Ferrielectricity in a Metal-Organic Ferroelectric

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Abstract

We report a paradigm of ferrielectricity in a single-phase crystal, TSCC -- tris-sarcosine calcium chloride [$(CH_3NHCH_2COOH)_3.CaCl_2$]. Ferrielectricity is well known in smectic liquid crystals but almost unknown in true crystalline solids. Pulvari reported it in 1960 in mixtures of ferroelectrics and antiferroelectrics, but only at high fields, and Unruh in1970 in ammonium sulphate. TSCC exhibits a second-order displacive phase transition near $T_c =$ 130 K that can be lowered to a Quantum Critical Point at zero Kelvin via Br- or I-substitution, and phases previously predicted to be antiferroelectric (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 clear Raman evidence for this transition. X-ray and neutron studies below $T_c =$ 130K show antiferroelectric displacement out of plane at two oxygen sites plus N+ displacement at N-H—Cl bonds, producing 0.363 $\mu C/cm^2$ polarization, in agreement with the measured 0.33 $\mu C/cm^2$.

I.   Introduction

Ferroelectrics and antiferroelectrics are well known among low-symmetry crystals and are directly analogous to ferromagnets and antiferromagnets, with polarizations P replacing magnetizations M. However, ferrielectrics, with approximately antiparallel dipole ordering but net polarizations are very rare, except among liquid crystals. TSCC (tris-sarcosine calcium chloride) has a second-order displacive paraelectric (PE) to ferroelectric (FE) phase transition near $T_c = 130$ K.[1] The main aim of the present work is to show that the ferroelectric 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 Guzman-Verri and Littlewood.[2]

There is no officially agreed-upon definition (e.g., IEEE standards) of "ferrielectricity." Here we define a ferrielectric as a polar crystal with two or more polar sublattices, having either different polarization magnitudes (and usually signs) in the same direction, or the same magnitude in different (but not exactly opposite) directions. TSCC has an unusual (perhaps unique) structure with 4 polarizations per unit cell in both its paraelectric and ferroelectric phase, permitting ferrielectricity without change in primitive cell size, e.g. three polarizations up and one down. Thus the present study provides what may become the standard textbook example of ferrielectricity.

The early history of ferroelectric 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 the present work are first, that the system is analogous to the four-sublattice model of Gleeson's group for liquid crystals, 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^{++} ion.

Early work by Bornarel and Schmidt[3] showed that tris-sarcosine calcium chloride also has a structural phase transition at ca. 700 MPa hydrostatic pressure at T=293 K and that the

phase boundary extrapolates to $<< 40K$ at atmospheric pressure (their studies were limited to $T > 77$ K). They suggested that the high-pressure phase is antiferroelectric (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 paraelectric and ferroelectric phases already have 4 formula groups (and 12 sarcosine molecules) per unit cell. Thus, an AFE distortion might realign the polarizations to be antiparallel (say, 2 up and 2 down) in contrast to the 4 parallel dipoles per ferroelectric unit cell. Such an unusual structure also could permit simultaneous FE and AFE ordering, either a ferrielectric canted arrangement (as in ferrimagnets[4]), or a Lieb-Mattis type antiferroic, un-canted linear polarization geometry with, for example, 3 polarizations up and 1 down. This would help explain the polarization data P(T) with strong built-in potential (bias field) reported by Fujimoto et al.[5] Although several authors have suggested that the high-pressure ambient temperature phase of TSCC is the same antiferroelectric 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 non-polar.

The present 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 antiferroelectric 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) together with known specific heat data to show that phases below T=130K are both ferroelectric, and that a four-state model analogous to that used by Gleeson's group for liquid crystals is a reasonable qualitative macroscopic model. Third, we examine X-ray and neutron structural data to show that both ferroelectric 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[6,7] revealed no additional vibrational modes in TSCC at $T = 4$ K compared with $T = 300$ 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 $T = 64$ K, as well as additional anomalies near $T = 47$ K, but no proof that these anomalies are phase transitions in either a crystallographic or thermodynamic sense. The existence of a phase transition at 64K 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 $T_c = 130$K. But dielectric and polarization anomalies at 48.0K are reproducible but much smaller.

One aim of the present report is to provide new electrical and Raman data that confirm the transition at 1 atmosphere pressure and T ca. 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 zero Kelvin (ca. 80% Br), and the quantum critical point dynamics are not quantitatively compatible with a conventional uniaxial ferroelectric; 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 ferrielectric crystal would offer a new kind of switching device, with single-polarity switching (both positive or both negative) and high threshold voltages.

The basic structure of TSCC is pseudo-hexagonal, as shown in Fig.1, with local polarizations orthogonal to the pseudo-sixfold axis.
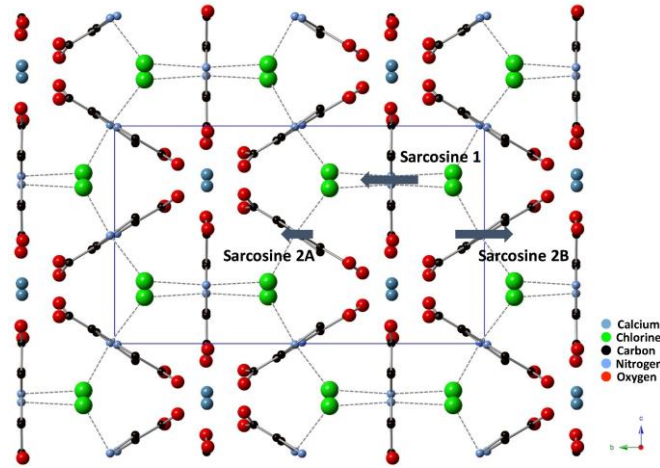
Fig.1. TSCC structure (modified from Ashida et al.[1]); the large arrows show the sarcosine molecule displacements below T_c from our neutron and X-ray data, discussed below.

II.   Earlier Experiments and Inconsistencies

1. Low temperature and high pressure (Roth et al.)[8]

Roth et al. 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 ferroelectric $Pna2_1$ phase or the paraelectric $Pnma$ phase, and therefore that it is probably an antiferroelectric non-polar $P2_1/a$ 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 ferroelectric and so-called antiferroelectric 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. And in addition, many of the modes in the ferroelectric 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 $Pna2_1$ and $P2_1/a$ phases. So rather than confirming the predicted

symmetry from Schmidt, the work of Rost et al. 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 antiferroelectric double hysteresis loops P(E) in TSCC in any phase. Definitions of antiferroelectricity generally require this.

The sole argument given by Roth et al. 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 Pna2$_1$ (C_{2v}).

Schmidt has published an argument[9,10] 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 antiferroelectric or not at temperature T does not depend upon whether its higher-temperature transition is first- or second-order.

