CRITICAL BEHAVIOUR OF SbSBr (*)

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ABSTRACT — A study of critical behaviour in SbSBr is presented and compared with reported data. Critical exponents β, δ, γ and γ' are determined. These values are in disagreement with those predicted by a mean field theory.

1 — INTRODUCTION

SbSBr is one of the $A_V B_{VI} C_{VII}$ ferroelectric compounds. At room temperature it has an orthorhombic structure described by D_{2h}^{16} space group [1]. It is photoconductive and becomes ferroelectric at low temperatures. There has been a large discrepancy on the reported values of the critical temperatures (T_c) of this material. Pikka et al. [1] and Nitsche et al. [2] reported a 'ferroelectric phase transition' at about 90K and Fridkin et al. [3] reported the existence of another phase transition at 178K. Raman scattering measurements suggested a critical temperature of about 39K [4]. Inushima et al. observed the ferroelectric phase transition

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at 22.8K by studying Raman scattering birefringence and electrical permittivity [5, 6, 7, 8].

This rather confusing situation is probably due to the sensitivity of dielectric properties in SbSBr on domains, mechanical strains and impurities.

SbSBr crystals are among the pure ferroelectric materials with lower critical temperature; it lies in the same range of the critical temperatures observed in $K\,Ta_{1-x}\,Nb_x\,O_3$ and $K_{1-x}\,Na_x\,TaO_3$ [9]. For such systems quantum-statistical fluctuations can be predominant and determine the range of stability of the polar phase [9]. The existence of quantum effects on ferroelectric transitions at very low temperatures is a matter of considerable interest and those effects in a quantum crystal can lead to a critical behaviour different from that in a classical crystal. In this work we report an experimental study of electrical permittivity (ε), hysteresis loops and pyroelectric effect, as a function of the temperature, in a SbSBr crystal grown by a vapour transport method. Particular attention is focused on the analysis of the critical behaviour of the electric permittivity and spontaneous polarization.

2 – EXPERIMENTAL

The sample studied was carefully cut with a thickness of 1.4 mm along the c axis (polar axis). The cross section area is 0.73 mm^2. The electrodes were made of silver paste.

Electrical permittivity was measured at a frequency of 10 kHz along the polar direction by using a Hewlett Packard LCR meter 4262A. Hysteresis loops were obtained with a modified Sawyer-Tower circuit at 0.2 Hz frequency.

Fig. 1 (a) shows the relative electrical permittivity (ε_r) as a function of the temperature. A clear anomaly is observed in $\varepsilon_r(T)$ and its maximum value takes place at $T_{max} = 23.8K$. A plot of ε_r^{-1} versus T can be seen in Fig. 1 (b). A detailed behaviour of ε_r and ε_r^{-1} versus T in the critical region are displayed in Fig. 2 (a) and Fig. 2 (b), respectively. Near T_c there is a deviation from the Curie-Weiss law over an appreciable range of temperatures, above and below T_c. In the higher temperature region of the paraelectric phase we remark a kind of saturation of $\varepsilon_r^{-1}(T)$.

Temperature dependence of the spontaneous polarization (P_s) in the same sample was determined by studying ferroelectric

