POLARIZATION REVERSAL OF SbSI (*)

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ABSTRACT — The ferro-paraelectric phase transition of SbSI has been studied by using very accurate measurements of spontaneous polarization and dielectric constant as a function of the temperature. There is strong evidence of a large discrepancy between the Curie temperature as determined from data above or below T_c.

1 – INTRODUCTION

The Landau theory for a second order phase transition is valid when the fluctuations of the order parameter are not too strong, i.e. for temperatures not too close to the critical temperature T_c, which coincides with the Curie temperature T_0. Ginzburg [1] has given a criterion which allows an estimate of the

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temperature range (around T_0) where this theory is not valid. When electric dipolar interactions are responsible for a phase transition, this should obey Landau theory except in a narrow "critical region" close to T_c, typically of the order of $\varepsilon = 10^{-4}$ to 10^{-5} where $\varepsilon = |T - T_0| / T_0$. For a first order transition the change of phase occurs at a temperature T_c which is different from T_0 The critical temperature T_c is higher than the temperature T_0 (stability limit of the paraelectric phase) and lower than the stability limit of the ferroelectric phase, T_0^- [2].

In a previous paper [3] we used the critical exponent associated with the spontaneous polarization of SbSI to test Landau theory in that compound. Here we have fitted experimental data on SbSI to the correct expressions of spontaneous polarization obtained from Landau theory. Experimental spontaneous polarization is obtained through pyroelectric effect and D-E hysteresis loops studies. Dielectric constant measurements as a function of the temperature were carried out in order to obtain the values of all parameters of Gibbs free energy in Landau theory.

2 – EXPERIMENTAL PROCEDURE

The pyroelectric coeficient (λ) is determined by measuring the d. c. discharge current (i) from a sample of known electrode area (s) subjected to a controlled rate of change of temperature (dT/dt). The pyroelectric coefficient is given by $\lambda = (i/s)(dT/dt)^{-1}$. The potential difference across a short circuiting resistor arising from the discharge current was measured with a P. A. R. model 134 electrometer [3]. The spontaneous polarization as a function of the temperature was also derived from 50 cps hysteresis loops obtained with a modifiel Sawyer-Tower circuit [4]. Dielectric loss (ε'') and dielectric constant (ε') were measured with a model 745 LEADER LRC meter. SbSI was polarized with a d. c. electric field while being cooled down through the transition temperature. The temperature was measured with a copper-constantan thermocouple with a precision better than 0.02 K. Samples were cut from thin rectangular prisms 10-20 mm long and about 0.4 mm^2 cross section. SbSI crystals were grown by vapour

transport reaction, the polar axis being along the long edge. Silver paste contacts were used as electrodes.

3 – EXPERIMENTAL RESULTS AND DISCUSSION

Experimental results of pyroelectric effect measured at an uniform heating rate of 4 mK s^{-1} in one sample of SbSI, here refered as sample (a), are shown in figure 1. As the temperature rises the current passes through a sharp maximum at $T_m = 288.9$ K and then gradually approaches zero. The temperature dependence of spontaneous polarization deduced from figure 1 can be seen in

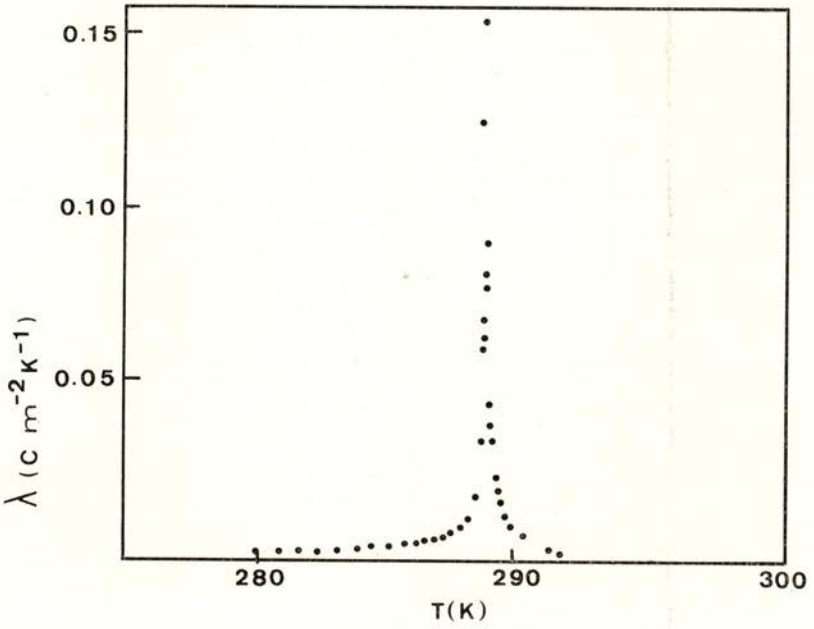

Fig. 1 — Temperature dependence of pyroelectric coefficient λ for SbSI (sample (a)).

figure 2. In figures 3 and 4 we can see pyroelectric coefficient and spontaneous polarization as a function of the temperature for another sample of SbSI, sample (b). For this sample the pyro-

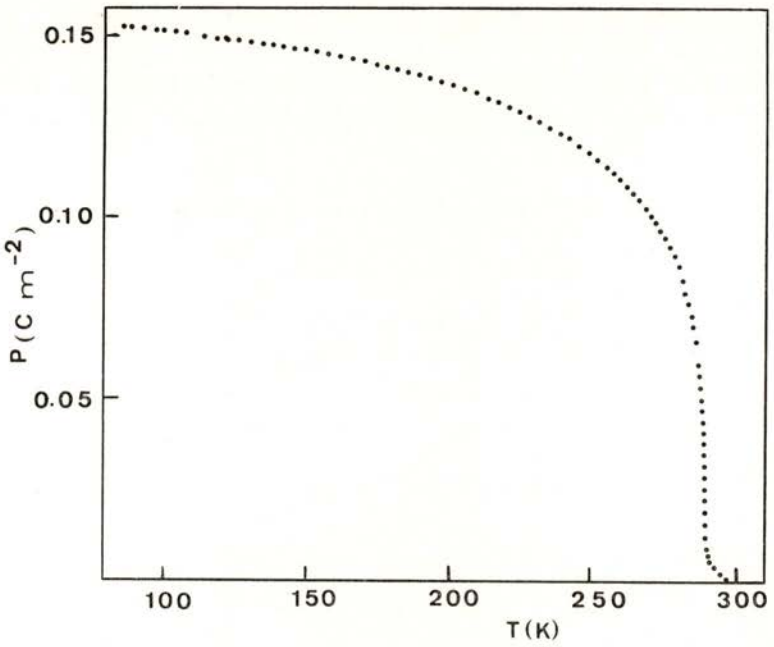

Fig. 2 — Temperature dependence of spontaneous polarization P_s for SbSI (sample (a)) obtained from pyroelectric coefficient data of figure 1.

