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Ferrielectricity in the metal-organic ferroelectric tris-sarcosine calcium chloride

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We report a paradigm of ferrielectricity in a single-phase crystal, tris-sarcosine calcium chloride [TSCC; $(CH_3NHCH_2COOH)_3CaCl_2$]. Ferrielectricity is well known in smectic liquid crystals but almost unknown in true crystalline solids. C. F. Pulvari [Ferrielectricity, Phys. Rev. **120**, 1670 (1960)] reported it in 1960 in mixtures of ferroelectrics and antiferroelectrics (AFEs), but only at high fields. Tris-sarcosine calcium chloride exhibits a second-order displacive phase transition near $T_c = 130$ K that can be lowered to a quantum critical point at 0 K via Br or I substitution and phases previously predicted to be AFE at high pressure and low temperatures. Unusually, the size of the primitive unit cell does not increase in the so-called AFE phase. We measure hysteresis loops and polarization below $T = 64$ K and provide clear Raman evidence for this paraelectric-ferrielectric transition.

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I. INTRODUCTION

Ferroelectrics (FEs) and antiferroelectrics (AFEs) are well known among low-symmetry crystals and are directly analogous to ferromagnets and antiferromagnets, with polarization P replacing magnetization M. However, ferrielectrics (FIs), with approximately antiparallel dipole ordering but net polarizations and with a switchable component are very rare, except among liquid crystals. Tris-sarcosine calcium chloride (TSCC) has a reported second-order displacive paraelectric (PE) to FE phase transition near $T_c = 130$ K [1–3]. The main aim of this paper is to show that the FE phase of TSCC is actually a textbook paradigm of ferrielectricity. A secondary point of broad interest is that it has the highest figure of merit for electrocaloric materials, according to the new model by Guzmán-Verri and Littlewood [4].

Tris-sarcosine calcium chloride has an unusual (perhaps unique) structure with four polarizations per unit cell in both its PE and FE phase, permitting ferrielectricity without change in primitive cell size, e.g. three polarizations up and one down. Thus, this paper provides what may become a standard textbook example of ferrielectricity.

We note that the definition of ferrielectricity is subtle (there is no official definition, i.e., IEEE standards committee). We use the term as closely analogous to ferrimagnetism to describe a crystal in which there are two or more sublattices with ordered polarizations, and these polarizations do not quite cancel—either because they are antiparallel but of different magnitudes (as with Lieb-Mattis ferrimagnetism), or because they are of the same magnitude but at angles different from 180°. That is a microscopic atomistic definition. In addition, we require that there be a switched polarization.

The early history of FE studies of TSCC is full of errors and *non sequiturs*. Without bogging down unduly in the refutation of false claims and incorrect suggested structures, we review these briefly below, before proceeding to an array of new data: Raman, dielectric, polarization switching, x-ray, and neutron studies. Principal conclusions of this paper are, first, that the system is analogous to the four-sublattice model of Jaradat *et al.* for liquid crystals [5,6] and, second, that contrary to almost all early work (pre-1980), the system is not a hydrogen-bonded order-disorder lattice (N-H…Cl bonds play a small role) but instead dominated by oxygen displacements of the ions surrounding the Ca^{2+} ion. In this paper, we demonstrate that, in TSCC, there is a large, nearly AFE, ordering of oxygens surrounding the Ca^{+2} ions, but their polar displacements do not quite cancel. Note that this is unrelated to the N-H…Cl hydrogen bonding assumed prior to 1975 to be responsible for ferroelectricity in TSCC. The net FE polarization calculated along the b axis from the oxygen displacements, assuming a zwitter-ion charge of +1 on the missing hydrogen, is $0.36\,\mu\mathrm{C/cm^2}$, in good agreement with our experimentally measured value.

Early work by Bornarel and Schmidt [7] showed that TSCC also has a structural phase transition at ~700 MPa hydrostatic pressure at $T = 293$ K and that the phase boundary extrapolates to ≪40 K at atmospheric pressure (their studies were limited to $T > 77$ K). They suggested that the high-pressure phase is AFE but offered no evidence for that. Some data on the hypothesized PE, AFE, FE triple point near $T = 177$ K and $P = 503$ MPa were provided, but the structures and full phase diagrams remain enigmatic. Those authors pointed out that an AFE structure in TSCC need not involve a doubling (or other multiplication) of the primitive unit cell, since the PE and FE phases already have four formula groups (and 12 sarcosine molecules) per unit cell. Thus, an AFE distortion might realign the polarizations to be antiparallel (say, two up and two down) in contrast to

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the four parallel dipoles per FE unit cell. Such an unusual structure also could permit simultaneous FE and AFE ordering, either a FI canted arrangement (as in ferrimagnets [8,9]), or a Lieb-Mattis type antiferroic, uncanted linear polarization geometry with, for example, three polarizations up and one down. This would help explain the polarization data $P(T)$ with strong built-in potential (bias field) reported by Fujimoto *et al.* [8,9]. Although several authors have suggested that the high-pressure ambient temperature phase of TSCC is the same AFE structure as the ambient-pressure low-temperature phase, that is impossible: We emphasize that Fujimoto *et al.* found that P remains nonzero down to very low T, ruling out a centric C_{2h} symmetry, but found that the phase at high pressures and ambient temperatures is probably C_{2h} and definitely nonpolar.

This paper is organized in the following way: First, we use Raman spectroscopy to show that the primitive unit cell does not double at low temperatures or high pressures, and hence that the structures are not AFE in the usual sense. These spectra also establish that the low-T and high-pressure phases are not the same. Second, we use dielectric and polarization measurements (both switching and pyroelectric current) together with known specific heat data to show that phases below $T = 130\,\text{K}$ are both FE, and that a four-state model analogous to that used by Jaradat *et al.* for liquid crystals [5,6] is a reasonable qualitative macroscopic model. Third, we examine x-ray and neutron diffraction data to show that both FE and antiferrodistortive displacements occur simultaneously at low T and, contrary to earlier speculations, involve the Ca-O part of the structure and not the N-H...Cl hydrogen bonds. Finally, we provide an argument why the unusual unit cell with four separate polarizations need not involve any improper ferroelectricity or coupling between two distinct order parameters.

Our earlier Raman studies [10–12] revealed no additional vibrational modes in TSCC at $T = 4\,\text{K}$ compared with $T = 300\,\text{K}$. This supported the idea that any low-T structure(s) had no increase in unit cell size. However, we found unambiguous evidence by other techniques for the so-called AFE transition at $T = 64\,\text{K}$, as well as additional anomalies near $T = 47\,\text{K}$, but no proof that these anomalies are phase transitions in either a crystallographic or thermodynamic sense. The existence of a phase transition at 64 K is marked by very strong mechanical losses (resonant ultrasonic spectroscopy), with a rise from 0.1 to >1.0% and a large specific heat anomaly, nearly half that at $T_c = 130\,\text{K}$. But dielectric and polarization anomalies at 48.0 K are reproducible but much smaller.