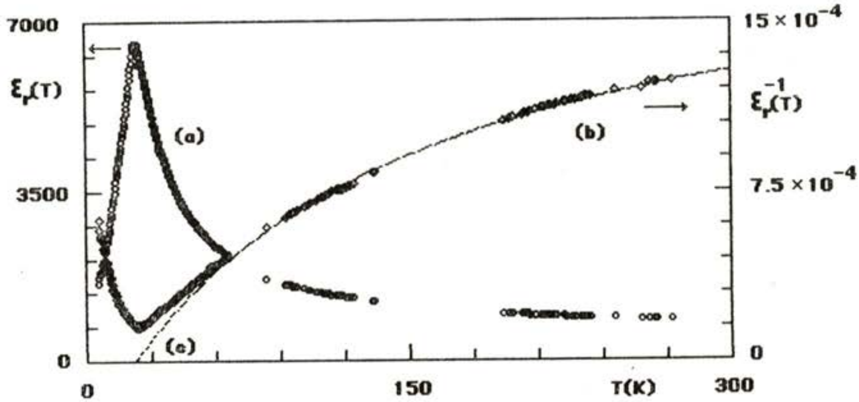

Fig. 1 — Temperature dependence of electrical permittivity parallel to c axis, ε_r (a) and inverse electrical permittivity (b), of SbSBr.

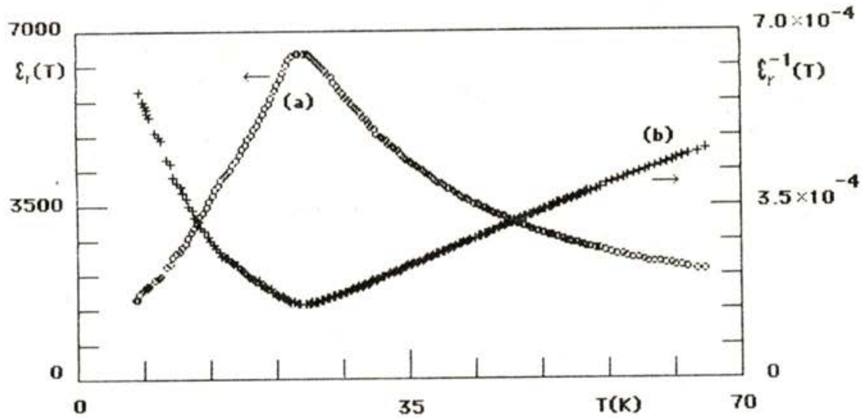

Fig. 2 — Temperature dependence of electrical permittivity parallel to c axis, ε_r (a) and inverse electrical permittivity (b), of SbSBr.

hysteresis loops. No double loops were observed. Fig. 3 shows a plot of P_s versus T; for $4 < T < 10K$, P_s is approximately constant and its value is 6 μCcm^{-2}. A very sharp decrease of P_s is observed around T_c, but above this temperature some residual polarization is still observed up to about 39K. We have also studied the pyroelectric effect in order to see if that important tailing off of polarization was an intrinsic effect or a polarization induced by

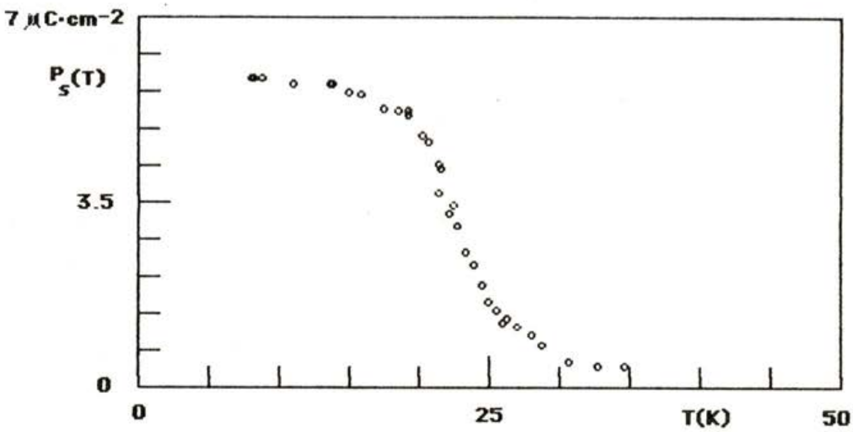

Fig. 3 — Temperature dependence of the spontaneous polarization (P_s) parallel to c axis of SbSBr, obtained from D-E hysteresis loops.

the applied a.c. electric field used to obtain the hysteresis loops. Preliminary results on the pyroelectric effect show a clear anomaly in the critical region (Fig. 4 (a)). Temperature dependence of P_s

