{4}/mcn \) (No. 140) at an \( x \)-dependent transition temperature \( T_r(x) \), which is significantly larger than the ferroelectric ordering temperature \( T_c \). Because the finite polarization in the ferroelectric state requires the absence of an inversion center, the transition at \( T_c \) necessarily involves a further symmetry reduction. The crystal structure in the ferroelectric phase was found to belong to the orthorhombic point group \( mm \).\(^14\)\(^\text{[15] [16]} \) and for \( x = 0.02, 0.04 \) the space group \( I\overline{2}2\text{m} \) (No. 46) was specified by x-ray diffraction.\(^21\)

Charge-carrier doping in pure \( \text{SrTiO}_3 \) by, e.g., a partial removal of oxygen or substitution of Sr (Ti) by La (Nb), induces metallic conductivity\(^22\)\(^\text{[23] [24]} \) and, for certain carrier concentrations, even superconductivity.\(^25\)\(^\text{[26] [27]} \)

In systems with both, calcium substitution and electron doping (\( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \)), the \( T_c \)-related anomalies of the ferroelectric insulating parent compound persist within the metallic and superconducting phase.\(^25\)\(^\text{[28] [29]} \)

Rischau et al. investigated the evolution of this ferroelectric-like transition with charge-carrier concentration \( n \) for \( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \) with \( x = 0.0022 \) and \( x = 0.009 \).\(^30\)

Based on minima in the resistivity data \( \rho(T) \), a decreasing \( T_c \) upon increasing \( n \) was derived and a disappearance of the ferroelectric-like phase above a critical carrier density \( n_c \) that depends on the calcium content \( x \). The mechanism behind this behavior remained unclear, but it was suggested that it could result from Friedel oscillations causing destructive interference of Ca-induced dipoles.\(^30\)

In fact, such a mechanism was discussed theoretically already much earlier by Glazhuk et al.\(^31\)\(^32\).

Rowley et al. discussed the appearance of ferroelectric order in insulating quantum paraelectrics in the context of quantum criticality,\(^33\) where for \( \text{SrTiO}_3 \) the quantum control parameter can be tuned either by stress,\(^33\) by chemical substitution like in \( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \), or by oxygen-isotope exchange.\(^33\)\(^34\)\(^35\) In such a scenario, the charge-carrier concentration \( n \) represents an additional control parameter towards a metallic ground state. The presence of a quantum phase transition is intrinsically tied to a diverging Grüneisen parameter.\(^36\) For pressure-dependent quantum phase transitions, this holds for the Grüneisen ratio \( \Gamma = \alpha/c_p \) with the thermal-expansion coefficient \( \alpha \) and the specific heat \( c_p \). In the vicinity of a quantum critical point \( \Gamma \) exhibits a sign change\(^37\) which results from a sign change of \( \alpha \), because \( c_p \) is always positive.\(^38\) Experimentally, such sign changes of \( \alpha \) are observed in diverse materials where the control parameter is either a magnetic field,\(^39\)\(^40\) a chemical or hydrostatic pressure,\(^40\) or the charge-carrier concentration.\(^17\)

Here, we present a detailed study of the evolution of the ground state of \( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \) with \( x = 0.009 \) as a function of the charge-carrier density \( n \) varying from the insulating parent compound to \( n \simeq 6 \times 10^{20} \text{cm}^{-3} \). Based on thermal-expansion measurements, we investigate the evolution of both the structural transition temperature \( T_s \) and the \( T_c \)-related transition as a function of carrier concentration \( n \). With increasing \( n \), \( T_s \) essen-
tially linearly decreases and the structural transition remains well defined over almost the entire doping range. In contrast, $T_C(n)$ and the corresponding anomalies in $\alpha$ rapidly decrease in the low-$n$ range up to a threshold carrier concentration $n^*$, above which broadened anomalies remain present up to the highest $n$. There is no evidence for a sign change in $\alpha$ as a function of $n$. This either suggests the absence of a sharp quantum phase transition, because the ferroelectric-like transition in Sr$_{1-x}$Ca$_x$TiO$_3$ is continuously vanishing, e.g. by varying from long range to short range, or the symmetry of the low-temperature order changes at some critical charge-carrier content $n^*$ without being directly reflected in the macroscopic uniaxial expansion $\alpha(T)$.