One aim of this paper is to provide new electrical and Raman data that confirm the transition at 1 atm pressure and $T \sim$64–70 K. Additional Raman and pyroelectric anomalies verify the transition near 50 K. These transitions are important because, in bromine- or iodine-substituted TSCC, replacement of Cl ions lowers T_c to 0 K ($\sim$80% Br), and the quantum critical point (QCP) dynamics are not quantitatively compatible with a conventional uniaxial FE; hence, the structure (AFE or other) below 47 K is pertinent, and in particular, one should clarify why it remains polar.

The general idea here is that a FI crystal would offer a new kind of switching device, with single-polarity switching (both positive or both negative) and high threshold voltages.

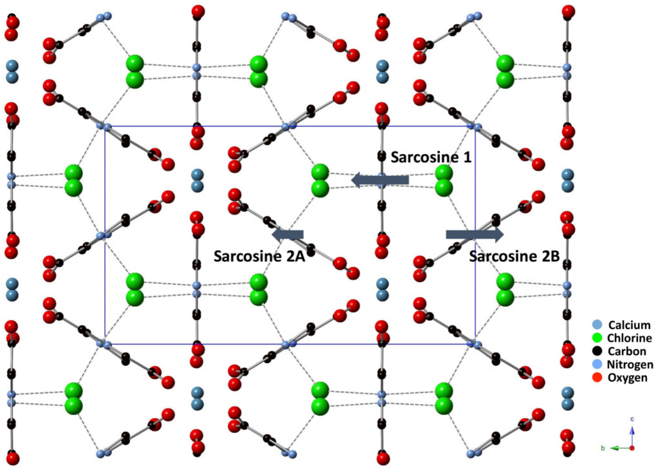

FIG. 1. TSCC structure (modified from Ashida *et al.* [3]); the large arrows show the sarcosine molecule displacements below T_c from our neutron and x-ray data, discussed below.

The basic structure of TSCC is pseudohexagonal, as shown in Fig. 1, with local polarizations orthogonal to the pseudosixfold axis.

II. EARLIER EXPERIMENTS AND INCONSISTENCIES

A. Low temperature and high pressure (Roth *et al.* [13])

Roth *et al.* [13] showed several things about the Raman spectra at low temperatures and high pressures: Firstly, they emphasized that the high-pressure phase had very nearly the same number of Raman lines as did the FE $Pn2_1a$ phase or the PE $Pnma$ phase and, therefore, that it is probably an AFE nonpolar $P2_1/a$ phase (C_{2h}) with the same $Z = 4$ formula groups (12 sarcosines) per primitive cell. In our opinion, this is at best a *non sequitur* and very likely incorrect. In fact, although the FE and so-called AFE phases would have nearly the same total number of vibrational modes, the supposed C_{2h} phase would have many fewer Raman-active modes. This arises for two reasons: The vibrations in C_{2h} have parity, and the odd-parity modes are not Raman-allowed, which would decrease the number of Raman lines by approximately half. In addition, many of the modes in the FE phase will be split into transverse-longitudinal doublets (TO/LO), giving rise to an even larger difference between the number of modes expected in the $Pn2_1a$ and $P2_1/a$ phases. So rather than confirming the predicted symmetry from Schmidt [14], the work of Roth *et al.* [13] actually contradicts it. The paradox here is that usually a FE/AFE transition doubles the unit cell and hence approximately doubles the number of Raman lines, but in this particular case, the predicted C_{2h} AFE structure would approximately halve the number of Raman lines. Hence, it probably can be ruled out, despite other evidence supporting it. The second important point is that no one has previously observed any AFE double hysteresis loops $P(E)$ in TSCC in any phase. Definitions of antiferroelectricity generally require this.

The sole argument given by Roth *et al.* [13] for monoclinic C_{2h} symmetry is that they found only two clear symmetry varieties of vibrational modes, whereas they argue polar structures should have four; however, this argument is generally false, and the subgroups C_2, C_s, or C_i each have only two. In any event, the low-T phase is strongly polar and hence is most likely C_2 or lower symmetry. The Raman selection rules show it cannot be $P2_1/a(C_{2h})$.

Schmidt has published an argument [7,14] claiming that the lack of double hysteresis loops is expected because the transition from PE to AFE or FE to AFE is first order. The collective view of the present authors is that the presence or absence of double loops in the hysteresis of an AFE material has nothing to do with the order of a transition to another phase from the AFE state. In fact, using the general arguments of Karl Popper or Thomas Kuhn, one cannot define a physical state by what happens at other conditions, such as higher temperature, but only from measurements in that state; therefore, whether a crystal is AFE or not at temperature T does not depend upon whether its higher-temperature transition is first or second order.

B. 64 K transition

There is now ample evidence for a structural phase transition at 64 K (about 73 K in TSCC with a few percent Br). Although the Raman spectra below 64 K are indeed very similar to those at high pressure, the phase boundary inferred by Bornarel and Schmidt [7] and by Schmidt [14] does not extrapolate to 64 K but to a much lower temperature.

It is worth noting that the soft mode in the FE phase abruptly vanishes at the high-pressure phase transition. This confirms that the transition is first order, but it raises symmetry questions about the point group of the high-pressure phase. In the FE phase, the soft mode is of totally symmetric symmetry; this is always a requirement for any nonreconstructive group-subgroup transition (Worlock's lemma [15]). If the high-pressure phase is a subgroup of the FE phase, the soft mode must remain Raman active. The fact that it is not seen implies either that it has become diffusive (order-disorder), or that the high-pressure phase has a higher symmetry than the low-pressure FE phase. Note that doubling of the primitive cell does not affect this argument.

C. Raman symmetries

Roth *et al.* [13] argue that they see only two kinds of Raman spectra, thus ruling out a $P2_12_12_1$ piezoelectric structure (which would have four) and supporting a C_{2h} $P2_1/a$ structure at low temperatures. This disagrees with our neutron scattering and polarization results, which show that the structure at low T is polar. In addition, this is still another *non sequitur*, since the correct symmetry argument does not reveal intensity ratios for different polarizabilities, merely which ones are nonzero. A transition from orthorhombic to orthorhombic is also not excluded by the data of Roth *et al.* [13].

To summarize previous work: A series of conjectures and *non sequiturs* has unfortunately led various authors to label both the room-temperature high-pressure phase and the low-temperature atmospheric-pressure phases of TSCC as AFE C_{2h}. This has been inconsistent with both the number and symmetry of Raman lines and the lack of double-loop hysteresis, and with the FE switching at low temperatures.