2. 64K 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 and by Schmidt does not extrapolate to 64 K but to a much lower temperature.

It is worth noting that the soft mode in the ferroelectric 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 ferroelectric

phase the soft mode is of totally symmetric symmetry; this is always a requirement for any non-reconstructive group-subgroup transition ("Worlock's Lemma"). If the high-pressure phase is a subgroup of the ferroelectric 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.

3. Raman symmetries

Roth et al. 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-orthorhombic is also *not* excluded by the data of Roth et al.

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 antiferroelectric 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 ferroelectric switching at low temperatures.

4. 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.2a and 2b. In Fig. 2a we see a strong decrease in intensity of the lowest-frequency modes near 65 cm^{-1} and increase in their splitting, and in addition a dramatic disappearance of the mode near 40 cm^{-1} at 76 K, together with the appearance of an intense new mode near 115 cm^{-1}. This new mode at ca. 115 cm^{-1} is sometimes an indication of the high-pressure phase, conspicuous in the data of Roth et al. It is a "signature mode" that lends some support to the idea that the phase at P = 1 atm and T<64K is similar to that at P>700 MPa and T=293K. However, it does imply that these two structures are the same.
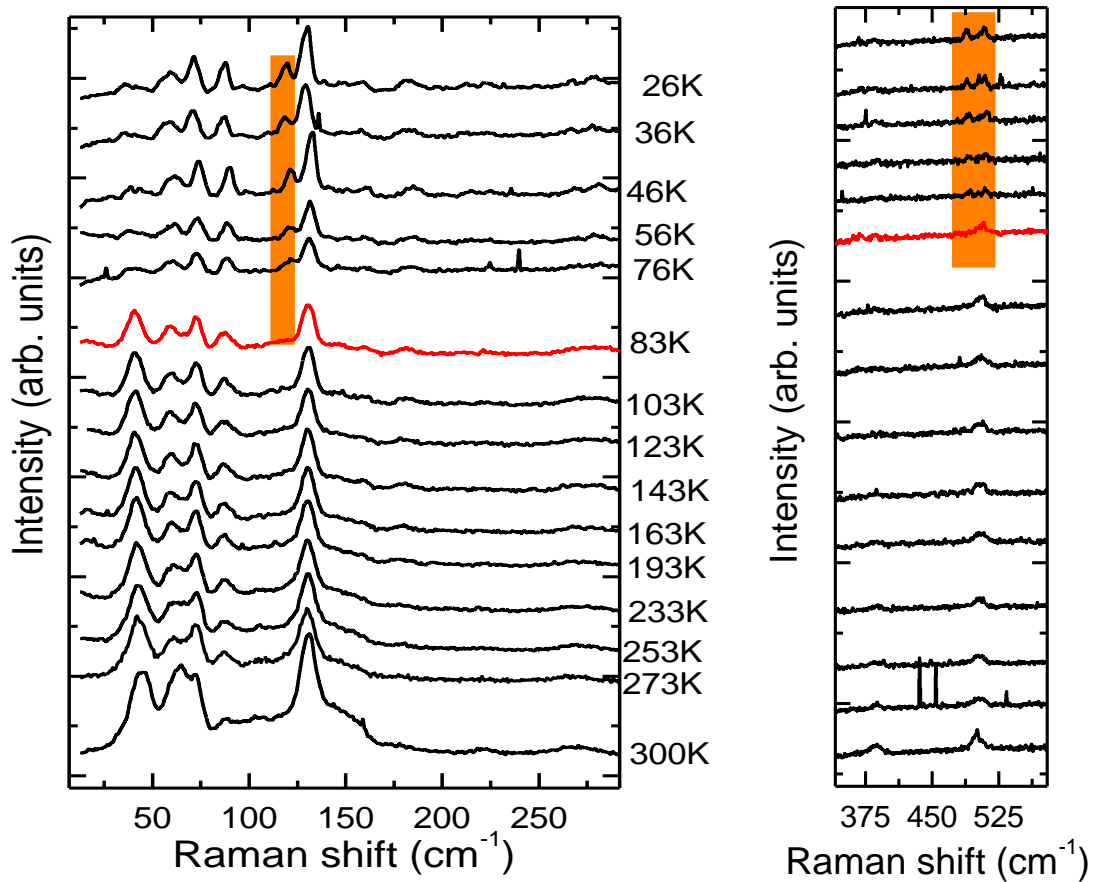
Fig. 2: (a) Left side. Raman data (intensity versus energy) in TSCC with 3% Br at various temperatures, showing anomalies in intensity and energy for low frequency vibrations near 40 and 115 cm^{-1} at ca. T = 75 K. (b) Right side. Raman data (intensity versus energy) in TSCC with 3% Br at various temperatures, showing anomalies near 500 cm^{-1} at ca. T= 50K.

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

We interpret the disappearance of the vibrational mode at 40 cm^{-1} and the appearance of a new mode near 115 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 cm^{-1} is not a removal of degeneracy, but could arise from changes in transverse-longitudinal (TO/LO) mode splittings.

III.   Electrical measurements

1. Switching polarization loops P(E)

In an effort to demonstrate antiferroelectric double-loop hysteresis, we subjected TSCC single-crystal samples up to 4.0 kV across 0.3-1.4 mm (E = 33 kV/cm) at T = 40 K. This is 10x 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 ferroelectric single loops between 130 K 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 antiferroelectric polar phase, one should see both FE single loops and AFE double loops. It is of course possible that the structure is ferrielectric[11] with canted polarizations or different numbers of dipoles up and down (say 3 up and 1 down per unit cell). Ferrielectricity is rare but has been known since the early work of Cross[11] and Pulvari.[12] The best example is in ammonium sulphate,[12] 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 $DyMn_2O_5$[13,14] and in $CuInP_2S_6$.[15] Ferrielectric transitions are also well known in ferroelectric liquid crystals. Gleeson's group has studied the study of a four-layer smectic that can be ferro-, ferri-, or antiferro-electric.[16,17] The four layers can be ordered 4-up, 3-up/1-down, or 2-up/2-down, possibly in analogy with the four polarizations per unit cell in TSCC. She emphasizes that the response of these systems is highly asymmetric with regard to voltage polarity.

Similarly, Gou and Rondinelli have considered[18] 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 33 kV/cm along the c-axis), we conclude that the phase below 64 K is ferroelectric and not antiferroelectric (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 work by Fujimoto et al.[4] but ignored in subsequent work by Roth et al.[8]

Note especially that the loop is not symmetric about V=0; instead an extremely large bias field is observed (built-in potential) such that the entire loop is shifted ca. 10 kV/cm to the +V side. We confirmed that this is an asymmetry between the (0 1 0) and (0 -1 0) axes (and not an artefact) by mechanically inverting the sample. The data in Fig.3 resemble those in an antiferroelectric, but with only one polarity switching. We suggest that this is not an accident, and that the correct description of this system is probably "ferrielectric," with two polarization components of the same magnitude, one of which switches and one of which does not because of quite different values of coercive field E_c.