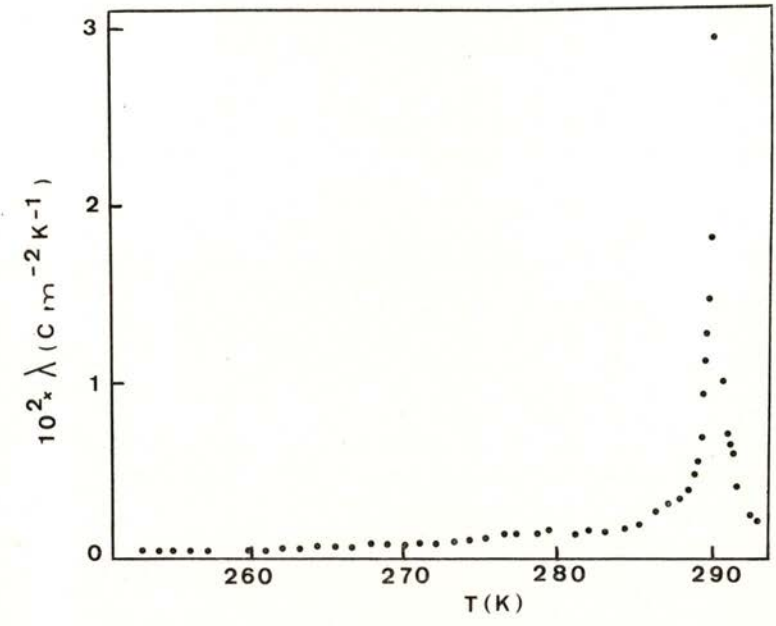

Fig. 3 — Temperature dependence of pyroelectric coefficient λ for SbSI (sample (b)).

electric coefficient shows a more pronounced tailing-off above $T_m = 290.1$ K. As is well known, Landau's theory for a first order

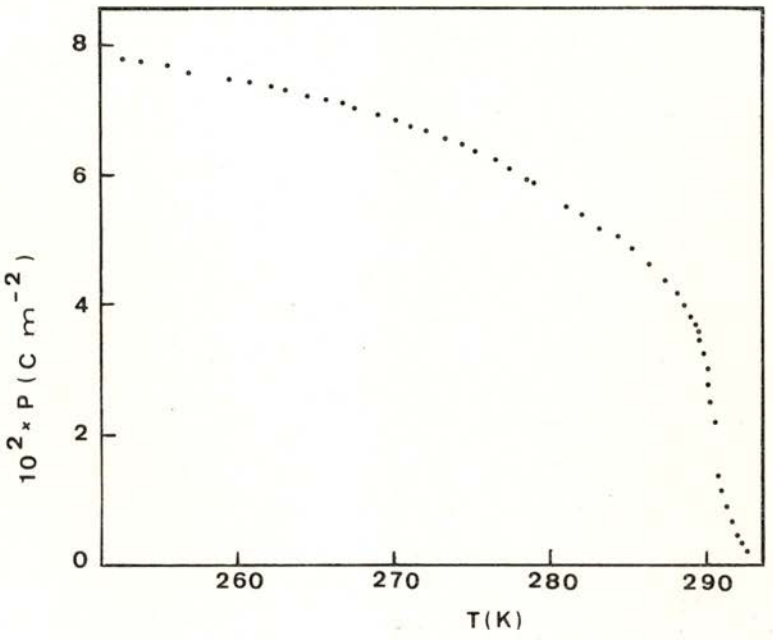

Fig. 4 — Temperature dependence of spontaneous polarization P_s for SbSI (sample (b)) obtained from pyroelectric coefficient data of figure 3.

transition requires the Gibbs free energy density to be expanded up to the sixth power of the order parameter P [2, 4] :

$$G = G_0 + a\ (T - T_0)\ P^2/2 + b\ P^4/4 + c\ P^6/6 \qquad (1)$$

The coefficient *a* and *c* are positive and *b* is negative. Standard calculations based on minimisation of the free energy give the following result :

$$a\ (T - T_0) + b\ P^2 + c\ P^4 = 0 \quad \text{for} \quad T < T_c = T_0 + 3\ b^2/16\ a\ c \qquad (2)$$

$$P = 0 \qquad \text{for} \quad T > T_c \qquad (3)$$

For a sample under an uniform electric field E_b expression (2) must be replaced by the following one :

$$a\,(T - T_0)\;P + b\,P^3 + c\,P^5 - E_b = 0 \qquad (4)$$

The reciprocal of the electrical susceptibility is given by

$$(\chi_T)^{-1} = 4\,a\,(T_0 - T) + (b^2/c)\,\{1 + [(\tilde{T} - T)/(\tilde{T} - T_0)]^{1/2}\} \quad \text{for} \quad T < T_c \qquad (5)$$

$$(\chi_T)^{-1} = a\,(T - T_0)\,, \quad \text{for} \quad T > T_c \qquad (6)$$

where

$$\tilde{T} = T_0 + b^2/4\,a\,c\,. \qquad (7)$$

Using a least squares method, data were fitted on a computer to expression (2). The best fitting to this expression yields the values