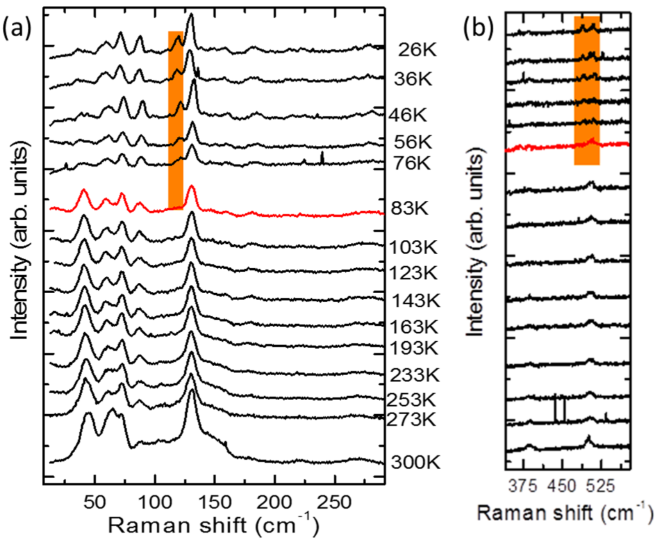

FIG. 2. (a) Left side. Raman data (intensity versus energy) in TSCC with 3% Br at various temperatures, showing anomalies in intensity and energy for low-frequency vibrations near 40 and $115\,\mathrm{cm}^{-1}$ at $\sim T = 75$ K. (b) Right side. Raman data (intensity versus energy) in TSCC with 3% Br at various temperatures, showing anomalies near $500\,\mathrm{cm}^{-1}$ at $\sim T = 50$ K.

D. New Raman work

Raman data as a function of temperature for a TSCC single crystal with 3% Br (chosen to match most recent work) are shown in Figs. 2(a) and 2(b). In Fig. 2(a) we see a strong decrease in intensity of the lowest-frequency modes near $65\,\mathrm{cm}^{-1}$ and increase in their splitting, and in addition, a dramatic disappearance of the mode near $40\,\mathrm{cm}^{-1}$ at 76 K, together with the appearance of an intense new mode near $115\,\mathrm{cm}^{-1}$. This new mode at $\sim 115\,\mathrm{cm}^{-1}$ is sometimes an indication of the high-pressure phase, conspicuous in the data of Roth *et al.* [13]. It is a signature mode that lends some support to the idea that the phase at $P = 1$ atm and $T < 64$ K is similar to that at $P > 700$ MPa and $T = 293$ K. However, it does imply that these two structures are the same.

In Fig. 2(b) (same temperature runs), we also see that a mode near $500\,\mathrm{cm}^{-1}$ splits into a doublet $\sim 25\,\mathrm{cm}^{-1}$ apart below $\sim T = 70$ K.

We interpret the disappearance of the vibrational mode at $40\,\mathrm{cm}^{-1}$ and the appearance of a new mode near $115\,\mathrm{cm}^{-1}$ as clear signatures of a phase transition near 70 K. This phase transition is unlikely to involve unit cell doubling, which would roughly double the entire number of Raman lines. It suggests instead a small reduction in symmetry, from say orthorhombic C_{2v} to monoclinic C_2. However, there are no degenerate vibrations in orthorhombic crystals; therefore, the small splitting in the mode near $500\,\mathrm{cm}^{-1}$ is not a removal of degeneracy, but could arise from changes in TO/LO mode splittings.

III. ELECTRICAL MEASUREMENTS

A. Switching polarization loops $P(E)$

In an effort to demonstrate AFE double-loop hysteresis, we subjected TSCC single-crystal samples up to 4.0 kV across

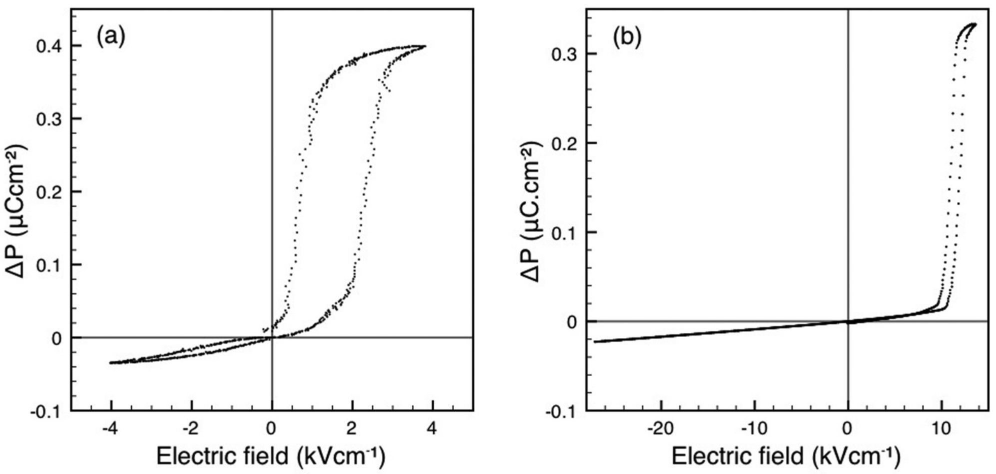

FIG. 3. Polarization data versus field $P(E)$ obtained at $T = 50$ K and 100 Hz for (a) undoped TSCC along the polar $+b$ axis; $E = 4$ kV/cm along [0 1 0]. Switching is observed in the form of a single AFE-like loop (i.e. a FE loop with a very large bias field) from ~8–12 kV/cm, in agreement with Ref. [9]. (b) For 30% Br-doped TSCC the bias voltage is larger (linearly proportional to Br%, approx. 10 kV/cm). However, this occurs only for positive voltages. For fields along the pseudohexagonal c axis, no hysteresis is observed up to 100 kV/cm.

0.3–1.4 mm ($E = 33$ kV/cm) at $T = 40$ K. This is 10× the known coercive field of 3 kV/cm for TSCC. Results are shown in Fig. 3.

If the phase at high P or low T is C_{2h}, what should be seen at such fields is FE single loops between 130 and 64 K and double loops or no loops at all below 64 K. On the other hand, if the low-T (or high-P) phase is a lower AFE polar phase, one should see both FE single loops and AFE double loops. It is of course possible that the structure is FI [16] with canted polarizations or different numbers of dipoles up and down (say, three up and one down per unit cell). Ferrielectricity is rare but has been known since the early work of Cross [16] and Pulvari [17]. The best example is in ammonium sulphate [18], where Unruh showed that the two polar sublattices produce a net polarization that actually changes sign with temperature. Most recently, it has been reported in multiferroic $DyMn_2O_5$ [19,20] and in $CuInP_2S_6$ [21]; however, none of these studies demonstrate an electrically switchable polarization required for ferrielectricity. Ferrielectric transitions are also well known in FE liquid crystals. Jaradat *et al.* have studied a four-layer smectic that can be FE, FI, or AFE [5,6]. The four layers can be ordered four up, three up/one down, or two up/two down, possibly in analogy with the four polarizations per unit cell in TSCC. Jaradat *et al.* emphasize that the response of these systems is highly asymmetric with regard to voltage polarity [5,6]. Similarly, Gou and Rondinelli have considered [22] the case of an artificial ABABAB... superlattice in which the two kinds of layers can have FE, FI, or AFE ordering.