2. Four-State Model Hypothesis:

TSCC has a complex structure with two inequivalent sarcosine sites, often designated S1 and S2. In analogy with the 4-state model of polarizations in smectic liquid crystal ferroelectrics,[16,17] we consider as a possibility a model for low-temperature TSCC that permits the four formula groups per unit cell (12 sarcosines) at the sites usually labelled S1 and S2 to order in pairs at different temperatures. (See also Gou and Rondinelli.[18])

As with the model of Gleeson's group, this would give four different states: At T > 130 K the Pnma paraelectric phase has no polarizations ordered.   As T is lowered below 130K, additional sarcosines might order. This model is strongly supported by the fact that the switched polarization at high fields shown in Fig.2 is 0.33 $\mu C/cm^2$, and the non-switching polarization obtained in Fig.5 by integrating pyroelectric current at very low

fields and low temperatures is also 0.33 $\mu C/cm^2$. This suggests that there is one

unit of polarization (viz. 0.33 $\mu C/cm^2$) that orders spontaneously below 130K (two +P up;

one –P down; one disordered), and a second unit that can be ordered at high fields (three +P
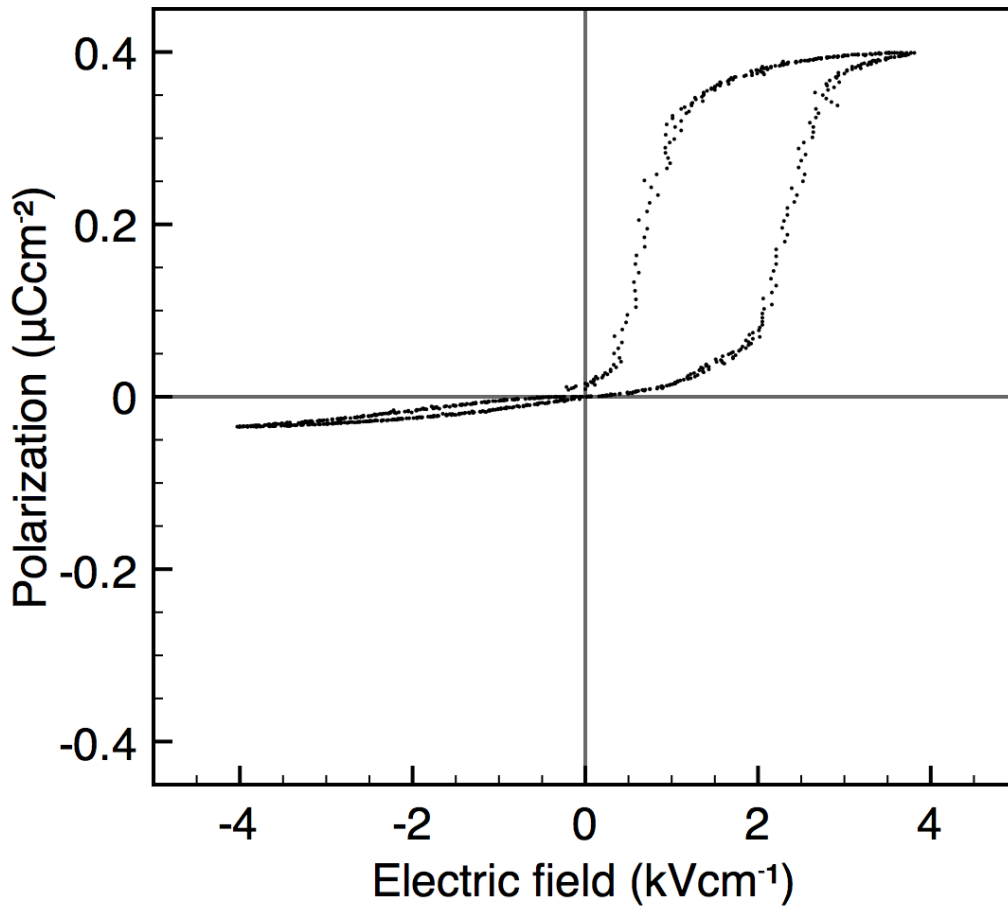
up; one –P down).
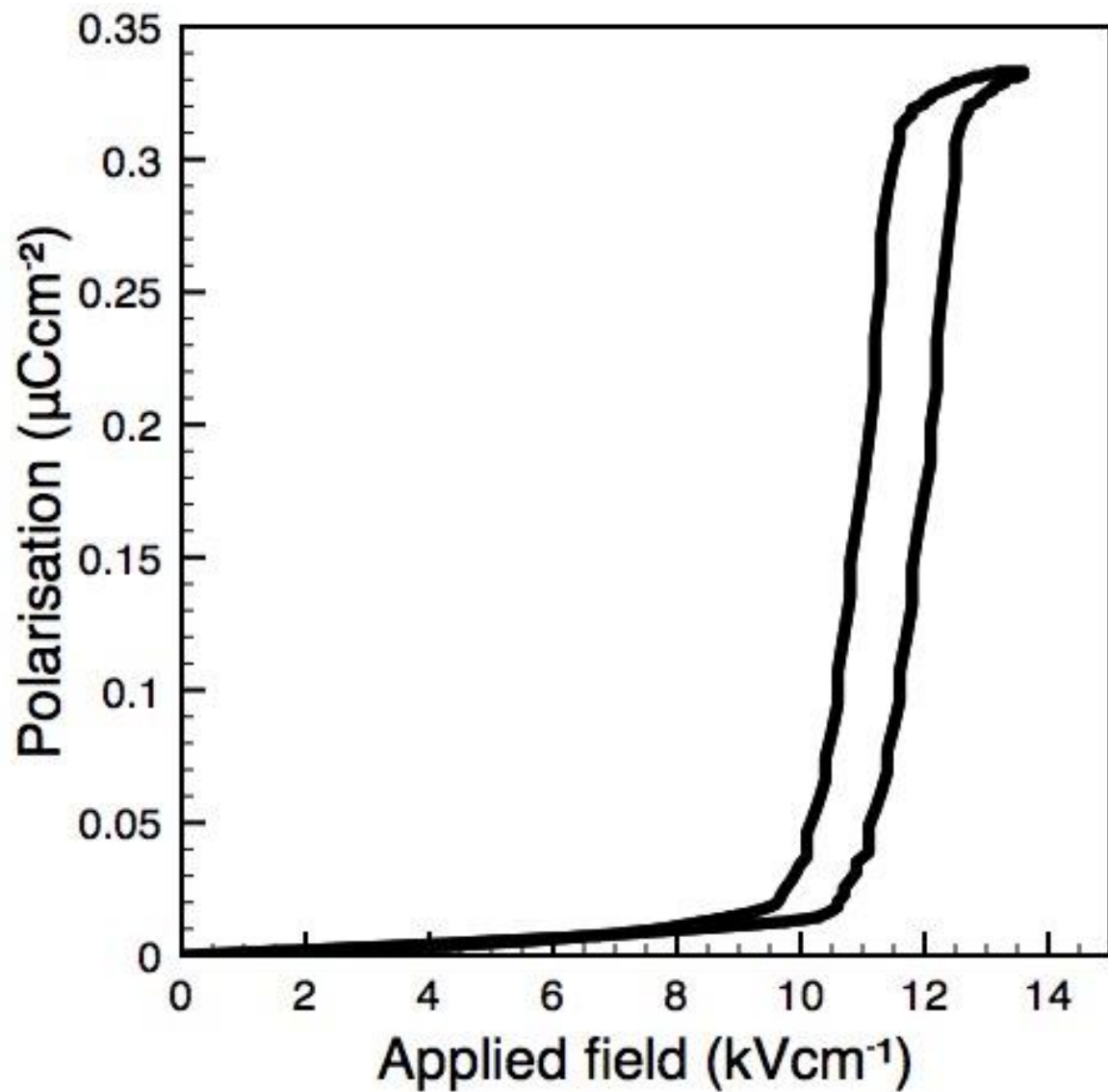
Fig. 3: (a) Polarization data versus field P(E) for TSCC:Br 30% along the polar +b-axis; E = 30 kV/cm along [0 1 0] with 4 kV across 1.4 mm at T = 40 K and 100 Hz. Switching is observed in the form of a single antiferroelectric-like loop (i.e. a ferroelectric loop with a very large bias field) from ca. 8-12 kV/cm, in agreement with ref.4. (b) For pure TSCC (no Br) the bias voltage is smaller (linearly proportional to Br%, but not zero – approx. 1.5 kV/cm). However, this occurs only for positive voltages. For fields along the pseudo-hexagonal c-axis no hysteresis is observed up to 100 kV/cm.