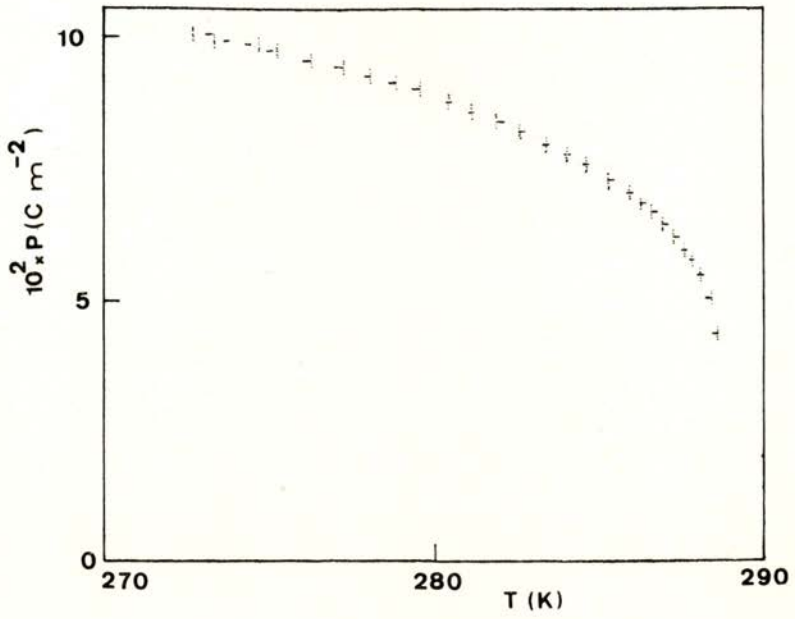

Fig. 5 — Theoretical fitting of P_s versus T (horizontal dashes) for SbSI (sample (a)). Vertical dashes: experimental data obtained from pyroelectric effect.

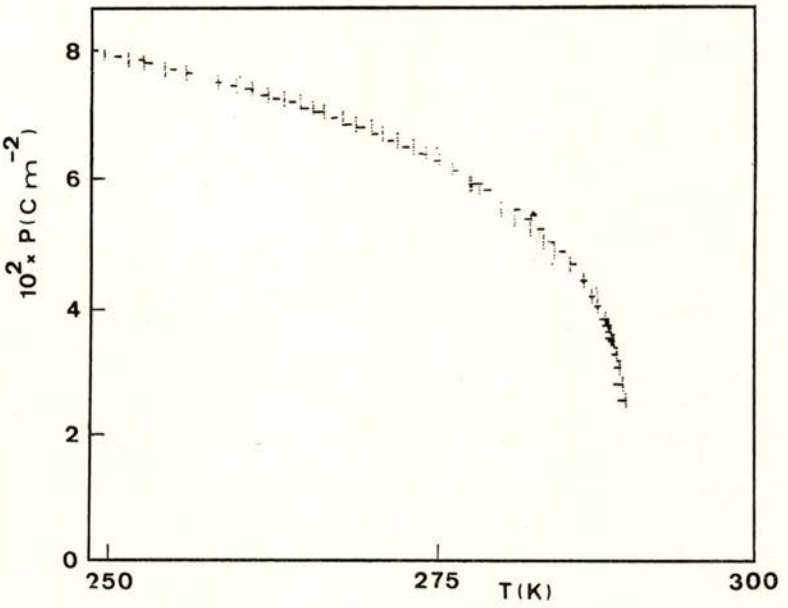

Fig. 6 — Theoretical fitting of P_s versus T (horizontal dashes) for SbSI (sample (b)). Vertical dashes: experimental data obtained from pyroelectric effect.

of b/a, c/a, T_0 and T_c listed in Table I. The horizontal dashes of figures 5 and 6 are drawn using those values. Vertical dashes represent experimental data.

TABLE I

	Sample (a)		Sample (b)
	Pyroelec. eff.	Hyst. loop	Pyroelec. eff.
b/a [$C^{-2}m^4K$]	-6.3×10^2	-1.4×10^2	-9.0×10^2
c/a [$C^{-4}m^8K$]	2.1×10^5	5.4×10^4	12×10^5
T_o [K]	288.2	289.4	289.5
T_c [K]	288.5	289.5	289.6
T_m [K]	288.9	—	290.1

The results obtained seem to show that SbSI follows Landau's theory for a first order transition. As the difference $T_c - T_0$ is very small the phase transition is very nearly a continuous one, as referred

by Glass and Lines [4]. By assuming that the tailing off in the pyroelectric effect above T_c could be explained by an internal electric bias field (E_b) we have also fitted the data to expression (4). The values of b/a , c/a , T_o , T_m and E_b/a obtained by a method similar to that referred above are listed in Table II. The horizontal dashes of figures 7 and 8 are drawn accordingly.

TABLE II

	Sample (a)		Sample (b)
	Pyroelec. eff.	Hyst. loop	Pyroelec. eff.
b/a [$C^{-2}m^4K$]	-4.3×10^2	-3.6×10^1	-6.9×10^2
c/a [$C^{-4}m^8K$]	2.0×10^5	0.64×10^5	9.2×10^5
T_o [K]	288.7	288.3	289.9
T_m [K]	288.9	—	290.1
E_b/a [$Cm^{-2}K$]	6.9×10^{-3}	3.35×10^{-2}	9.1×10^{-3}

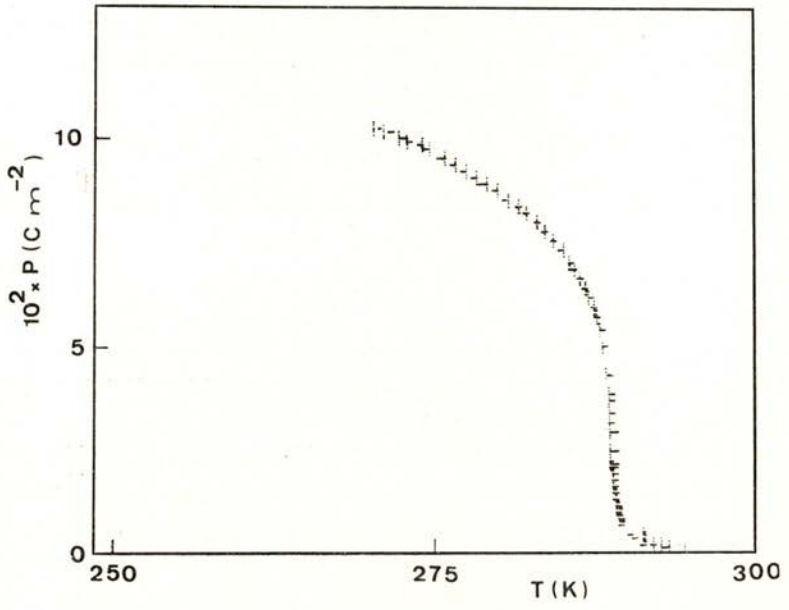

Fig. 7 — Theoretical fitting of P_s versus T including a bias internal electrical field E_b (horizontal dashes) for SbSI, (sample (a)). Vertical dashes: experimental data obtained from pyroelectric effect.