The discussion of our results is split into two parts. Section IIIA discusses the symmetry changes at the structural and the ferroelectric transition of the pristine insulating material in order to clarify how the macroscopic uniaxial expansion $\alpha(T)$ is related to a (partial) twinning occurring at both transitions, which sets the basis for the discussion of the evolution of both transitions as a function of the charge-carrier concentration in IIIB.

## II. EXPERIMENTAL

A commercial Sr$_{1-x}$Ca$_x$TiO$_3$ single crystal with $x = 0.009$ was used for this study. The nominal Ca content was confirmed by secondary ion mass spectrometry (SIMS) as described previously. The crystal was cut into cuboid pieces with all faces being cubic (100) planes and dimensions optimized for Hall effect measurements (typically $0.5 \times 2.5 \times 5 \text{mm}$). In order to induce electron doping the samples were annealed under vacuum ($\lesssim 10^{-3}$mbar) for 1 to 2 hours at temperatures between 700°C and 1000°C depending on the intended charge-carrier concentration. Resistivity and Hall effect measurements were carried out via a standard six-probe method using the commercial physical property measurement system (PPMS by Quantum Design) and most of these data have been published in Ref[39]. On the same samples we studied the uniaxial thermal expansion by measuring the length change $\Delta L(T)$ using a home-built capacitance dilatometer. The samples were continuously heated from liquid-helium temperature to 180 K at a rate of about 0.1 K min$^{-1}$ and the thermal-expansion coefficient $\alpha = (1/L_0)(\partial L/\partial T)$ was determined numerically. The heat-capacity measurement of pristine Sr$_{1-x}$Ca$_x$TiO$_3$ was performed using the microcalorimeter option of the PPMS.

## III. RESULTS AND DISCUSSION

### A. Pristine Sr$_{0.991}$Ca$_{0.009}$TiO$_3$

Figure 1 (a) shows the specific heat $c_p/T$ of pristine Sr$_{0.991}$Ca$_{0.009}$TiO$_3$. The insets depict enlarged views of the temperature ranges around both the structural and ferroelectric transition temperature $T_s$ and $T_C$, respectively, which were determined from thermal-expansion data [see Fig. 1 (b) and (c)]. In agreement with previous publications[29,43], the structural transition at $T_s$ is clearly visible by a small but distinct $c_p$ anomaly, but no anomaly can be resolved in $c_p(T)$ around $T_C$.

Figure 1 (b) shows the thermal-expansion coefficients $\alpha_i/T$ of pristine Sr$_{0.991}$Ca$_{0.009}$TiO$_3$ measured along all
three of the cubic (100) directions (solid lines) that are parallel to the sample’s dimensions $L_i$. Figure 1 (c) displays the corresponding uniaxial length changes $\Delta L_i/L_0$ adjusted to the cubic lattice parameter at 150 K. The $\alpha_i$ are identical at high temperatures and show pronounced anomalies around 139 K and 27 K. The upper temperature can be identified with the cubic-to-tetragonal transition temperature $T_s$. Pure SrTiO$_3$ becomes tetragonal around $T_s \approx 105$ K and in Sr$_{1-x}$Ca$_x$TiO$_3$, $T_s$ increases with increasing $x$. The transition temperature $T_s \approx 139$ K of our pristine sample with $x = 0.009$ is in agreement with findings in the literature.[21,23,25] The high-temperature cubic phase has the space group $Pm3m$ (No. 221) while in the tetragonal phase it is $I4/mcm$ (140). This transition is antiferrodistortive due to a tilting of the TiO$_6$ octahedra around the $c$ axis[20,25] corresponding to $(a'^0,b'^0,c'^-)$ in the classification of Glazer.[50,51] where $a'^0$ denotes the absence of a tilting around the $a$ axis and $c'^-$ represents an anti-phase tilting around the $c$ axis. The inset in Fig. 1 (b) illustrates the octahedra tilt in a top view of the tetragonal $ab$ plane. Titanium ions (blue) define the corners of the cubic unit cell (dotted square). At $T_s$, the oxygen ions (red) move as indicated by the arrows and consequently, the tetragonal unit cell (dashed square) is doubled in the $ab$ plane and rotated by 45°. Due to the anti-phase tilting in the $c$ direction, the $c$ axis is doubled as well. Thus, the cubic axes $a_t$ and the tetragonal axes $a_i, c_t$ are related by $a_t \approx \sqrt{2}a_i$ and $c_t \approx a_i$. It is evident, that the sample’s dimensions $L_i$ which are parallel to the cubic (100) directions, point along (110) with respect to the tetragonal axes $a_t$. The lower transition at 27 K signals the ferroelectric phase transition that was characterized by $P(E)$ hysteresis loops.[20] While the structural transition at $T_s$ is seen mainly in the sample’s short direction $L_{short}$, the ferroelectric transition at $T_C$ predominantly along the sample’s medium and long direction $L_{medium}$ and $L_{long}$, respectively.