Based upon the loops observed in Fig. 3, and the absence of any $P(E)$ loops along the other crystallographic axes (up to 30 kV/cm along the c axis), we conclude that the low-temperature phase is FE in the sense that it has a switchable polarization and not AFE (it could be both simultaneously with canted polarizations P), but the Raman data and polarization data prove that it is not C_{2h}.

This was established previously in very nice paper by Fujimoto *et al.* [8,9] but ignored in a subsequent paper by Roth *et al.* [13]. Note especially that the loops are not symmetric about $V = 0$; instead a large bias field is observed (built-in potential) such that the entire loop is shifted ~2 and 10 kV/cm to the $+V$ side for undoped and 30% Br-doped TSCC, respectively. We confirmed that this is an asymmetry between the (0 1 0) and (0 −1 0) axes (and not an artifact) by mechanically inverting the sample. It is worth emphasizing that the $P(E)$ response only measures the change in polarization under an applied field and these hysteresis loops should also be displaced in the positive y axis by ~0.25–0.3 μC/cm^2 due to the spontaneous (zero field) polarization as determined from pyroelectric current measurements (discussed later). The data in Fig. 3 resemble those in an AFE, but with only one polarity switching. The data demonstrate a textbook example of a FI with two polarization components of the approximately the same magnitude, one of which switches and one of which does not because of quite different values of coercive field E_c.

B. Four-state model hypothesis

Tris-sarcosine calcium chloride has a complex structure with two inequivalent sarcosine sites, often designated S1 and S2. In analogy with the four-state model of polarizations in smectic liquid crystal FEs [5,6], we consider a model for low-temperature TSCC that permits the four formula groups per unit cell (12 sarcosines) at the sites usually labeled S1 and S2 to order in pairs at different temperatures (see also Gou and Rondinelli [22]).

As with the model of Jaradat *et al.* [5,6], this would give four different states: At $T > 130$ K, the *Pnma* PE phase has no polarizations ordered. As T is lowered below 130 K, additional sarcosines might order. This model is strongly supported by the fact that the switched polarization at high fields shown in Fig. 3 is 0.3–0.4 μC/cm^2, and the nonswitching polarization obtained in Fig. 4 (discussed below) by integrating pyroelectric current is 0.25 μC/cm^2 for undoped TSCC and 0.33 μC/cm^2 (approximately equivalent to the switchable polarization) for 30% Br doped. This suggests that there is one unit of polarization (~0.3 μC/cm^2) that orders spontaneously below

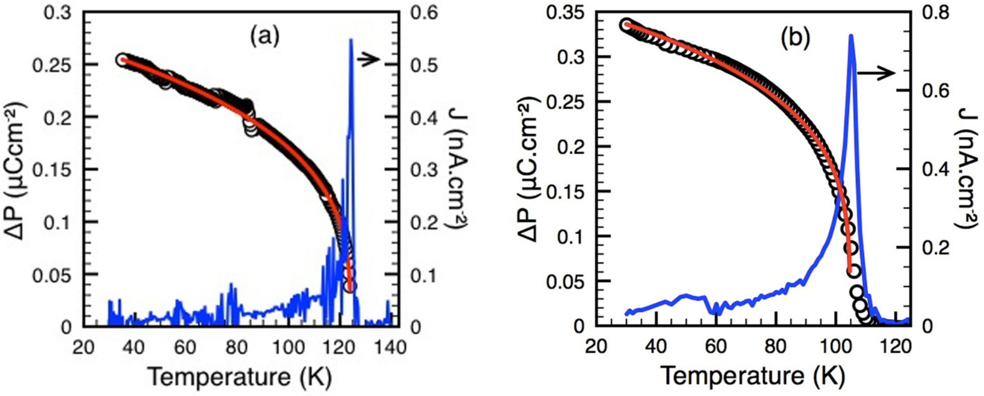

FIG. 4. Pyroelectric current J (blue curve) and spontaneous polarization P (open circles) as a function of temperature for (a) undoped and (b) 30% Br-doped TSCC. Red curve denotes fit of $P(T)$ proportional to the mean-field tricritical dependence $(T_c - T)^\beta$. Fitted parameters are $T_c = 124\,\mathrm{K}, \beta = 0.30$, and $T_c = 105\,\mathrm{K}, \beta = 0.25$ for 30% Br-doping. Note that the maximum spontaneous (zero-field) polarization P measured in this way is comparable in magnitude to the switchable polarization observed in the $P(E)$ loops in Fig. 3 and that the lowest temperature phases are pyroelectric, and in fact that P increases in these phases.

130 K (perhaps two $+P$ up, one $-P$ down, one disordered) and a second unit that can be ordered at high fields (three $+P$ up, one $-P$ down). However, this is a conjecture simply in analogy with liquid crystal studies; our x-ray studies, discussed below, yield only average polarization values per cell and cannot tell us how many sarcosines are polarized up, down, or disordered.

This model is compatible with the original discoveries of the transition near 64 K, first by Haga *et al.* [23] and subsequently by Lee *et al.* [24]; the former was via specific heat and yielded an entropy change of 1.16 J/mol.K (about half that of 2.51 J/mol.K at $T_c = 130\,\mathrm{K}$; both of these are less than the value $R\ln 2 = 5.8\,\mathrm{J/mol.K}$ expected for an order-disorder transition), but incorrectly inferred that this low-T phase is the same as the high-pressure phase, whereas the latter suggested that it was an effect of proton dynamics and not a static structural phase transition. Regrettably, that study did not show data below $T = 50\,\mathrm{K}$ (an unusual stopping point), an unfortunate coincidence since we found [10,11] some indication of another transition near 48 K.

C. Other AFE-like transitions with only one loop

Very recently, Randall's group at Penn State have also found AFE-like loops that occur for only one voltage polarity in the famous AFE sodium niobate, "which in fact is an AFE structurally, but as it switches under the forward electric coercive field, remains in a metastable FE state and avoids the switch back to the AFE, thereby missing the telltale features of the double hysteresis loop" [25]. Sodium niobate is one of the two materials originally described by Pulvari as FI [17]. In calcium zirconate/sodium niobate, they observe [26,27] a related smooth FE-AFE transition with increasing Ca/Zn %.

D. Pyroelectric measurements

If we invoke a polar structure at temperatures below 64 K, it is useful to measure the absolute polarization and show that it is nonzero. This can be done via second harmonic generation or by pyroelectric measurements.