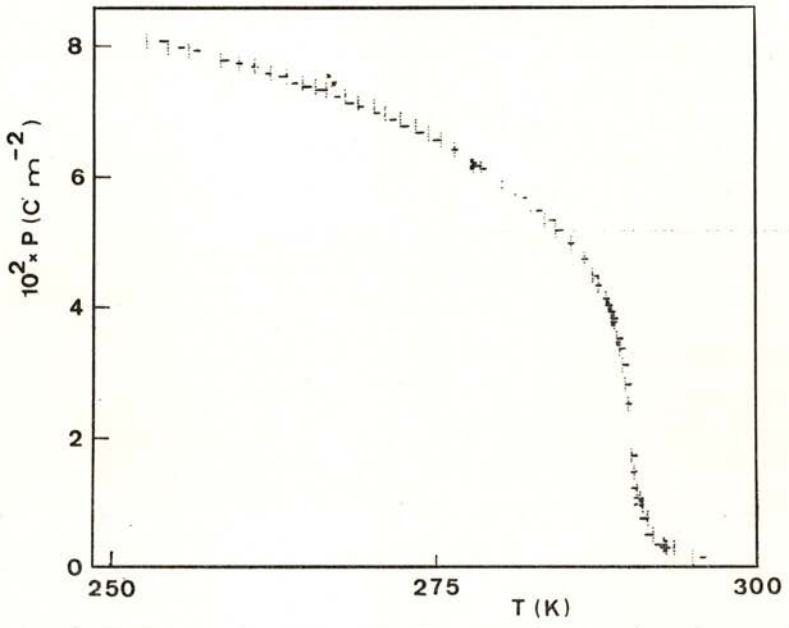

Fig. 8 — Theoretical fitting of P_s versus T including a bias internal electrical field E_b (horizontal dashes) for SbSI (sample (b)). Vertical dashes: experimental data.

In figure 9 we can see some hysteresis loops, at different temperatures, for sample (a). We have not observed double hysteresis loops as reported by S. Kawada [5] in SbSI samples with a critical temperature higher than in our samples. Vapour grown non-stoichiometric crystals with a slight excess of sulfur together with oxygen impurities show a transition temperature around 24.7 C [6]. The results we obtained are very similar to those reported by Fattuzo and Merz [7]. Spontaneous polarization obtained from hysteresis loops is seen in figure 10. The results exhibited in figure 11 for increasing and decreasing temperature do not show appreciable thermal hysteresis, which is consistent with the small difference between T_0 and T_c. Table I also lists the values of b/a, c/a, T_0 and T_c obtained by fitting the polarization obtained from hysteresis loops for sample (a) to expression (2); and in Table II are presented the corresponding values by fitting

the same data to expression (4). In figure 12 the horizontal dashes represent the fitting of the experimental data to expression (2) and in figure 13 the horizontal dashes represent the fitting of the experimental data to expression (4).

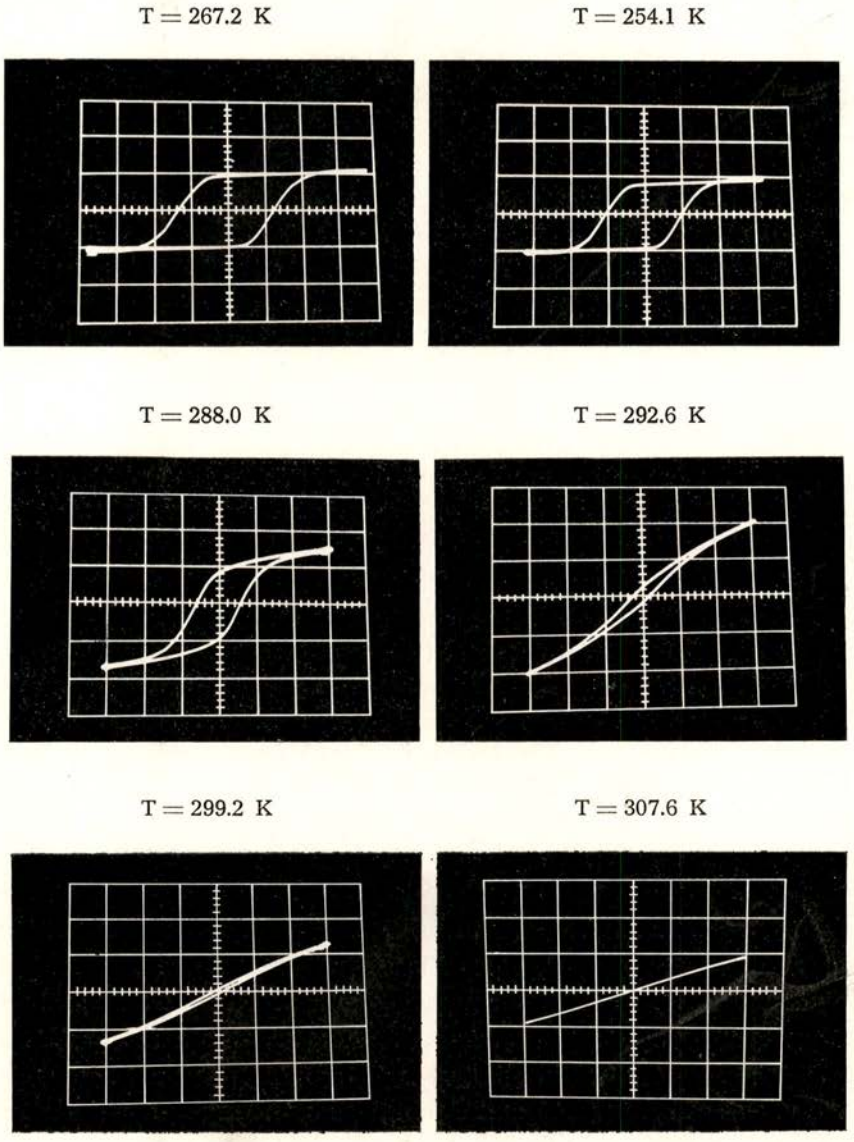

Fig. 9 — SbSI hysteresis loops, at different temperatures, for SbSI (sample (a)).