This model is compatible with the original discoveries of the transition near 64 K, first by Haga et al.[19] and subsequently by Lee et al.;[20] 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 $T_c = 130$ K; both of these are less than the value R ln 2 = 5.8 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 K (an unusual stopping point), an unfortunate coincidence since we found[2,6] some indication of another transition near 48 K.

3. 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 antiferroelectric structurally, but as it switches under the forward electric coercive field, remains in a metastable ferroelectric state and avoids the switch back to the antiferroelectric, thereby missing the tell-tale features of the double hysteresis loop."[21] Sodium niobate is one of the two materials originally described by Pulvari as ferrielectric. In calcium zirconate/sodium niobate they observe[22,23] a related smooth FE-AFE transition with increasing Ca/Zn %.

4. 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. Here we measure P(T) at T = 77 K as 0.33 $\mu C/cm^2$, in agreement with earlier work. Below ca. 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. 4. The transition is second-order but very close to tricritical. For pure TSCC polarization P(T) varies as $(T_c-T)^\beta$ with $\beta = 0.32$ +/- 0.02; for 3% Br we found 0.28 +/- 0.02;

for three other specimens. As we show in a subsequent section, oxygen-ion positions around the Ca^{++} ion rotate near T$_c$ with the same dependence ($\beta = 0.3$).
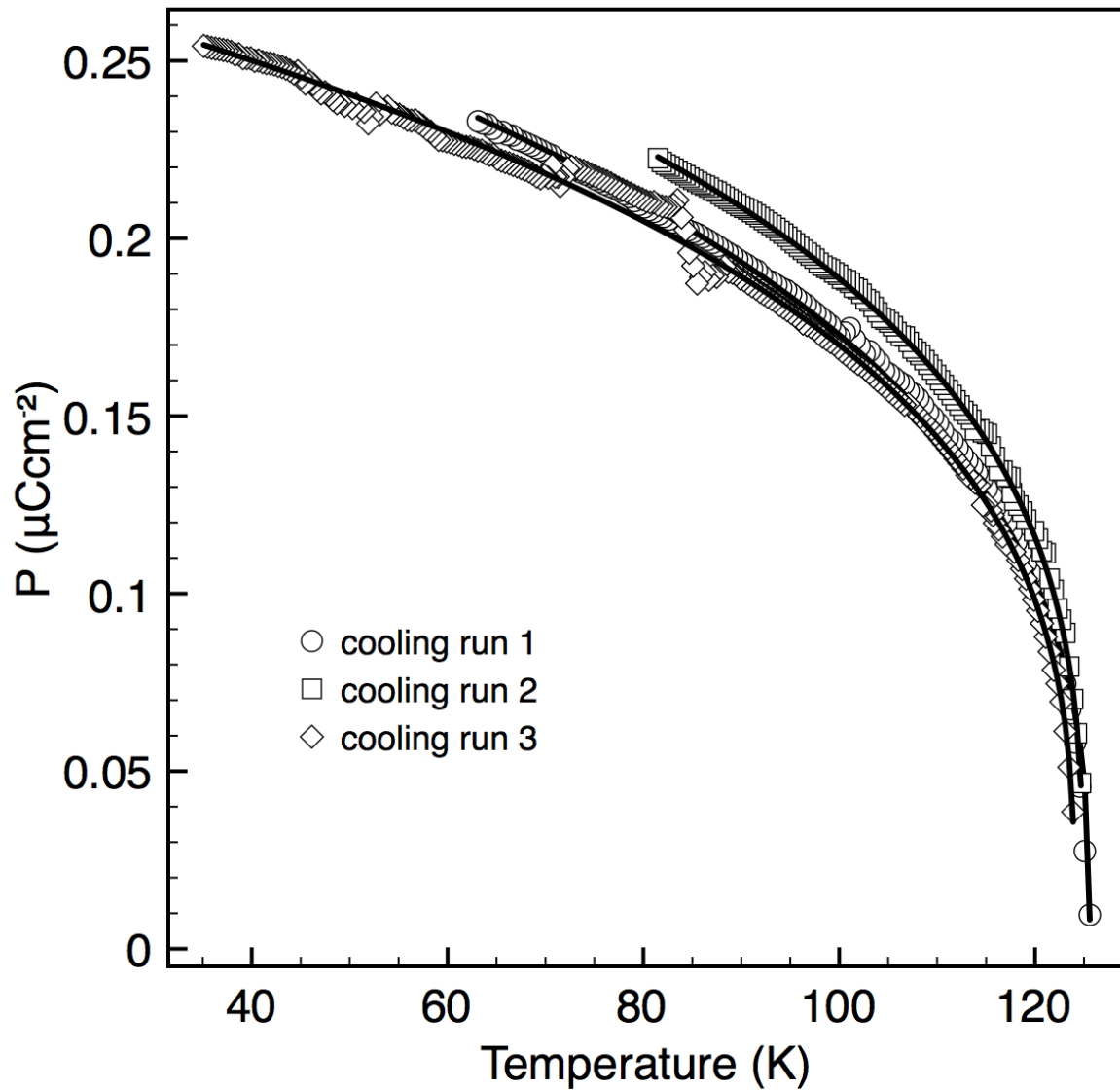