The latter are summarized in Fig. 4 for both undoped and 30% Br-doped TSCC. Integration of the pyrocurrent, $J(T)$ gives $P(T)$ with a measured spontaneous polarization at $T = 77\,\mathrm{K}$ of the order $0.25-0.3\,\mu\mathrm{C/cm}^2$, in agreement with earlier work. Below ~64 K, the polarization does not vanish (ruling out any centric structure); instead it increases an additional 10% as temperature lowers, in agreement with Ref. [9]. The transition is probably second order but very close to tricritical. For pure TSCC polarization, $P(T)$ varies as $(T_c - T)^\beta$ with $\beta = 0.30 \pm 0.02$; for 30% Br, we found 0.25 ± 0.02. As we show in a subsequent section, oxygen-ion positions around the Ca^{2+} ion rotate near T_c with the same dependence ($\beta = 0.3$).

E. PUND data

Whenever FE polarization hysteresis data are unusual, it is wise to record PUND data. PUND is an acronym describing separate measurements of the four parts of a switching loop, first employed by Ramtron Corp. [28]: P = positive nonswitching voltage, U = up − switching voltage from $-P$ to $+P$, N = negative nonswitching voltage, D = down-switching voltage. It reliably discriminates between true FE polarization reversal [which is actually detected as a charge, by integrating displacement current $i(t)$] and artifacts such as real injected charge [also detected by integrating leakage current $J(t)$]. Our PUND data are shown in Fig. 5. Here, we employ a triangular voltage drive, with intentional separation of 1 s between the $+V$ and $-V$ pulses; two measurements with the same voltage rise time were collected to discount any transient current effects. We conclude that there are no artifacts.

The fact that the polarization that can be switched is $0.33\,\mu\mathrm{C/cm}^2$ and that the underlying polarization that cannot be switched but can be measured via pyroelectric techniques is similar ($0.3\,\mu\mathrm{C/cm}^2$ for Br-doped TSCC) suggests a mesoscopic model in which the polarization comes in lumps of $0.3\,\mu\mathrm{C/cm}^2$, similar to the four-state liquid crystal model from Jaradat *et al.* [5,6] described earlier. However, this is in part a pedagogical convenience, since FE polarizations are not

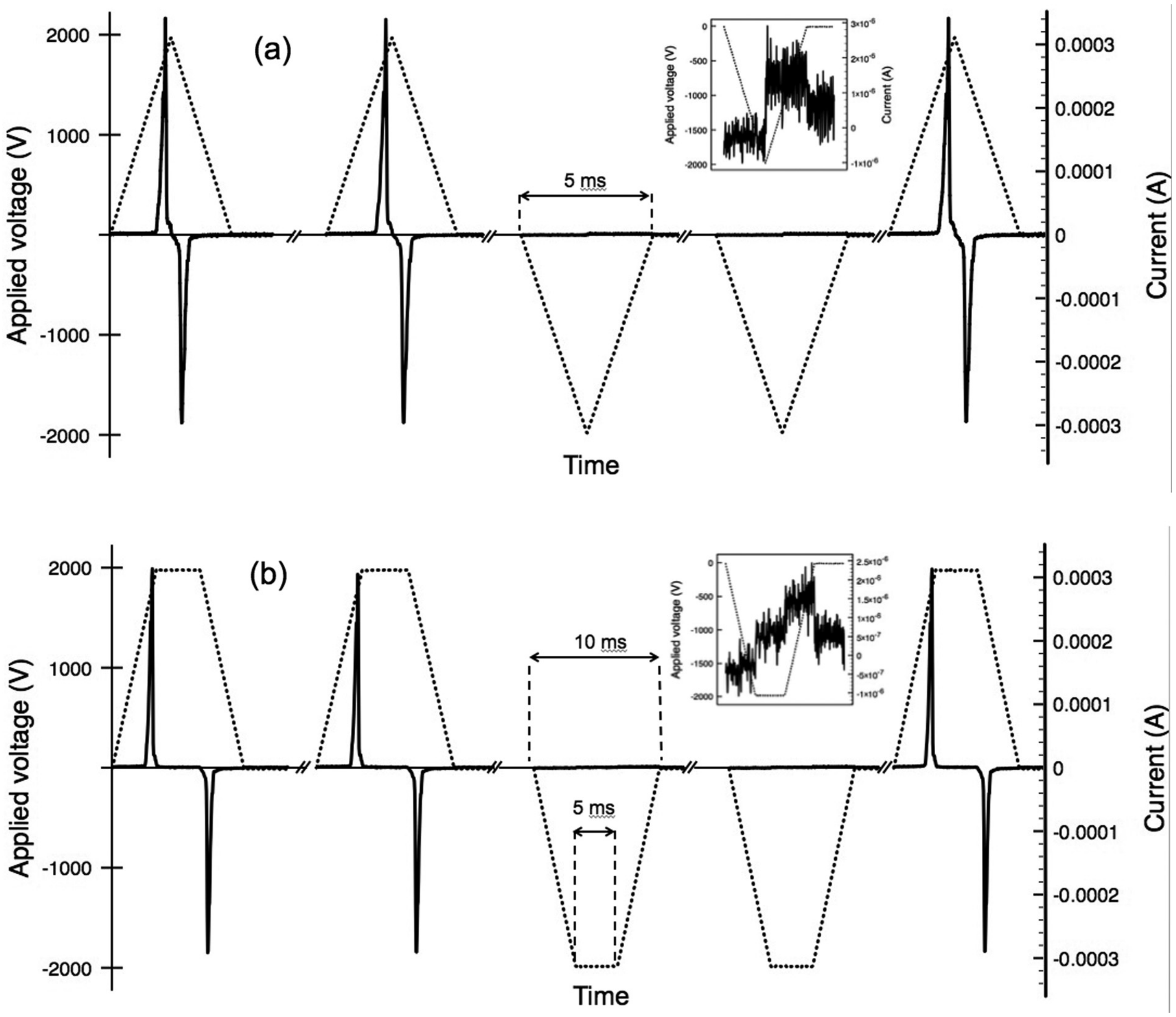

FIG. 5. Polarization PUND data on 30% Br-doped TSCC at $T = 50$ K. (a) Triangular and (b) trapezoid pulses of equivalent rise time were employed to discount transient current and/or charge injection effects. All pulses were separated by a wait time of 1 s. The current responses are identical for both pulse chains with clear switching events consistent with Fig. 3(b); a magnified view of the nonswitching current observed under negative bias is also shown (inset).

exactly spatially localized. We emphasize that ferrielectricity in smectic liquid crystals is not rare, although the crystal community never cites it.

IV. THE TRANSITION AT 47 K

An additional phase transition near 47 K at atmospheric pressure was first inferred from dielectric and thermal data by the present group [10,11]. However, in retrospect, if we go back and scrutinize the early specific heat data of Haga *et al.* [23], it seems likely that the divergence near 64 K has a complexity (change of slope) on its low-temperature side, perhaps indicative of another phase transition with weak entropy change (<0.5 J/mol), see Fig. 6. More accurate specific heat data were reported by Lashley *et al.* [11], together with thermal relaxation times and thermal expansion; these show large anomalies (~1%) at 61.0, 49.3, and 46.7 K. On these, we have superimposed in Fig. 7 new dielectric and polarization data, showing anomalies very near 48 K. We emphasize that our x-ray and neutron data show no structural changes at these temperatures.