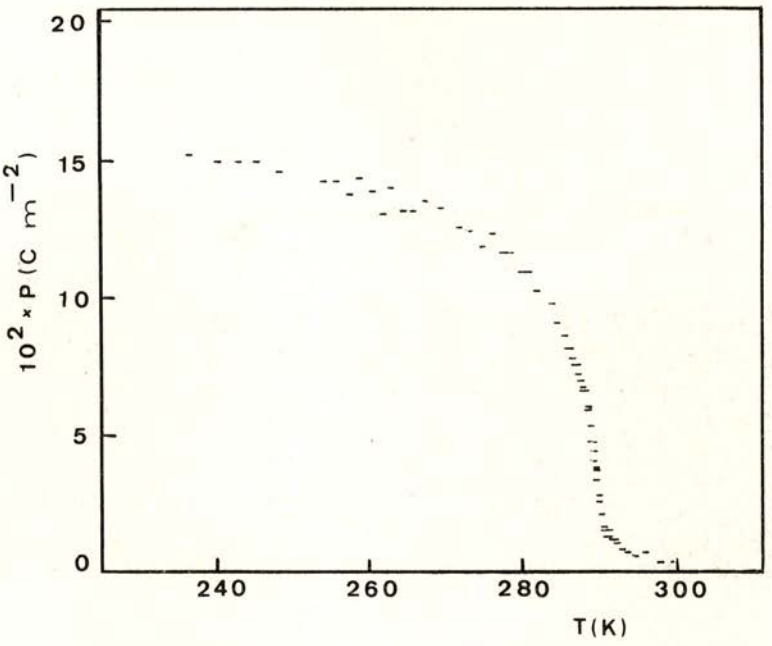

Fig. 10 — Temperature dependence of spontaneous polarization of SbSI (sample (a)) obtained from hysteresis loops.

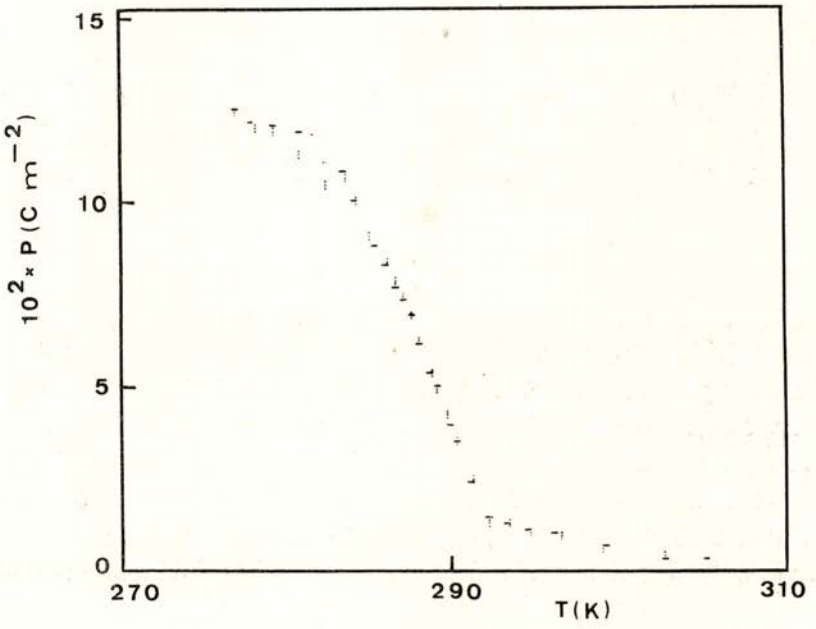

Fig. 11 — Temperature dependence of spontaneous polarization of SbSI (sample (a)), determined for increasing temperatures (vertical dashes) and decreasing temperatures (horizontal dashes).

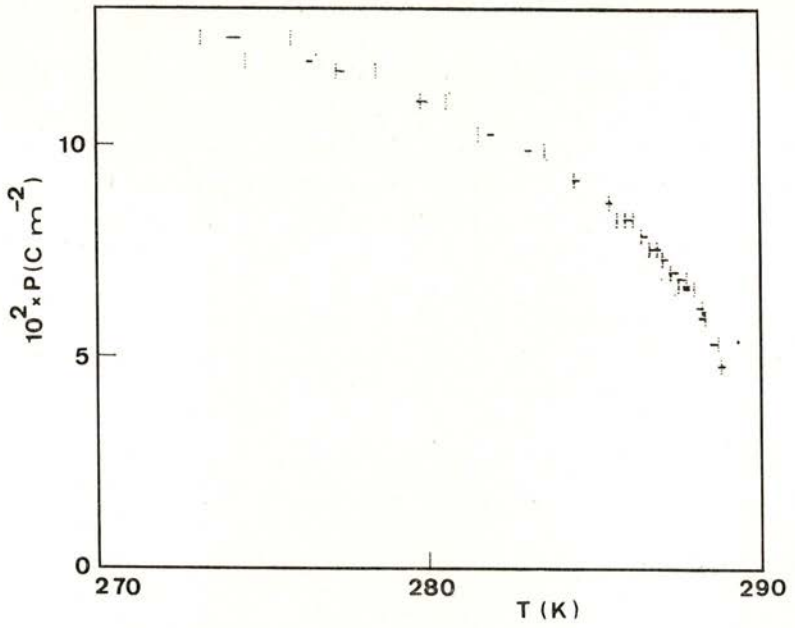

Fig. 12 — Theoretical fitting of P_s versus T (horizontal dashes) for SbSI (sample (a)). Vertical dashes: experimental data obtained from hysteresis loops.

