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DIELECTRIC OBSERVATION OF A PROBABLY ANTIFERROELECTRIC HIGH PRESSURE PHASE IN THE FERROELECTRIC TRIS-SARCOSINE CALCIUM CHLORIDE (TSCC)

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Dielectric susceptibility and ferroelectric hysteresis measurements on TSCC show that the 2nd-order paraelectric-ferroelectric (PE-FE) phase boundary beginning at (130.8 K, 1 bar) runs with pronounced curvature to (176.8 K, 5.03 kbar), where a new phase of low dielectric susceptibility appears. This phase is hypothesized to be antiferroelectric (AFE) with 3 possible structures: orthorhombic ($P2_12_12_1$, piezoelectric) or monoclinic ($P2_1/a$ or $P2_1/n$, centrosymmetric). The FE-AFE phase boundary was determined down to (81.0 K, 2.60 kbar) and the PE-AFE boundary up to (225.5 K, 6.82 kbar). Both the FE-AFE and PE-AFE transitions are of 1st order over the range studied.

Tris-sarcosine calcium chloride (TSCC) is a ferroelectric with several unusual properties. It grows from aqueous solution in the paraelectric (PE) phase with a structure which is orthorhombic[1] (D_{2h}^{10} - Pnma) but so nearly hexagonal that the crystal is ferroelastic; uniaxial stress along $\underline{c}$ near 200°C can in effect rotate the structure about the pseudo-hexagonal $\underline{a}$ axis[2].

The structure[1] in the PE phase has 4 formula units of $(CH_3NH_2^+CH_2COO^-)_3\,CaCl_2$ per unit cell, with the Ca^{++} ions and 4 of the 12 sarcosine dipoles in (probably disordered) positions corresponding to the mirror plane perpendicular to $\underline{b}$. Below the ferroelectric (FE) transition temperature T_c this mirror plane must vanish because $\underline{b}$ becomes the FE axis; it has been assumed[3] that the structure of the FE phase is orthorhombic C_{2h}^9-$Pn2_1a$, $Z = 4$. No superstructure was found[4] in recent X-ray diffraction studies of the FE phase[4], consistent with Z remaining 4 in that phase.

The Curie-Weiss constant C_3 and spontaneous polarization P_s are quite small[3,5]. Nuclear magnetic resonance (NMR)[6] and electron paramagnetic resonance (EPR)[7,8] results have been interpreted in terms of an order-disorder transition, but recent Raman scattering results[9,10] revealed a soft mode below T_c which indicates that the transition is at least partly displacive. The pressure dependence of T_c has an unusually large positive initial slope and negative curvature[11,12]. The reported[12] disappearance of the dielectric anomaly above 4 kbar was the motivation for the present search for a third phase of TSCC at high pressure.

The crystals used in these measurements were recrystallized by evaporation of an aqueous solution of TSCC crystals grown from 98% pure sarcosine and reagent grade $CaCl_2.2H_2O$. Absence of ferroelastic twins[2] and optically observable defects was verified by means of a polarizing microscope. The crystals were polished on wet filter paper into plates whose faces perpendicular to the FE $\underline{b}$ axis were covered with evaporated gold electrodes. The first crystal is 1.4 mm thick along $\underline{b}$ with electroded faces of area 18.3 mm^2, while the second has thickness 2.95 mm and area 37.8 mm^2.

Contacts to these electrodes were provided by weakly spring-loaded brass pistons inside the sample holder, which in turn was placed inside a stainless steel pressure cell having two 4-wire electrical inputs. The cell was pressurized with helium by means of a compressor and intensifier which could attain 6 kbar. For later experiments with the second crystal, another intensifier provided nearly 7 kbar before leaks from connections became excessive. A manganin cell and transducer permitted pressure measurement to 1% accuracy. The crystals were cooled at rates as slow as -0.2 K/min by sending pulses of liquid nitrogen each minute through passages provided in the cell, which was thermally insulated only by a layer of styrofoam. Shorter nitrogen pulses were employed in some warming runs while in others the natural warming rate of about 0.5 K/min was used. Sample temperature was determined within $\pm$1 K by measuring with the 4-terminal method the resistance R(p) of a platinum resistor at pressure p inside the cell near the crystal, then applying the approximate correction formula $R(0) = (1 + 0.002\,p)\,R(p)$ with p in kbar to allow use of the T vs. R(0) tables, and finally correcting for the thermal lag (2 to 5 min., increasing with T) of the crystal as found from comparing dielectric results for warming and cooling runs.

The small-signal dielectric susceptibility of both crystals was measured with a Wayne-Kerr B221 "magic eye" bridge operating at 3 V rms and angular frequency $\omega = 2\pi f = 10^4$/sec, with sensitivity 0.01 pf and 10^{-4} micromho. Provi-

sion for dc bias fields up to ±2000 V/cm was added for some of the later measurements on the first crystal. Chart recorder traces of hysteresis loops were obtained for the first crystal, using a 0.05 Hz source supplying peak fields up to 2000 V/cm. Both the susceptibility and hysteresis measurements were made at intervals ranging from 1 minute near the transitions to 5 minutes farther from the transition.