Fig.4. Pure TSCC, with P(T) proportional to the mean-field tricritical dependence (T$_c$-T)$^{0.28}$. Note that the maximum polarization P measured this way of 0.33 μC/cm^2 agrees with that from the polarization switching loops in Fig.3 and that the lowest temperature phases are pyroelectric, and in fact that P increases in these phases.

5. PUND data

Whenever ferroelectric 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.:[24] P – Positive non-switching voltage; U – Up switching voltage from –P to +P; N – Negative non-switching voltage; D – Down switching voltage. It reliably discriminates between true ferroelectric 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 5 ms between the +V and −V pulses. We conclude that there are no artifacts.
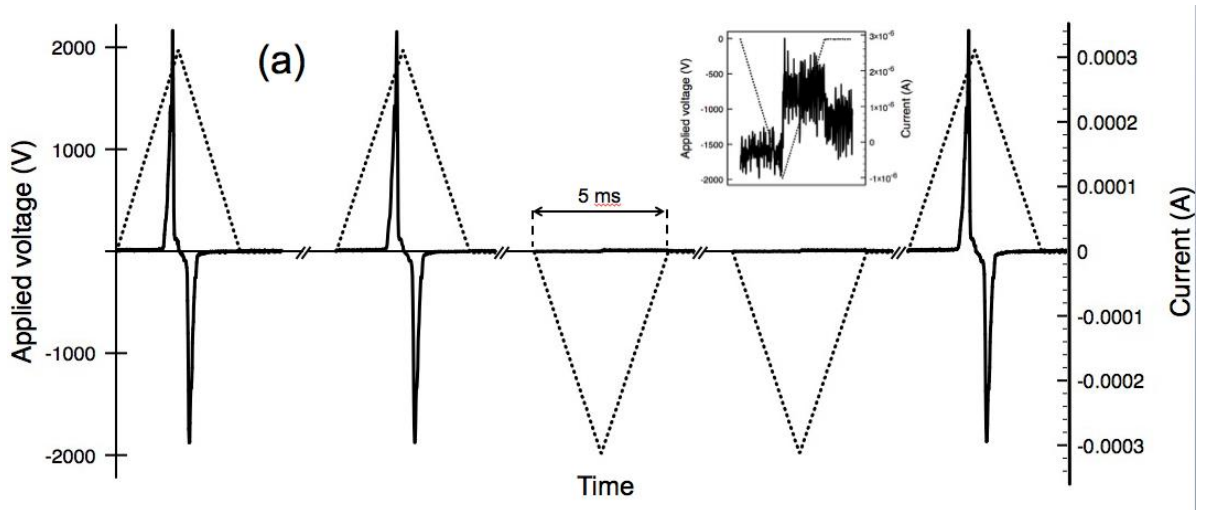

Fig. 5. Polarization "PUND" data on TSCC at T=55K.

IV.   The transition at 47K

An additional phase transition near 47K at atmospheric pressure was first inferred from dielectric and thermal data by the present group.[2,6] However, in retrospect, if we go back and scrutinize the early specific heat data of Haga et al.,[19] 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.,[6] together with thermal

relaxation times and thermal expansion; these show large anomalies (ca. 1%) at 61.0K, 49.3K and 46.7K. On these we have superimposed in Fig.10 new dielectric and polarization data, showing anomalies very near 48K. We emphasize that our X-ray and neutron data show no structural changes at these temperatures.
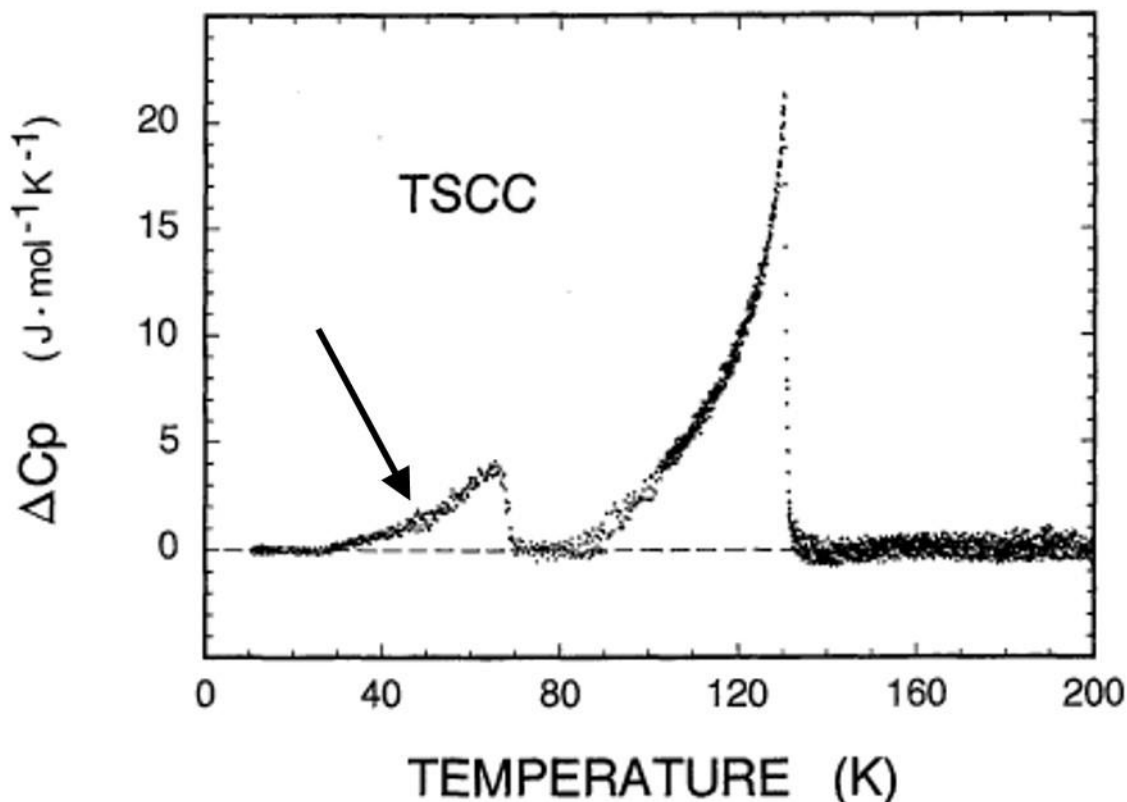