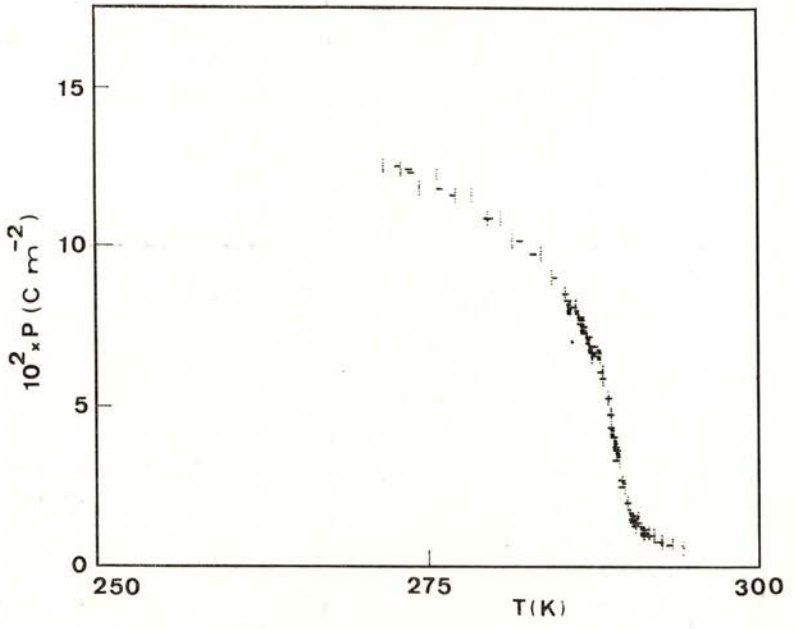

Fig. 13 — Theoretical fitting of P_s versus T including a bias internal electrical field E_b (horizontal dashes) for SbSI (sample (a)). Vertical dashes: experimental data obtained from hysteresis loops.

We have also measured dielectric loss (ε'') and dielectric constant (ε') as a function of the temperature in sample (a) (figure 14). ε' has a maximum value at $T_m = 288.2$ K. The reciprocal of dielectric constant is approximately described by $(\varepsilon')^{-1} \simeq a'(T - T'_0)$ with $a' = 1.66 \times 10^5\ F^{-1}\,K^{-1}m$ and $T'_0 = 277.3$ K for $T > T_c$ (figure 15). For $T < T_c$, we have $(\varepsilon')^{-1} = a''(T - T''_0)$ with $a'' = 1.26 \times 10^6\ F^{-1}\,K^{-1}m$ and $T''_0 = 290.3$ K (figure 15). Measurements of dielectric constant with increasing and decreasing temperature show a very small thermal hysteresis as can be seen in figures 16 and 17.

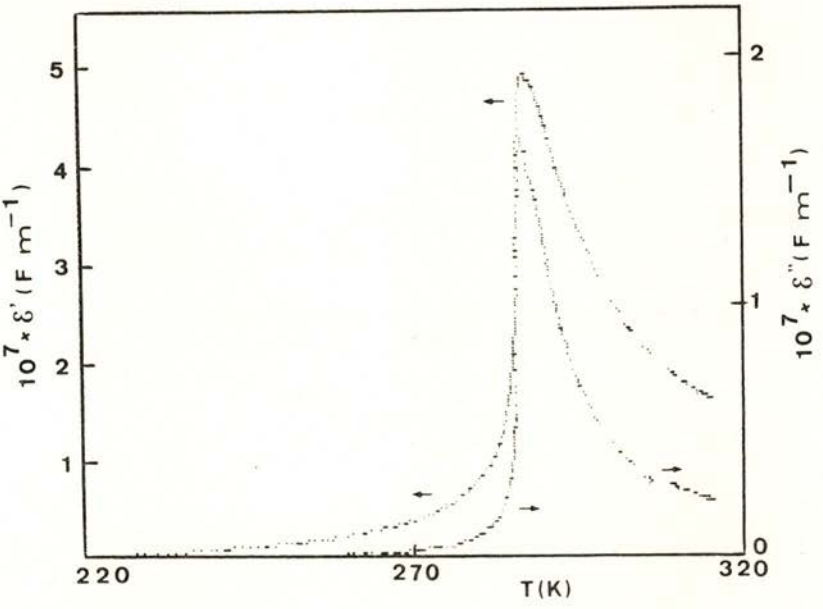

Fig. 14 — Temperature dependence of dielectric constant, ε', and dielectric loss, ε'', for SbSI (sample (a)).

As we can see in figure 18 the reduced dielectric susceptibility obtained with the values listed in Table II (pyroelectric effect) for sample (a) and using expression (5) are in fair agreement with the experimental data.

Landau's theory predicts that $T'_0 = T_0$. Previous results reported for SbSI gave a value of the order of 10 K [8-10] for

the difference $T_c - T'_0$ which is consistent with the result we have obtained for SbSI. To identify T'_0 with T_0, as it is sometimes done, does not seem consistent with the small thermal hysteresis observed in SbSI. Given the large value of 10 K for $T_c - T'_0$ the difference of the stability limits of ferro and paraelectric phase ($T_0 - T_0^-$) would be of the same order of magnitude and so a

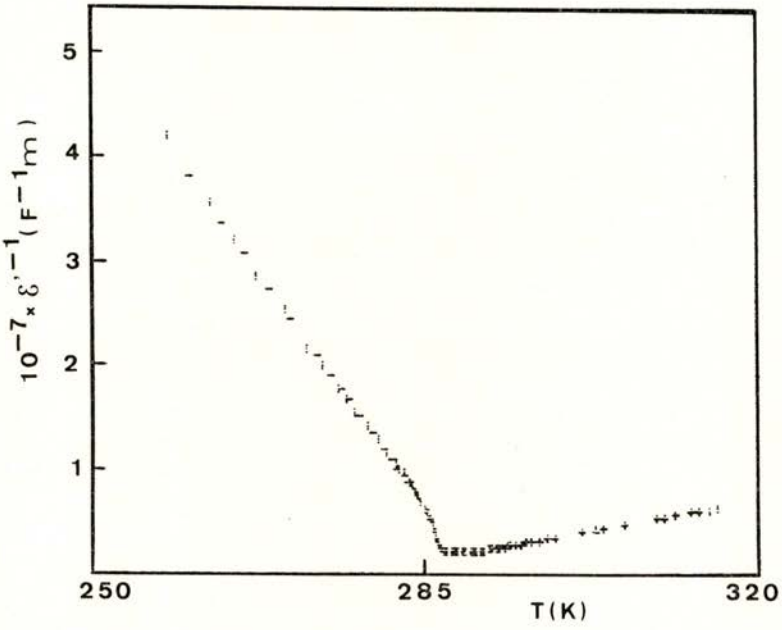

Fig. 15 — Temperature dependence of the reciprocal of dielectric constant for SbSI (vertical dashes). Theoretical fittings (horizontal dashes): see text.

much larger thermal hysteresis should be observed. Stokka *et al* [11], in measurements of specific heat for increasing temperatures, in SbSI, found $T_m - T_0 \sim 1$ K, and a thermal hysteresis of the order of magnitude of 1 K. These results are consistent with those we obtained.