The primary result of these experiments is the discovery of a third, probably antiferroelectric (AFE), phase of TSCC which exists only at high pressure as shown in Fig. 1. This work also supplements previous studies of dielectric properties[3,5,6] at ambient pressure and of the *pressure dependence of the paraelectric-ferro*electric (PE-FE) transition temperature T_c[11,12].

best fits to the expression

$$T = t_o + t_1 p + t_2 p^2 \qquad (1)$$

were made for the transition temperatures T(p) for each of the three phase boundaries. These three parabolas come within 0.01 kbar and 0.1 K of intersecting at a single point located at p_t = 5.03 kbar, T_t = 176.8 K, which was then imposed as the common point *for each transition in the expression*

$$T = T_t + T_1(p - p_t) + T_2(p - p_t)^2. \qquad (2)$$

The best-fit parameters T_1 and T_2 were then found for the PE-FE and FE-AFE transitions. Finally, this best-fit T_1 for the FE-AFE line

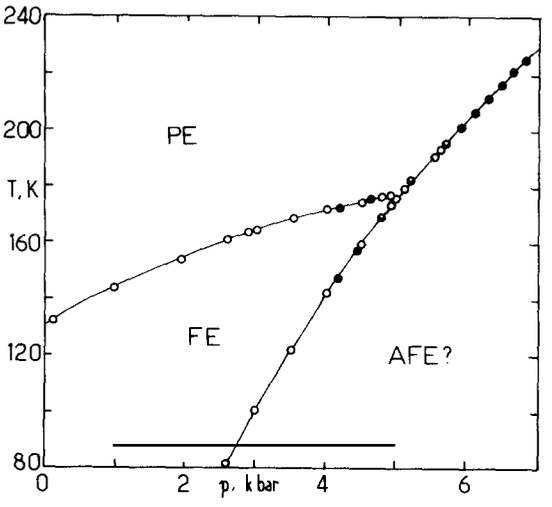

Figure 1

Phase diagram for tris-sarcosine calcium chloride (TSCC), showing the paraelectric (PE), the ferroelectric (FE), and the probably antiferroelectric (AFE) high-pressure phase. The PE-FE transition is probably 2nd order, while the PE-AFE and FE-AFE transitions are 1st order. Some closely adjacent experimental points have been combined for clarity. Open and filled circles represent data from the 1st and 2nd crystal respectively, while half-filled circles represent data from both crystals.

The PE-FE phase boundary was determined by the temperature at which the inverse susceptibility $(\varepsilon - \varepsilon_o)^{-1}$ vanishes on linear fits using a 20°C interval above T_c, or by the onset of hysteresis. The PE-AFE boundary was marked by a sudden change in ε, while the FE-AFE boundary was located by such change or by the sudden disappearance of hysteresis loops.

*Mathematical expressions for the phase boun*daries were determined as follows. Because results from the first crystal were the most extensive for *the PE-FE and FE-AFE boundaries,* they were used to determine the PE-FE-AFE common point and then the PE-FE and FE-AFE boundary expressions. First, separate 3-parameter

was imposed also as the initial slope T_1 for the PE-AFE line, and the best-fit T_2 was then found for that line using data from both crystals. This common-slope assumption is required if the PE-FE transition is 2nd-order and the PE-AFE and FE-AFE transitions are first-order, as indicated by the dielectric results. A posteriori justification for this assumption and *the parabolic form for Eq. (2) is that this* 7-parameter fit to all the data cannot be substantially improved by introducing additional parameters.

The best-fit parameters found by the above procedure appear in Table I, together with parameters found previously[11] for the PE-FE transition.

Table I. Coefficients t_i and T_i in Eqs. (1) and (2) for pressure dependences of phase transition temperatures in TSCC, including coefficients found previously (Ref. 11) over the 0 to 2.1 kbar pressure range

Transition	t_o, K	t_1, K/kbar	T_1, K/kbar	$T_2(=t_2)$ K/kbar^2
PE-FE*	128.6±0.2	13.2±0.4		-0.5±0.2
PE-FE	130.8±0.4	14.5±0.3	3.82±0.2	-1.06±0.04
PE-AFE			29.2±0.5	-0.99±0.1
FE-AFE			29.2±0.5	-4.16±0.3

*Ref. 11

The t_o (ambient-pressure T_c) values differ as is typical for two crystals from different sources, and the initial slopes t_1 and curvatures t_2 also differ somewhat outside experimental error. The initial slope T_1 of 14.5 K/kbar is unusually large, but what is more striking is the strong curvature which reduces the slope to 3.82 K/kbar at the common point, and which would give a maximum T_c of 180.2 K at only 6.83 kbar if the AFE phase did not intervene. Qualitatively similar slope and curvature were found by Hegenbarth and Schmidt[12], but they noted disappearance of the dielectric anomaly at only 4 kbar.