Structural phase transitions generally involve transformation twinning.[21,23] For a cubic-to-tetragonal transition one expects the emergence of three twin domains enabling different $\alpha_i$ to partially compensate each other. Therefore, a completely twinned sample should exhibit an isotropic uniaxial thermal expansion $\alpha$, which is related to the volume expansion $\beta = 3\alpha$. In general, $\beta = \sum_i \alpha_i$, where $\alpha_i$ denote the uniaxial expansion coefficients along a set of three pairwise orthogonal directions and for a tetragonal lattice, $\beta = 2\alpha_{at} + \alpha_{ct}$ with the (usually anisotropic) main-axis expansion coefficients $\alpha_{at}$ and $\alpha_{ct}$ along the tetragonal axes $a_t$ and $c_t$, respectively. As shown by $\bar{\alpha} = \beta/3$ (black dashed line in Fig. 1 (b)), the transition at $T_s$ is almost volume-conserving, i.e., the expansion in the long direction roughly compensates the contraction along the short and medium direction. A nearly volume-conserving transition is also reported for SrTiO$_3$ where the temperature-dependent lattice parameters around $T_s$ were determined by high-resolution x-ray diffraction.[25] The anisotropic $\alpha_i$ and the nearly volume conservation indicate highly unequal twinning fractions in our crystal. The usage of a capacitance dilatometer naturally requires the application of a certain uniaxial stress that can be sufficient to achieve a (partial) detwinning of the crystal.[23,24] This is apparently not the case in our sample. Here, the presence of a dominating twin is not triggered by external conditions but rather predetermined by intrinsic crystal defects.[25]

We can estimate the fraction of the tetragonal axes $a_i$ and $c_t$ along the sample’s dimensions $L_i$ by comparing the anomalies of the thermal-expansion coefficients of our measurements with the slope changes of the temperature-dependent lattice parameters around $T_s$ from x-ray diffraction measurements. For this comparison, we use the high-resolution x-ray data of SrTiO$_3$[25] which at $T_s$ show an $a_1$-axis contraction that corresponds to a change $\Delta \alpha_a \approx 8 \times 10^{-6}$ K$^{-1}$ and a $c_1$-axis expansion corresponding to $\Delta \alpha_c \approx -16 \times 10^{-6}$ K$^{-1}$. By comparing these values to our thermal-expansion anomalies $\Delta \alpha_i$ at $T_s$ we estimate that the sample’s short axis $L_{short}$ contains approximately 0.9$a_i$ and 0.1$c_t$, whereas the long axis contains 0.5$a_i$ + 0.5$c_t$, and the medium axis contains 0.6$a_i$ + 0.4$c_t$. From this estimate we reconstruct the tetragonal pure-axes compositions $a_t = 1.25L_{short} - 0.25L_{long}$ and $c_t = 2.25L_{long} - 1.25L_{short}$. Figures 1 (b) and (c) show the temperature-dependent lattice parameters around $T_s$ in our sample. Here, the presence of a dominating twin is not triggered by external conditions but rather predetermined by intrinsic crystal defects.[25]