Fig. 6. Specific heat data near 64K and 130K in TSCC, modified from Haga.[19]

V.   Structural determination

TSCC has a complex structure with two inequivalent sarcosine sites, designated S1and S2, in the ambient temperature paraelectric phase (space group *Pnma*). 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.[6] reported a transition to polar space group $Pn2_1a$ with three sarcosines (here designated S1, S2a, S2b) on general positions. That study noted that deviations of all atomic positions between the paraelectric and polar phases was very small (less than 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 of the methyl and O atoms are relatively high. This is suggestive of possible disorder around the methyl groups and the CaO_6 octahedron. Earlier work[20] has suggested that a possible driver for the 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 behaviour. The optimal means of probing these possibilities crystallographically is neutron diffraction, which is highly sensitive to H-atom positions. Our study shows no unusual behaviour 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 all the X-ray refinements being below 3%, and no anomalous structural artefacts. 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 (see ESI for details). 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 ferroelectric 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 Figure 7.
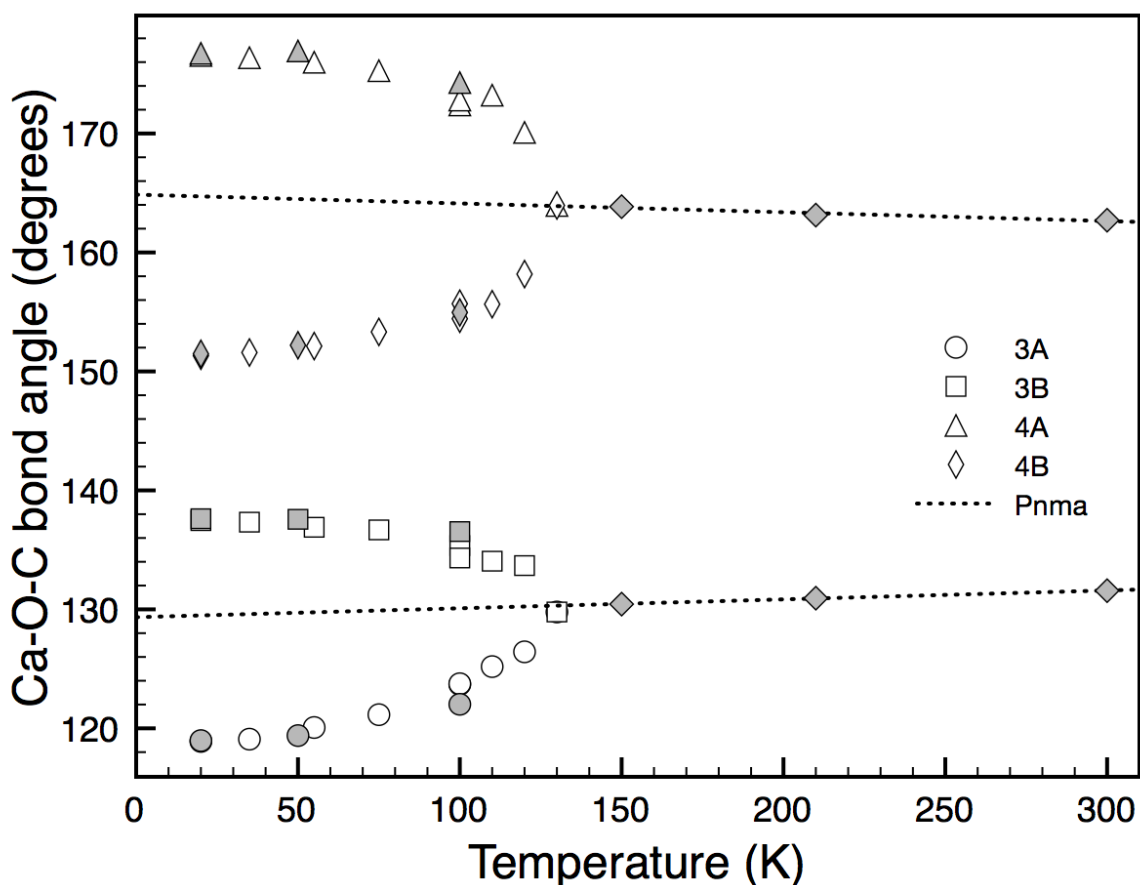
Fig. 7. Change in Ca-O-C bond angle in pure TSCC near T_c. [X-ray data are open symbols; neutron data are shaded.] This may be considered the microscopic order parameter, proportional to the macroscopic order parameter $<P(T)>$. 3AB and 4AB designate different oxygen sites. Dotted lines extrapolate angles from the paraelectric phase.

A smooth evolution of these displacement parameters is seen from 100 K 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. 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 Figure 8, 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 behaviour

does support the assertion that TSCC is ferrielectric below Tc, with antiparallel, but not cancelling, displacements of the three sarcsosines ('two-up, one-down'). The nature of this ferrielectric distortion is reminiscent of that seen in hexagonal $YMnO_3$. In the present case the distortion arises from a single active polar mode, whereas the mechanism in $YMnO_3$ is a 'hybrid improper' one[20b] due to coupling of a non-polar and a polar mode. The present crystallographic study gives a clear picture of the nature of the PE-FE transition at Tc, 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 analysed the changes in atomic displacement parameters (ADPs) versus T, in particular for those atoms suggested to have relatively high ADPs by Mishima. Although relatively large throughout the regime 20 – 100 K, we see no evidence for anomalies (Figs. 9-11). The suggestion 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 are therefore if due to long-range structural re-arrangements, must be very small distortions indeed and probably involve only hydrogen ions, and in particular rotations of the methyl groups.[20] 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 64K and 48K are due to local structural or dynamic effects