The FE-AFE boundary extrapolates to 1.14 kbar at 0 K, so the AFE phase can be presumed to exist only at high pressure. The curvature is greater than that of the PE-AFE boundary because of the progressively lower free energy of the FE phase compared to the PE phase as one moves down along the FE-AFE boundary.

The dielectric susceptibility results, within the limitations imposed by the rapid rate of temperature change and relatively high frequencies used, indicate a 2nd-order PE-FE transition as reported previously[3,5]. Straight Curie-Weiss plots of $(\varepsilon - \varepsilon_\infty)^{-1}$ vs. T were obtained for the first 20° above T_c at all pressures, including 5.6 kbar where the Curie-Weiss behavior is interrupted by the appearance of the AFE phase. The Curie-Weiss constant C in $\varepsilon - \varepsilon_\infty = C/(T - T_c)$ was 31 ± 2 K with no noticeable pressure dependence for the first crystal, and 30 ± 4 K at 4.18 kbar for the second crystal. These values are within the wide range 17 to 58 found by others[3,5,6].

The peak dielectric constant at T_c for the first crystal was in the 300 to 500 range, increasing with pressure as noted previously[12]. This increase can be explained in terms of a defect-induced spread in local pressure inside the crystal[13], which gives correspondingly smaller transition temperature spreads ΔT_c as pressure increases because of the decreasing dT_c/dp. The crystal, acting as a series-parallel combination of tiny crystals each with its own T_c, then has higher peak ε as ΔT_c decreases. The second crystal had peak ε of over 1000 at 4.16 kbar.

Below T_c the Curie-Weiss constants were near 200 for the first crystal and 80 for the second, and the loss tan δ was quite large. Both effects probably resulted from domain wall motion at the relatively large field (3 V/cm) and low frequency (1592 Hz) used. The loss decreases with decreasing temperature below T_c. Application of dc bias reduced both the dielectric susceptibility and loss as expected, but within the limited thermal accuracy had no effect on any transition temperatures.

The PE-AFE and FE-AFE transitions appear to be of first order, because there are no anomalies in the PE or FE behavior until the onset of the AFE phase, which has a small dielectric susceptibility without noticeable temperature or pressure dependence.

The hysteresis loops, studied only for the first crystal, were very thin and S-shaped just below T_c. With decreasing T they became wider and rounded at the tips, indicating that even 2000 V/cm was insufficient field for saturation. At still lower temperature the loops again became narrower and regained their pointed tips.

At 1 bar pressure the spontaneous polarization was near 0.11 microcoul/cm^2 and the coercive field near 300 V/cm, at 0.05 Hz and E_{peak} of 900 V/cm. Both values are smaller than reported by Sorge and Straube[5].

No double hysteresis loops were seen in the AFE phase, in accord with the assumed first-order nature of the FE-AFE transition.

The new phase probably exhibits ordering of the structural elements that are in high-symmetry positions in the PE phase. There are 4 such elements in the PE unit cell each consisting of a calcium ion and sarcosine dipolar molecule lying in a mirror plane perpendicular to b. These can order pairwise in 4 ways as shown in Table II.

Table II. Possible structures of TSCC phases. The Dipolar Arrangement (Dip. Arr.) column shows the signs of the b-axis components of the dipole moments associated with the 4 sarcosine molecules (AB CD) which in the PE phase lie in mirror planes perpendicular to b. Molecules A and B lie in one such plane, while C and D lie in another. Molecules B and C are connected by a one-dimensional network of N-H...Cl hydrogen bonds running along b as shown in Ref. 1, while A and D lie in two other such networks.

Phase	Dip. Arr.	Structure	Nature	Status
PE	00 00	orth. Pnma	centrosym.	meas.
FE	++ ++	orth. $Pn2_1a$	ferroel.	probable
AFE	+- -+	orth. $P2_12_12_1$	piezoel.	possible
AFE	+- +-	mono. $P2_1/n$	centrosym.	poss.
AFE	++ --	mono. $P2_1/a$	centrosym.	poss.

One order type was proposed by Makita[3] as the FE structure. In the other 3 structures the dipole moments of the ordered elements cancel, and each structure permits 2 domain types, so these structures are all AFE.

These 3 possible space groups can be distinguished in principle by X-ray or neutron diffraction studies, both of which are planned. Knowledge of the order type would aid in determining which short range dipolar interactions are most important.

The above AFE structure hypotheses require a 1st-order FE-AFE transition in accord with the present findings but do not restrict the other transitions. The PE-AFE transition was also found to be 1st-order, but could exhibit a tricritical point at higher pressure. The

PE-FE transition which is 2nd-order at 1 bar [5] appears to remain 2nd order over its whole pressure range, but more accurate measurements are needed for certainty.

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