In contrast to the transition at $T_s$, the ferroelectric transition at $T_C$ is not volume conserving as is clearly demonstrated by the pronounced anomaly in the averaged uniaxial expansion $\bar{\alpha}$ (see black dashed line in Fig. 1 (b)). Furthermore, our reconstructed pure-axis data suggest that the volume-expansion anomaly essentially arises from a $c$-axis expansion upon cooling below $T_C$, while the transition is roughly area-conserving with respect to the $ab$ plane. The latter is naturally expected for a tetragonal-to-orthorhombic transition with opposite expansion anomalies of similar magnitudes along the orthorhombic $a$ and $b$ axes. Note that the ferroelectric polarization is expected to be aligned along one of these orthorhombic axes, as it has been discussed in the literature.[13,21,169] In this context, it is also worth to mention that a tetragonal-to-orthorhombic transition increases the number of possible twin domains by a factor of two. However, the uniaxial length change measured along the tetragonal [110] direction cannot distinguish between multi-domain and single-domain orthorhombic samples, because $\alpha_{[110]} = (\alpha_a + \alpha_b)/2$ in both cases.
Figure 2 shows the thermal-expansion coefficients $\alpha/T$ versus $T$ of Sr$_{0.991}$Ca$_{0.009}$TiO$_{3-\delta}$ with different charge-carrier concentrations up to $n \leq 57.9 \times 10^{19}$ cm$^{-3}$ together with $\alpha/T$ of the pristine sample already shown in Fig. 1. For clarity, the curves are shifted by $7.5 \times 10^{-8}$ K$^{-2}$ with respect to each other. On each sample, we measured $\alpha_i$ along $L_{\text{long}}$. Since all samples were obtained by parallel cuts from the original single crystal it appears plausible that the distribution of twin domains does not vary too much over the individual samples. This assumption is essentially confirmed by the fact that all samples, apart from the one with highest $n$, show clear anomalies of the same sign and similar shape signaling the structural phase transition at $T_s$. With increasing $n$ the transition temperature linearly decreases from $T_s \simeq 139$ K in pristine Sr$_{0.991}$Ca$_{0.009}$TiO$_3$ to $\approx 116$ K for $n = 22.6 \times 10^{19}$ cm$^{-3}$ [see Fig. 2(b)]. A linear decreasing $T_s(n)$ is known from reduced SrTiO$_{3-\delta}$ and a decreased $T_s$ was also seen in reduced EuTiO$_{3-\delta}$, suggesting that this is a generic trend in these almost cubic perovskite titanates. An extrapolation of the linear $T_s(n)$ dependence to the highest doping $n = 57.9 \times 10^{19}$ cm$^{-3}$ matches the kink at 80 K in the $\alpha/T$ curve of the corresponding sample. This suggests that the structural transition remains present in the entire series of Sr$_{0.991}$Ca$_{0.009}$TiO$_{3-\delta}$ samples, but the highest-doped sample apparently has an essentially homogeneous distribution of twin domains and, consequently, the averaged uniaxial expansion $\bar{\alpha}$ hardly shows any anomaly at this volume-conserving transition as discussed above.

The transition at $T_C$ is clearly identifiable for the lower-doped samples (left panel of Fig. 2) and shifts from $T_C \approx 27$ K for pristine Sr$_{0.991}$Ca$_{0.009}$TiO$_3$ down to 18 K for $n = 1.3 \times 10^{19}$ cm$^{-3}$. For the higher-doped samples (right panel of Fig. 2) the $\alpha/T$ anomalies become much less pronounced and rather broad: except for the sample with $n = 12.4 \times 10^{19}$ cm$^{-3}$. Despite this broadening a signature of the transition remains present in $\alpha/T$ of all doped samples. For example, in the more homogeneously twinned sample with $n = 57.9 \times 10^{19}$ cm$^{-3}$ the clear minimum of $\tilde{\alpha}/T$ around 17 K signals the spontaneous volume expansion resulting from the low-temperature transition, whereas $\alpha/T$ only shows a kink at $T_s$ of the high-temperature structural transition, which is volume conserving.