It is not easy to understand the large difference between T_0 and T'_0. As is well known, some ferroelectric properties of SbSI and ABO_3 perovskites, namely the temperature dependence of the soft mode, can be well understood by assuming an anisotropic polarizability of the oxygen and sulfur ions [12].

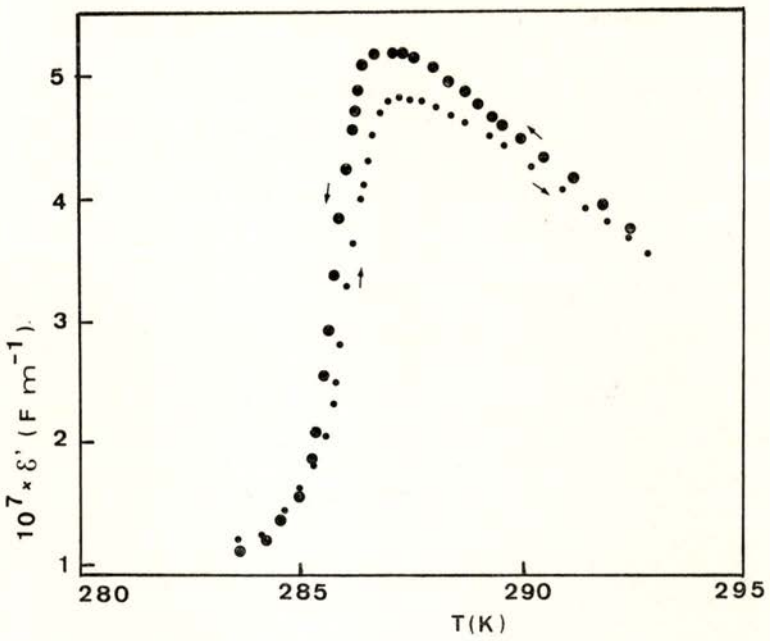

Fig. 16 — Temperature dependence of dielectric constant for sample (a); dots: increasing temperatures; circles: decreasing temperatures.

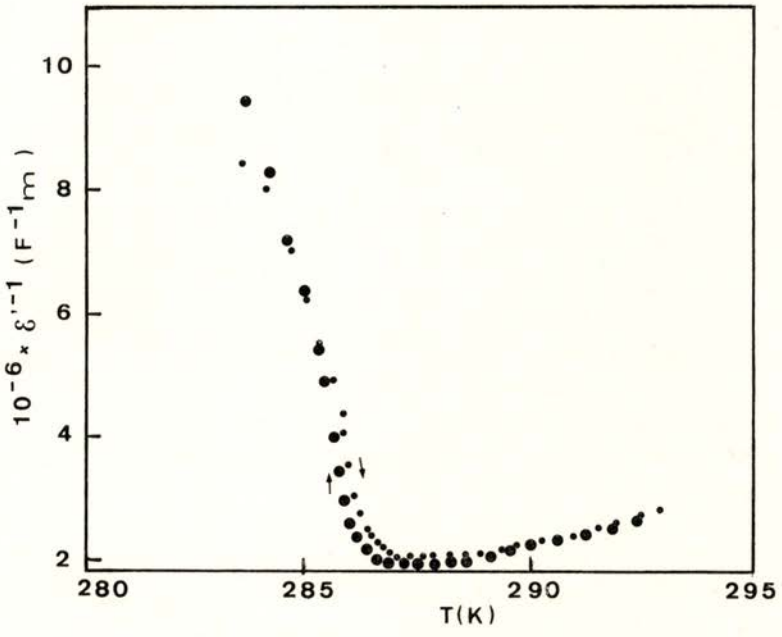

Fig. 17 — Temperature dependence of the reciprocal of dielectric constant for sample (a); dots: increasing temperatures; circles: decreasing temperatures.

Bilz *et al.* consider a quasi-one dimensional shell model, where one sublattice with rigid cations (Sb) is interacting with another sublattice of polarisable anions (S). The third lattice component (I) may be neglected in a first approximation. All long range forces are simulated by nearest neighbor forces, while the

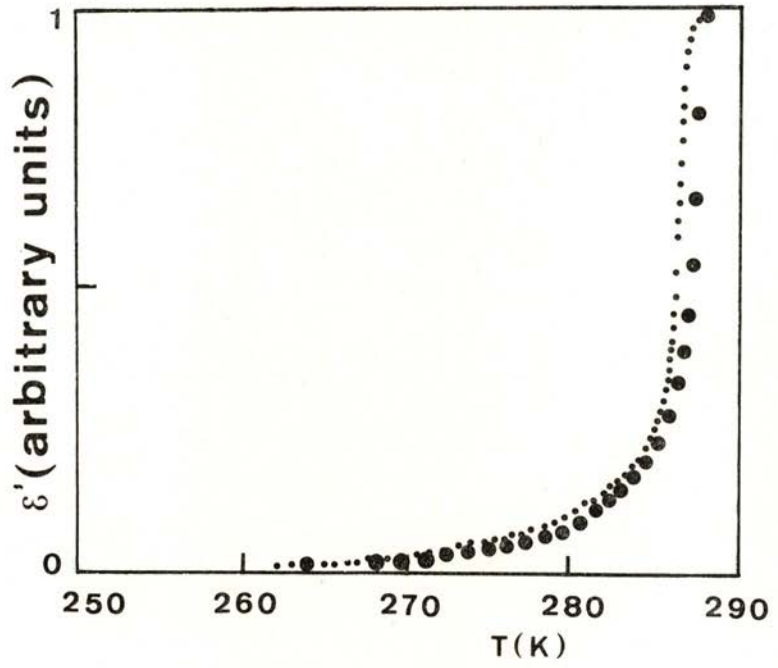

Fig. 18 — Circles: temperature dependence of reduced dielectric susceptibility obtained with values listed in table II for sample (a) ; dots: temperature dependence of reduced dielectric constant exhibited in figure 14.