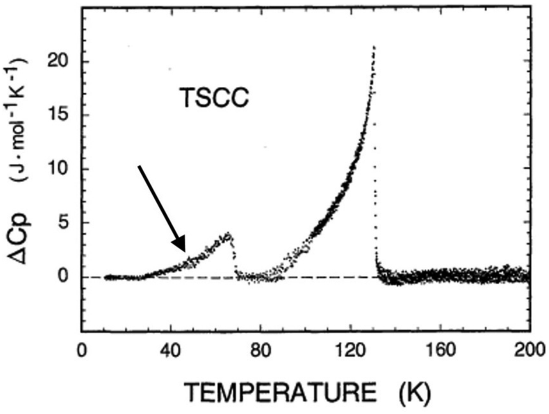

FIG. 6. Specific heat data near 64 and 130 K in TSCC, modified from Haga *et al.* [23].

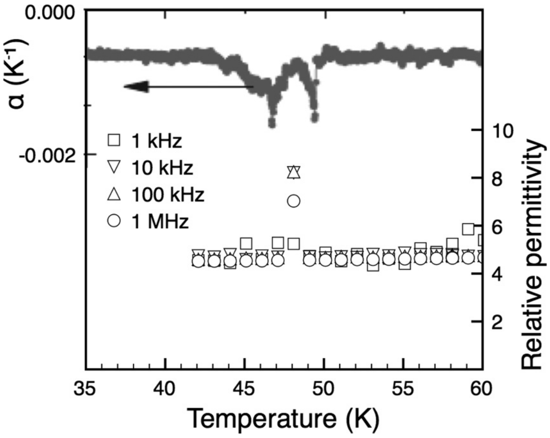

FIG. 7. Preliminary evidence for a phase transition in TSCC near 48 K. Upper trace is thermal expansion coefficient, and lower trace is dielectric response. The latter show only a few data points at 48.0 K.

V. STRUCTURAL DETERMINATION

Tris-sarcosine calcium chloride has a complex structure with two inequivalent sarcosine sites, designated S1and S2, in the ambient temperature PE phase (space group *Pnma*). Here, S1 sits on the mirror plane (four molecules per unit cell), and S2 sits on a general position (eight molecules per unit cell). Sarcosine exists in the zwitterionic form. Six different sarcosine molecules act as ligands to the Ca and bridge adjacent CaO_6 octahedra to form infinite chains along the a axis. The Cl^- ions occupy the resulting a-axis channels and are loosely bound via N-H. . .Cl hydrogen bonds. At 118 K (i.e. well below T_c), Mishima *et al.* [29] reported a transition to polar space group $Pn2_1a$ with three sarcosines (here designated S1, S2a, S2b) on general positions. That paper noted that deviations of all atomic positions between the PE and polar phases were very small (<0.17 Å), with the largest deviations concerning the methyl groups and the oxygen atoms coordinated to Ca. They also commented that (i) the Ca-O bond lengths are unusually short, and (ii) the atomic displacement parameters (ADPs) of the methyl and O atoms are relatively high. This is suggestive of possible rotational disorder of the methyl groups and of the CaO_6 octahedron. Earlier work [24] has suggested that a possible driver for some of the postulated phase transitions seen in TSCC may be due to the orientational motion of the methyl group or changes to the H-bonding behavior. The optimal means of probing these possibilities crystallographically is neutron diffraction, which is highly sensitive to H-atom positions. This paper shows no unusual behavior of the methyl groups (only an expected reduction of thermal motion on lowering T) and no significant changes in N-H. . .Cl bonding. The present diffraction experiments cover a wider range of temperatures (down to 20 K) than previous work. Most importantly, we see no evidence for a further change of unit cell or symmetry down to the lowest temperature studied: The $Pn2_1a$ model remains valid at 20 K, with R factors for both neutron and x-rays refinements in the expected range for a correct modelling of the data. The most significant temperature-dependent changes seen in both the neutron and x-ray experiments relate to the coordination around the CaO_6 octahedron, in particular, in evolution of the Ca-O-C bond angles versus T. These angles show variations of up to 18° between ambient and 20 K; however, there appears to be no direct correlation between these structural changes and the observed electrical properties. Instead, it is instructive to look at more global structural features in order to correlate bulk crystal structure with the observed properties. Any FE properties arise from polar displacements along the b axis in space group $Pn2_1a$. Hence, we calculated atomic displacements along the b axis for all non-H atoms using the present x-ray data, referred to a fixed origin at the Ca site. Only minor changes are seen in the relative displacements of the Cl^- ions. However, more significant changes are seen in the summed displacements of the atoms within each of the three independent sarcosine molecules. The thermal evolution of these polar displacements is plotted in Fig. 8.

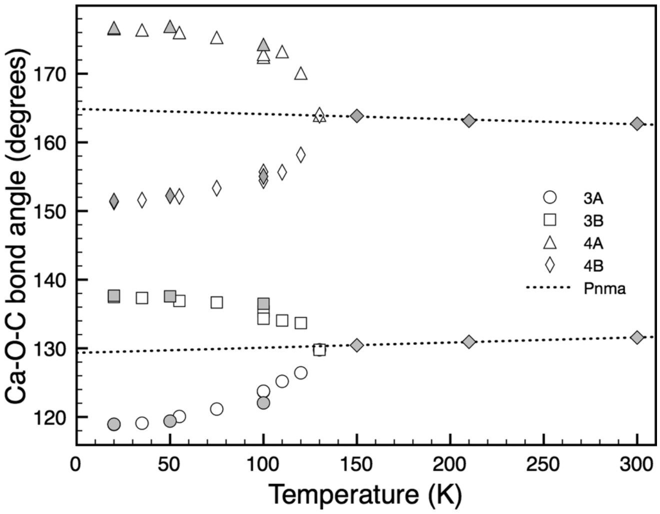

FIG. 8. Change in Ca-O-C bond angle in pure TSCC as a function of temperature. X-ray data are open symbols; neutron data are shaded. This may be considered the microscopic order parameter, proportional to the macroscopic order parameter $\langle P(T)\rangle$. Here, 3AB and 4AB designate different oxygen sites. Dotted lines indicate extrapolated angles from the PE phase.