Figure 3 compares the evolution of both transition temperatures $T_s$ and $T_C$ as a function of charge-carrier density $n$. The linear shift of $T_s$ and the weak broadening of the structural transition with increasing $n$ indicate that both the distribution of oxygen vacancies and the resulting charge-carrier density are rather homogeneous in the studied samples. Nevertheless, the low-temperature transition shows a complex behavior. The ferroelectric transition of the insulating pristine sample causes a very sharp $\alpha/T$ anomaly, which remains sharp for the low-doped metallic samples but broadens above $n = 1.3 \times 10^{19}$ cm$^{-3}$. As a criterion to define $T_C$, we take the maximum slope of $\alpha/T$ and use the temperature difference to the minimum of $\alpha/T$ as a measure of the transition width, which is shown as error bars in Fig. 3(a,b). The corresponding $T_C(n)$ curve is concave for $n \leq 1.3 \times 10^{19}$ cm$^{-3}$, as indicated by the dotted line in Fig. 3(a) and essentially saturates for larger $n$. As a further measure of this transition, we use a smooth background $\alpha_{\text{bg}}$ and calculate $\varepsilon = \int (\alpha - \alpha_{\text{bg}}) \, dT$, which yields the spontaneous elongation resulting from the low-temperature transition. For $\alpha_{\text{bg}}(T)$ we measured the thermal expansion $\alpha_{\text{STO}}$ on a single crystal of SrTiO$_3$, which remains in the tetragonal phase and scaled this $\alpha_{\text{STO}}(T)$ curve such that it matches $\alpha(T \approx 25$ K) of the respective Sr$_{0.991}$Ca$_{0.009}$TiO$_{3-\delta}$ sample. This is shown for 2 exemplary charge-carrier contents in Fig. 3(e,f) and the resulting $\varepsilon(T)$ are displayed in Fig. 3(g) with every second measurement skipped for clarity. The evolution of $\varepsilon(T = 4.2$ K, $n)$ as a function $n$ is summarized in Fig. 3(c,d); the corresponding error bars express the sensitivity of $\varepsilon(T = 4.2$ K, $n)$ on variations of the individual scaling factors used for $\alpha_{\text{STO}}$. We see that $\varepsilon(T = 4.2$ K, $n)$ rapidly decreases at $n \leq 1.3 \times 10^{19}$ cm$^{-3}$ and then levels off at a value of about 15% of the spontaneous elongation measured in the ferroelectric phase of pristine Sr$_{0.991}$Ca$_{0.009}$TiO$_3$. This behavior is qualitatively similar to that of $T_C(n)$, which saturates, however,
FIG. 3. Phase diagram of Sr$_{0.991}$Ca$_{0.009}$TiO$_3$-$\delta$. Open symbols refer to weak anomalies. (a) Detail view of the low-$n$ regime with guide to the eye for $T_C(n)$ (dotted curve). (b) Complete range of $n$ with linear fit of $T_C(n)$ (black solid line). Note the scale breaks in panels (a) and (b). (c, d) Spontaneous strain $\varepsilon$ as a function of $n$. (e, f) We used $\alpha(T)$ of pure SrTiO$_3$ as background (gray curves) and integrated the difference to $\alpha(T)$ of the respective Sr$_{0.991}$Ca$_{0.009}$TiO$_3$-$\delta$ sample, exemplary shown for $n = 0$ (e) and $n = 19.5 \times 10^{19}$ cm$^{-3}$ (f). (g) Temperature dependence of $\varepsilon$ of selected samples.

at a comparatively larger value of about 60% of $T_C$ of the insulating pristine material.

These are the main findings of the present study, which extends our previous work suggesting the existence of a ferroelectric quantum phase transition inside the superconducting dome of Sr$_{1-x}$Ca$_x$TiO$_3$-$\delta$. As already discussed there, a true ferroelectric order cannot exist in metals, because the mobile electrons screen any static electric polarization. However, characteristic features of the ferroelectric order in Sr$_{1-x}$Ca$_x$TiO$_3$ are still observed upon weak charge-carrier doping suggesting a ferroelectriclike transition that vanishes via a quantum phase transition as indicated by minima in the resistivity data $\rho(T,n)$. The aim of the present study was to further clarify this issue via thermal-expansion measurements, which are a sensitive thermodynamic probe to detect and characterize pressure-dependent quantum phase transitions. The existence of a well-defined ferroelectric-like transition in the metallic samples is clearly confirmed by the pronounced $\alpha/T$ anomalies (see Fig. 2) up to at least $n = 0.72 \times 10^{19}$ cm$^{-3}$, i.e., the transition remains present in metallic samples which finally become superconducting at lower temperatures. On further increasing $n$, however, the $\alpha/T$ anomalies do not vanish and, in particular, our data do not give any indication for a sign change of the $\alpha/T$ anomalies as a function of $n$. Thus, the general behavior of $\alpha$ and the corresponding Grüneisen ratio $\Gamma = \alpha/C_p$ is different from other materials showing quantum phase transitions as a function of magnetic field, pressure, or $n$ as external control parameter. On the one hand, this could mean the absence of a quantum phase transition, if the ferroelectriclike order changes just continuously disappears towards larger $n$. On the other hand, however, it is also clear from Figs. 2 and 3 that the shape and width of the $\alpha/T$ anomalies strongly change around $n = 1.3 \times 10^{19}$ cm$^{-3}$. This could mean that the symmetry change of the structural transition is different above and below a critical doping $n^*$ in the range of $1.3 \times 10^{19}$ cm$^{-3}$. A similar situation is, in fact, observed in the undoped Sr$_{1-x}$Ca$_x$TiO$_3$ where, as a function of $x$, the symmetry of the low-temperature ordered phase changes from polar ferroelectric (space group $Ic2m$; No. 46) via relaxor ferroelectric to antiferroelectric with inversion symmetry ($Pbcm$, No. 57) above $x \simeq 0.12$ [13,17]. Such a microscopic change is not necessarily reflected in the thermal-expansion coefficient. In the simplest case, this could be an experimental problem, because a more or less vertical phase boundary in an $n$-$T$ phase diagram is difficult to measure as a function of $T$. More generally, anomalies in the uniaxial expansion $\alpha$ require a finite dependence of the respective transition temperature on uniaxial stress along this direction [23]. In this context, it is also important that the polarization of Sr$_{1-x}$Ca$_x$TiO$_3$ is in the orthorhombic $ab$ plane [12,15,16], such that a change of the in-plane symmetry will have minor influence on the observed $\alpha/T$ anomaly, because it arises from a spontaneous elongation of the $c$-axis component in our partially twinned crystals, as discussed above in the context of Fig. 1. Thus, detailed structural analysis of the low-temperature phases for different charge-carrier concentrations would be necessary to resolve this puzzle.