non-linear polarisability of the anions is described by a quartic (electronic) shell-ion coupling [13]. This model leads to the following expression for dielectric constant as a function of the temperature (Barret formula) :

$$B / (\varepsilon' - A) = (T_f / 2) \coth (T_f / 2T) - T_c \qquad (7)$$

where A and B are parameters, T_f the temperature equivalent to the frequency (ω_f) of the soft mode at the zone boundary in the disperson relation $\omega_f (\mathbf{q})$.

By taking $T_c = 288\,K$ and for different values of T_f we can see in figure 19 a plot of $(T_f/2)\coth(T_f/2T) - T_c$ as a function of T. For $T_f = 200\,K$ we found $T_c - T_0' \simeq 10\,K$, but the value $T_f = 200\,K$ corresponds to a wave number $140\,cm^{-1}$ which is too high compared to the known values of the soft mode frequencies [10]. That model does not give a complete explanation for the observed behaviour in the critical region and so we must find an additional reason for the existence of such a difference between T_0' and T_c.

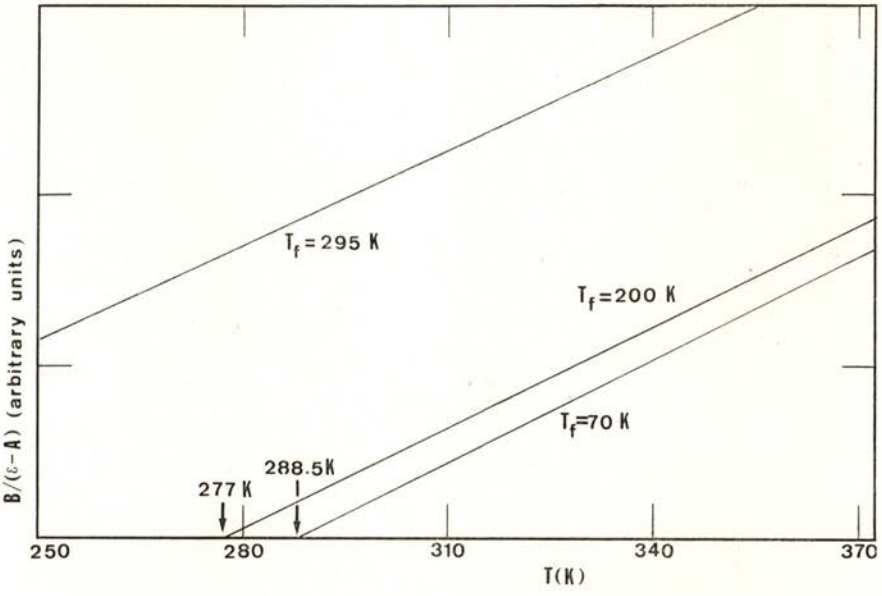

Fig. 19 — A plot of $B/(\varepsilon' - A) = (T_f/2)\coth(T_f/2T) - T_c$ with $T_c = 288\,K$, for several values of T_f.

As there exists strong experimental evidence for a mixing of the soft mode with higher vibration modes, leading to the observation of interesting optical properties in SbSI, it seems that (figure 20) the softening of the low frequency mode is driven by one or two other modes coupled with it [14]. The transition actually occurs when the frequency of the soft mode vanishes at T_c, a few degrees above the paraelectric Curie temperature. The transition

is somewhat "clamped" between T_0' and T_c and this might result from a strong phonon-phonon interaction. This interpretation is well supported by the study of Raman spectra of the ferroelectric transition in SbSI induced by hydrostatic pressure, where one observes a tailing-off of the soft mode above a crossing point, due to a strong interaction between phonons [14]. It might also be possible that a diffuse character in the SbSI transition could explain the large difference between T_0 and T_0'.

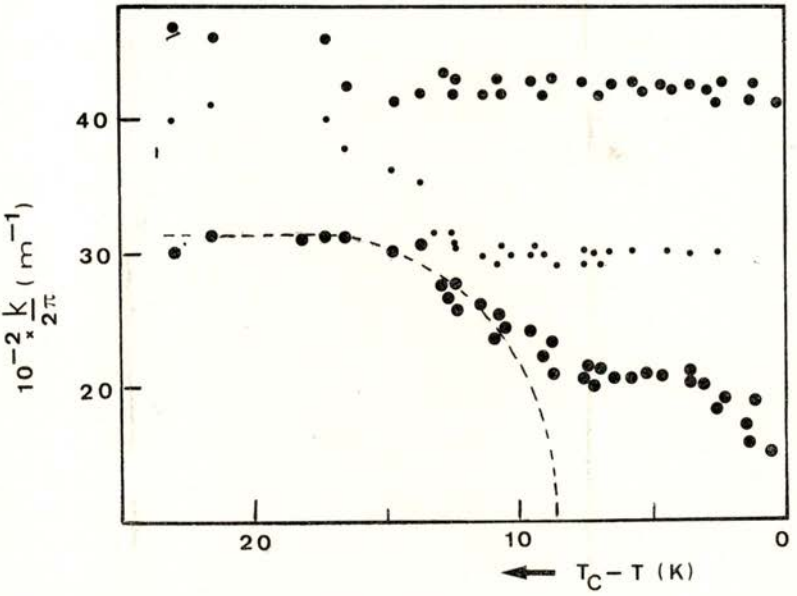

Fig. 20 — A plot of wave numbers versus $T_c - T$ for SbSI. Dots and circles: experimental data taken from reference [14]. The dashed line is a possible curve for the temperature dependence of the uncoupled soft mode wave number.

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