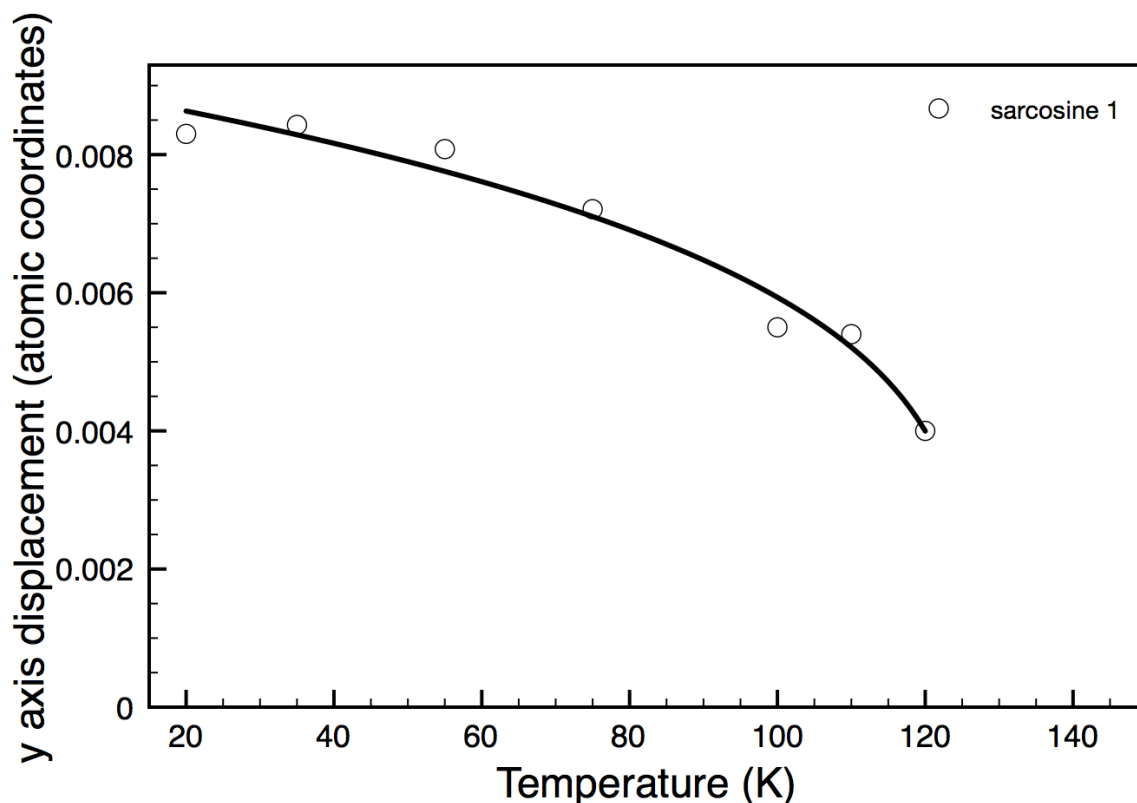1. Neutron structural data: Figure 8-10.

Fig. 8. Sarcosine molecule displacement with respect to Ca-ion (X-ray data); ordinate axis units are % of the b-axis lattice constant. The temperature exponent is $\beta = 0.27$. One outlying data point near T=100K has been removed.

The neutron scattering data were intended to determine the space group symmetries below T=48K and for 48K < T < 64K. It had been suggested that perhaps only H-ions move, and since the entropy change at 64K is significant (Fig.6), an order-disorder transition was suspected. The fact that the entropy change at 64K is nearly half that at 130K 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 rotation angle of ca. 18 degrees. The proton NMR data[20] show the 64K transition more conclusively, however, and also reveal that the CH_3 end groups on the sarcosines rotate above $T_c = 130$K, not detected in the neutron or X-ray data.

Fig. 7 shows that the two sarcosines (2a, 2b) on the mirror plane above T_c do not move in

opposite antiferroelectric 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 ferroelectric polarization, as shown in Fig. 7 the main displacements are out of phase (antiferroelectric). Fig. 8 shows this more clearly and provides a measure of the order parameter versus temperature, which is proportional to the O3 bond angle; in the paraelectric pseudo-hexagonal orthorhombic phase, the oxygen ion angle around the Ca^{++} ion is ca. 130 degrees. Fig. 9 shows these oxygen displacements on a larger cell with view down the pseudo-hexagonal axis. These data by themselves are insufficient to determine whether the transition is first-order, but data in earlier publications[6,19] 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 ferroelectrics are often highly contentious, especially in strontium barium niobate (SBN), where several papers show clearly that the ferroelectric transition is first-order, but some authors maintaining that it is continuous and evaluating "critical" exponents. For example, work by Dec's group[25a] give a large, precise discontinuity in volume $\Delta V = 0.6989\ A^3$ and a mean-field exponent for thermal expansion of 0.53+/-0.15, whereas earlier work co-authored with Kleemann claim a continuous transition and much smaller, highly non-mean-field exponents.[25c,d] It is difficult to understand second-order transitions with large volume discontinuities! And trying to fit continuous power laws to small jumps[25e] always gives small fictitious exponents ca. 0.1. The discontinuous character of the SBN transition is also shown clearly in Raman data.[25b] In TSCC and TSCC:Br the thermal expansion[6] and specific heat[19] are not proportional to each other near T_c, giving a non-constant Gruneisen ratio, which violates classical Landau theory and supports defect-mediated dynamics.[6]

2. Estimation of local polarization from X-ray and neutron data

Figs. 9 and 1 show the resulting TSCC structure in the ferroelectric phase. The ferroelectric polarization <P> in a displacive system is a non-local 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, the carboxyl group is a zwitter ion, and the H detaches 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.6-8. 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 hypothesising that it is approximately -1.0e 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 ions (COO^-) [which shifts 0.62% along b] and the nitrogen ion [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 x 1.746 x 1.0265 nm^3, gives a local polarization change <P> for each sarcosine of 0.363 $\mu C/cm^2$ in the correct polar b-direction. The experimental value of 0.33 $\mu C/cm^2$ is remarkably close to this value and hence suggests that the polarization in the ferroelectric phase may arise primarily from these sarcosine-calcium displacements (both measured at ca. T=50K), and not from the N-H-Cl hydrogen bonding, as had historically been supposed[3,4]despite the fact that P was known to be in the wrong direction (orthogonal to the polar b-axis) from the hydrogen bond.
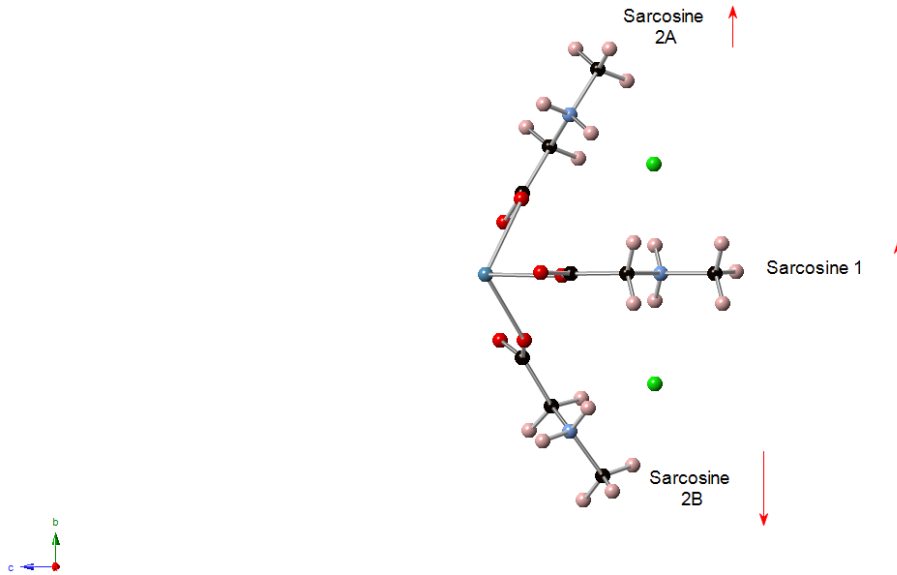
Fig. 9. Resultant TSCC structure below Tc = ca. 120K.