IV. SUMMARY

In conclusion, we present a detailed thermal-expansion study on Sr$_{1-x}$Ca$_x$TiO$_3$-$\delta$ ($x = 0.009$) with charge-carrier density tuned from the pristine, insulating parent compound to $n \simeq 60 \times 10^{19}$ cm$^{-3}$. Both the cubic-to-tetragonal transition $T_c$ and the ferroelectric transition $T_C$ display pronounced anomalies in the thermal-expansion coefficient $\alpha(T)$ of the pristine crystal. As a function of charge-carrier density $n$, $T_c$ decreases linearly from 139 K to 80 K and the related anomalies in $\alpha/T$
remain distinct and of similar magnitude across almost the entire doping range. Despite the presence of mobile charge carriers, the $T_C$-related anomaly survives for $n > 0$. However, $T_C$ decreases rapidly upon increasing $n$ and the associated anomalies in $\alpha(T)$ become very broad above $n \approx 1.3 \times 10^{19} \text{cm}^{-3}$. Whether the evolution of $T_C$ across this carrier concentration is continuous or passes a phase transition at a critical $n^*$ is not directly seen in $\alpha(T)$ but needs to be clarified by a structure analysis.

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The divergence and sign change of α/cₚ require a finite pressure dependence of the underlying quantum phase transition, which, for example, may result from a pressure-dependent quantum critical magnetic field.

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When measuring along $L_{\text{long}}$, the force applied via the dilatometer acts on the smallest cross-sectional area of our sample and consequently produces the largest pressure, whereas along $L_{\text{short}}$ the force acts on the largest cross section producing the smallest pressure. Nevertheless, we observe an expansion along $L_{\text{long}}$ and a compression along $L_{\text{short}}$ when cooling across $T_s$, which indicates the absence of stress-induced detwinning.

The decrease of $T_s$ is, however, not a direct consequence of the charge-carrier doping, because $n$-type doping by chemical substitution like in SrTi$_{1-x}$Nb$_x$O$_3$ increases $T_s$. On our twinned SrTiO$_3$ crystal we find a smooth $\alpha(T)$ low-temperature behavior. In contrast, thermal-expansion data on SrTiO$_3$ measured under strong uniaxial compressive stress result in single-domain tetragonal samples with very different expansion. The corresponding $\alpha(T)$ curves show a minimum between 20 K and 30 K, which resembles the data of our Ca-doped samples. Because SrTiO$_3$ is known to develop a stress-induced ferroelectric order, the anomalous $\alpha(T)$ curves observed probably arise from ferroelectric order that is induced in those SrTiO$_3$ crystals by the application of the uniaxial compressive stress.

This follows from general thermodynamics via Clausius-Clapeyron (Ehrenfest) relations for first- (second-)order phase transitions.