A smooth evolution of these displacement parameters is seen from 100 to 20 K, with no direct evidence of further phase transitions below T_c. However, it is perhaps surprising that there is an asymmetric relative displacement of sarcosines 2a and 2b, in particular. Here, S1 undergoes a relatively large displacement from the mirror plane, S2a undergoes a much smaller relative displacement, in the same sense, but S2b undergoes a large displacement antiparallel to these two molecules and almost cancels out the displacement S1. This is shown pictorially in Fig. 9, where the relevant fragment of the unit cell is shown, with relative displacements of the three sarcosines arrowed. It should be borne in mind that these two figures represent atomic displacements only (i.e. distances), not polarizations (charge distribution is not considered). Nevertheless, it can be seen that the structural behavior does support the assertion that TSCC is FI below T_c, with antiparallel, but not canceling, displacements of the three sarcsosines (two up, one down). The nature of this FI distortion is reminiscent of that seen in hexagonal $YMnO_3$. In the present

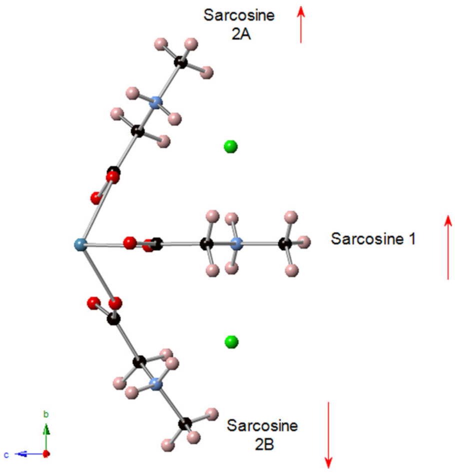

FIG. 9. Resultant TSCC structure below $T_c = \sim 120$ K.

case, the distortion arises from a single active polar mode, whereas the mechanism in $YMnO_3$ is an improper one [30] due to coupling of a nonpolar and a polar mode. The present crystallographic study gives a clear picture of the nature of the PE-FE transition at T_c, but does not offer any rationalization of the additional phase transitions observed in the present Raman data and other previous studies.

As a further attempt to detect any crystallographic response to these events, we analyzed the changes in ADPs versus T, in particular for those atoms suggested to have relatively high ADPs by Mishima *et al.* [29]. Although relatively large throughout the regime 20–100 K, we see no evidence for anomalies. The conclusion from the present crystallographic study is that there is a single structural phase transition at T_c; we observe no abrupt anomalies in the evolution of any structural parameter at any other temperature and no evidence for a further change of crystallographic symmetry. The anomalies at 64 and 48 K therefore, if due to long-range structural rearrangements, must be very small distortions indeed and probably involve only hydrogen ions [24]. We note in this context that the relevant Landau theory suggests that the low-symmetry phase be monoclinic with C_2 point group symmetry, and that C_2 is also compatible with the two Raman phonon symmetries (and intensities) observed experimentally and not the four which would be required by orthorhombic C_{2v}. This makes it less likely that the experimental anomalies near 64 and 48 K are due to local structural or dynamic effects

A. Neutron structural data

The neutron scattering data were intended to determine the space group symmetries below $T = 48$ K and for $48\text{ K} < T < 64$ K. It had been suggested that perhaps only H atoms move, and since the entropy change at 64 K is significant (Fig. 6), an order-disorder transition was suspected. The fact that the entropy change at 64 K is nearly half that at 130 K may not be a coincidence and may also relate to the two different sarcosine sites. However, as described above, no lower phase transition is observed, only a continuous smooth increase in Ca-O-C bond rotation angle of ∼18°.

Figure 8 shows that the two sarcosines (2a, 2b) on the mirror plane above T_c do not move in opposite AFE directions, as might be expected in an AFE transition. Instead, one (site 2a) moves almost not at all, whereas the second (site 2b) moves in a way to compensate the off-plane displacement of sarcosine S1, which is already out of plane above T_c. However, they move by slightly different amounts $y(T)$, adding to a net (small) polarization along the polar axis. This is probably the origin of the large $P(V)$ bias field observed in Fig. 3; the bias field $E_b(T)$ scales with this net displacement $y(T)$. However, since we do not know the effective charge of the displaced ions, we cannot yet confirm that this small net displacement gives the measured quantitative $E_b(T)$. Although there is a small net FE polarization, as shown in Fig. 8, the main displacements are out of phase (AFE). Figure 10 shows this more clearly and provides a measure of the order parameter versus temperature, which is proportional to the O3 bond angle; in the PE pseudohexagonal orthorhombic phase, the oxygen ion angle around the Ca^{2+} ion is ∼130°. Figure 9 shows these oxygen displacements on a larger cell with view down the pseudohexagonal axis. These data by themselves are insufficient to determine whether the transition is first order, but data in earlier publications [11,23] establish clearly that it is continuous, and an exponent describing thermal expansion near T_c has been precisely measured in the preceding sections. Such measurements in FEs are often highly contentious, especially in strontium barium niobate (SBN), where several papers show clearly that the FE transition is first order, but some authors maintaining that it is continuous and evaluating critical exponents. For example, work by Wolkuska *et al.* [31] give a large, precise discontinuity in volume $\Delta V = 0.6989\,\text{Å}^3$ and a mean-field exponent for thermal expansion of 0.53 ± 0.15, whereas earlier work by Dec *et al.* and Kleemann *et al.* claims a continuous transition and much smaller, highly nonmean-field exponents [32,33]. It is difficult to understand second-order transitions with large volume discontinuities! Trying to fit continuous power laws to small jumps [34] always gives small fictitious exponents ∼0.1. The discontinuous character of the SBN transition is

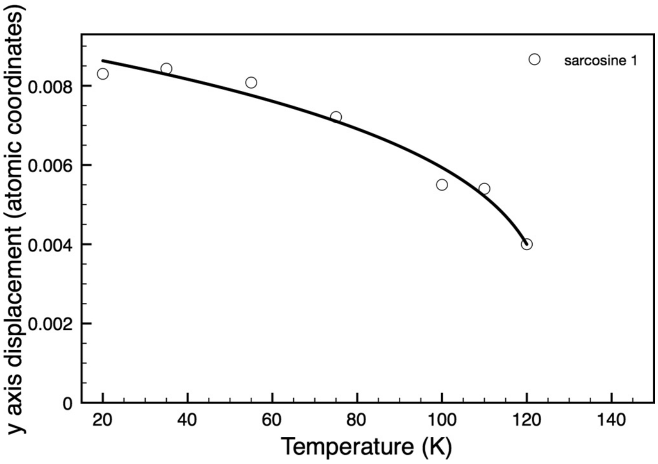

FIG. 10. Sarcosine molecule displacement with respect to Ca-ion (x-ray data); ordinate axis units are percent of the b axis lattice constant. The temperature exponent is $\beta = 0.27$. One outlying data point near $T = 100$ K has been removed.

also shown clearly in Raman data [35]. In TSCC and TSCC:Br, the thermal expansion [11] and specific heat [23] are not proportional to each other near T_c, giving a nonconstant Gruneisen ratio, which violates classical Landau theory and supports defect-mediated dynamics [11,12].