VI. Landau theory and comparison with ε-WO₃

Ferrielectric structures are extremely rare in inorganic single crystals. A notable exception is the low temperature phase ε-WO₃. The structure consists heavily tilted octahedral with the approximate centrosymmetric space group I2/c. The tungsten positions are shifted from the centre 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[25] over four W sites is 0.52 ± 0.16 eA². While ferrielectricity is rare in uniform materials, it is common in nano-structured samples. Domain wall-related polarity is often ferrielectric and complex nano-structures fail even for large samples to fully compensate local dipole moments.[26,27] Generally one expects large unit cells and flexible molecular structures to develop ferrielectric 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 ferroelectric with weak polarization driven by coupling to an antiferroic mode, i.e. free energy term proportional to

$$G(P,T) = P(q=0) \, \phi(q=\pi/a) \, \phi(q=-\pi/a), \qquad (1.)$$

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 -- ferroelectric eigenvector and polarization P at q=0, and hence excess Gibbs free energy of form[26,27]

$$\Delta G = A \, \theta_s[(\coth(\theta/T) - \coth(\theta_s/T_c))P^2 + 1/4 \, B \, P^4 + 1/6 \, CP^6 \qquad (2.)$$

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

$$B^2/(4ACT_c) = 8.2K/130K = 0.060 \qquad (3.)$$

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

VII.   Relation to QCP (Quantum Critical Point)

Recently we showed[7] 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 ($0.33 \, \mu C/cm^2$ at 77 K), which makes the system behave as if it were only negligibly ferroelectric at low T, similar to pseudo-cubic $SrTiO_3$ or $KTaO_3$.

VIII.   Summary

We present polarization hysteresis loops in TSCC below its known phase transition at 64 K (pure TSCC; ca. 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.; 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 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. The low-temperature structure is complicated by a probable additional transition near 48 K. Fig.10 compares the precise (resolution of a few mK) thermal expansion data of Lashley et al.[6] with new unpublished dielectric data. The latter [Fig.10] exhibit a peak at 48.0K, 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 64K or near 48K, 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 β = 0.29 +/- 0.04, compatible with the predicted mean-field tricritical value of ¼.
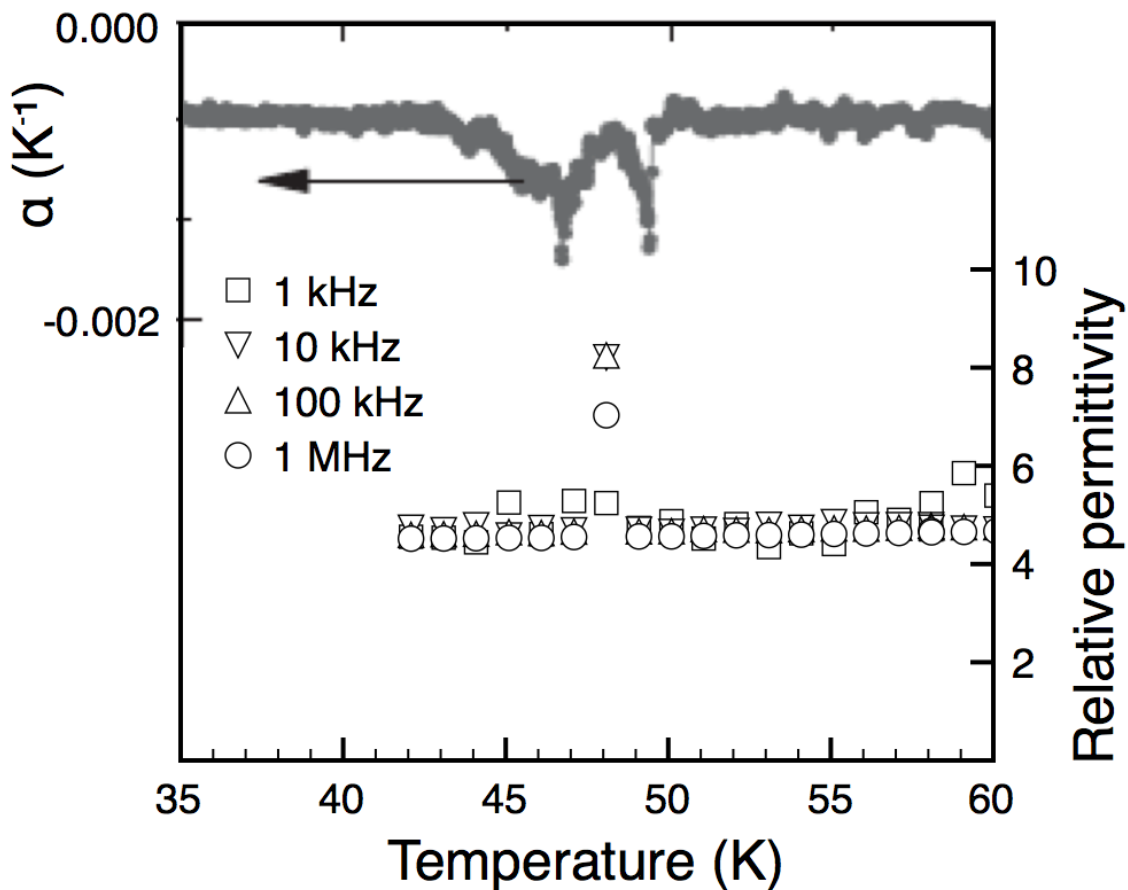
Fig. 10. Preliminary evidence for a phase transition in TSCC near 48K. Upper trace is thermal expansion coefficient, and lower trace is dielectric response. The latter show only a few data points at 48.0K.

A semantic question arises as to how best to describe "ferroelectrics" for which the bias field E_b >> the coercive field E_c: these crystals have no ferroelectric properties for voltages near zero. These are well known as arising from defects and substitutional ions in materials such as TGS (tri-glycine sulphate), but they may also arise from a ferroelectric structure with several inequivalent polar sites (e.g., sarcosine S1 and S2 sites in the present work). 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.[28]

Acknowledgements

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