B. Estimation of local polarization from x-ray and neutron data

Figures 1 and 9 show the resulting TSCC structure in the FE phase. The FE polarization $\langle P\rangle$ in a displacive system is a nonlocal function. It can roughly be compared with the structural distortions and the relevant Born effective charges. Sarcosine molecules are polar, with a methyl group at one end and a carboxyl -COOH at the other. In its crystalline form, TSCC retains its zwitterion form and the H is detached to form an N-H...Cl hydrogen bond elsewhere in the structure. Considering only this charge removal, we can estimate the local polarization produced by the sarcosine displacements shown in Figs. 8–10. The sarcosine displacements from Ca ions shown are 0.8% of the b axis lattice constant, namely 0.014 nm. We do not know the Born effective charge for the COO^- group at the end of each sarcosine molecule nearest the Ca ions, but hypothesizing that it is approximately $-1.0\,e$ from the zwitter-ion H from each carboxyl COOH that moves to the sarcosine N-H...Cl bond, leaving the N ion an extra $+e$ and the oxygen $-e$, we can see if this polarization is sufficient to plausibly account for the measured polarization. An estimate can be made by measuring not the average sarcosine ion shift from the Ca ion, but instead only the end sarcosine oxygen atoms (COO^-, which shifts 0.62% along b) and the nitrogen atom (which shifts 0.701% along $-b$). These shift in opposite directions from the Ca ions and have opposite charges so that their polarization components add constructively. Using this formal charge as an estimate of the Born charge, and using the unit cell volume $0.916 \times 1.746 \times 1.0265\,\mathrm{nm}^3$, gives a local polarization change $\langle P\rangle$ for each sarcosine of $0.36\,\mu\mathrm{C/cm}^2$ in the correct polar b direction. The experimental total polarization value of $\sim 0.3\,\mu\mathrm{C/cm}^2$ is close to this value and hence suggests that the polarization in the FE phase may arise primarily from these sarcosine-calcium displacements (both measured at $\sim T = 50\,\mathrm{K}$) and not from the N-H...Cl hydrogen bonding, as had historically been supposed [7–9].

VI. LANDAU THEORY AND COMPARISON WITH ε-WO_3

Ferrielectric structures are extremely rare in inorganic single crystals. A notable exception is the low-temperature phase ε-WO_3. The structure consists of heavily tilted octahedral with the approximate centrosymmetric space group $I2/c$. The tungsten positions are shifted from the center of the octahedral. These shifts follow almost the same antiferrodistortive pattern with each two octahedra containing shifts in opposite directions. Careful structural investigations by neutron scattering revealed that the shifts along the crystallographic c direction are not fully compensated, however, so that the true space group is Pc. This example shows ferroelectricity whereby the local dipole moments in the up-down directions are almost identical with a small preference for the up direction. The final moment on the unit cell is hence primarily along c, and summed [36] over four W sites is $0.52 \pm 0.16\,\mathrm{eA}^2$. While ferrielectricity is rare in uniform materials, it is common in nanostructured samples. Domain wall-related polarity is often FI and complex nanostructures fail even for large samples to fully compensate local dipole moments [36–39]. Generally, one expects large unit cells and flexible molecular structures to develop FI polarization more commonly than inorganic materials with relatively few atoms in the crystallographic unit cell.

It is important to note that TSCC is not the case of an improper FE with weak polarization driven by coupling to an antiferroic mode, i.e. free energy term proportional to

$$G(P,T) = P(q=0)\phi(q=\pi/a)\phi(q=-\pi/a), \tag{1}$$

where q is wave vector, a is lattice constant, and ϕ is the antiferroic order parameter (oxygen displacement). Because of its large unit cell, the antiferroic displacements are not at the Brillouin zone boundary. Rather it is a case of a single normal mode with a single order parameter—FE eigenvector and polarization P at $q = 0$, and hence excess Gibbs free energy of form [36–39]

$$\begin{aligned}\Delta G = {} & A\theta_s[\coth(\theta/T) - \coth(\theta_s/T_c)]P^2 \\ & + \tfrac{1}{4}BP^4 + \tfrac{1}{6}CP^6,\end{aligned} \tag{2}$$

with no coupled order parameter (and very small B). In our fitting of data to Eq. (2), the value of θ is very small, so coth $x = x$ (quantum low-T effects are negligible), and the ratio of

$$B^2/(4ACT_c) = 8.2\,\mathrm{K}/130\,\mathrm{K} = 0.060, \tag{3}$$

which is a quantitative measure of how very nearly tricritical the transition is (i.e., exactly 6% from tricritical).

VII. RELATION TO QCP

Recently, we showed [12] that, despite being uniaxial, TSCC exhibits a critical exponent γ for its isothermal susceptibility (dielectric constant) of $\gamma = 2$, rather than the predicted 3. This was inferred to arise from the ultra-weak polarization in TSCC ($\sim 0.3\,\mu\mathrm{C/cm}^2$ at 77 K), which makes the system behave as if it were only negligibly FE at low T, similar to pseudocubic $SrTiO_3$ or $KTaO_3$.

VIII. SUMMARY

We present polarization hysteresis loops in TSCC below its known phase transition at 64 K (pure TSCC; ~70–76 K in TSCC with a few percent Br). These data show that the low-temperature phase cannot be C_{2h} point group, as proposed by Roth *et al.* [13]; it cannot be centric at all. This inference is supported by Raman data. The latter show some similarities with the high-pressure, room-temperature phase, but the structures are not identical; and we emphasize that Schmidt's [14] extrapolated phase boundary does not predict that the high-pressure phase can be reached at 1 bar even at $T = 0$, and Fujimoto *et al.* show that this phase is not polar [8,9]. The low-temperature structure is complicated by a probable additional transition near 48 K. Figure 10 compares the precise (resolution of a few milli-Kelvin) thermal expansion data of Lashley *et al.* [11] with new unpublished dielectric data. The latter (Fig. 10) exhibit a peak at 48.0 K, about midway between the two peaks in thermal expansion coefficient, but our dielectric cryostat lacks the temperature stability to permit closer comparisons and probably overshoots one of the probable closely spaced transitions on cooling or heating. However, the x-ray and neutron structural study reveals no distortion to crystal class lower than orthorhombic, either near 64 or near 48 K, and so further study is merited. The present data are too scanty to permit an accurate value of the order-parameter critical exponent β to be evaluated, but both polarization $P(T)$ and sarcosine (oxygen ion) shifts versus T vary as $\beta = 0.29 \pm 0.04$, compatible with the predicted mean-field tricritical value of ¼.

A semantic question arises as to how to best describe FEs for which the bias field $E_b \gg$ the coercive field E_c: These crystals have no FE properties for voltages near zero. These are well known as arising from defects and substitutional ions in materials such as triglycine sulphate (TGS), but they may also arise from a FE structure with several inequivalent polar sites (e.g. sarcosine S1 and S2 sites in this paper). In the latter case, they may have two local polarizations, one of which switches and the other of which does not; they are reminiscent of Lieb-Mattis models of ferrimagnetism [40].

Experimental details are available in the Supplemental Material [41]. Crystallographic information files (CIFs) of TSCC structures (refined from diffraction data) have been deposited in the CCDC, deposition numbers CCDC 1536726-1536742.

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