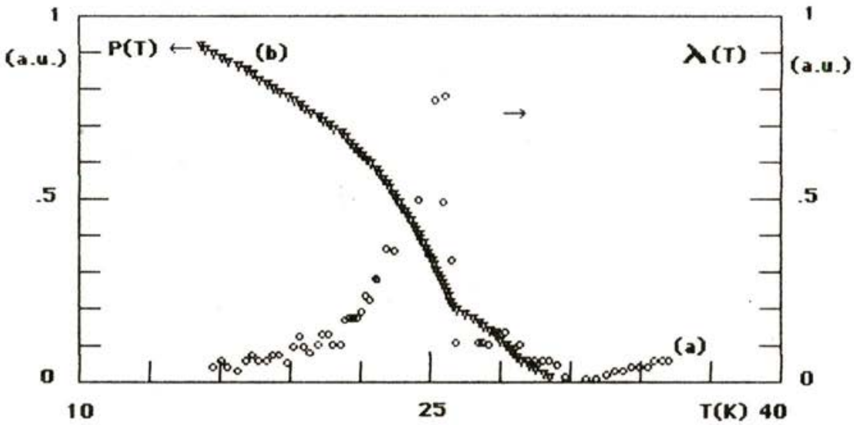

Fig. 4 — Temperature dependence of the pyroelectric coefficient λ (a) and spontaneous polarization, P_s (b) parallel to c axis, of SbSBr.

deduced by integration of the pyroelectric coefficient is similar to that obtained by the hysteresis loops study (Fig. 4 (b)).

In Fig. 5 we can see a plot of the coercive electric field versus temperature and remark a coercive field tailing off.

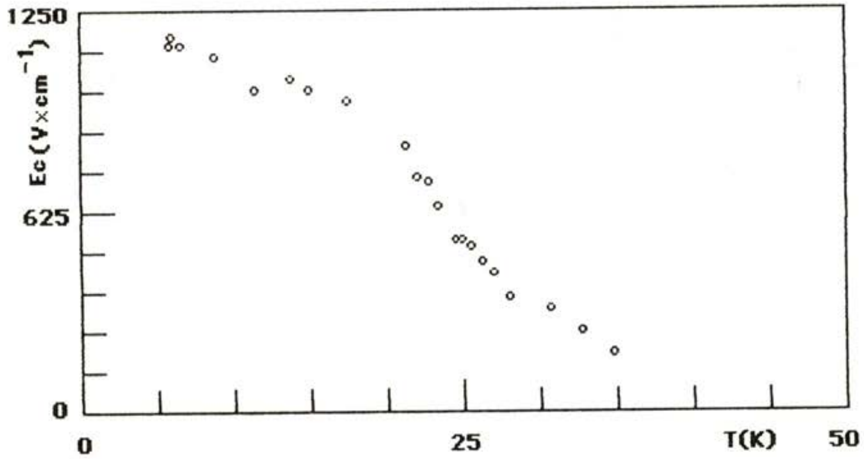

Fig. 5 — Temperature dependence of the coercive electric field (E) in SbSBr.

3 – ANALYSIS AND DISCUSSION

Our experimental results are in good agreement with those previously found in samples of SbSBr, $T_c \sim 23K$ [8]. In all these results we can observe clear deviations from Landau theory predictions and so it seems meaningless to analyse the experimental results in the scope of that theory. It seems that short range interactions must be taken into account for a better understanding of data. Those interactions can arise from intrinsic properties associated with a peculiar behaviour of fluctuations and correlation functions in ferroelectrics with low T_c. Point defects, spatial charges or internal strains in the sample, can also give an important contribution to the critical behaviour.

In order to see to what extent short range interactions would be important, our analysis of the experimental results focuses on the question of existence of single exponent laws and the determination of those exponents.

It is difficult to find an experimental criterion to determine the critical temperature from a study of hysteresis loops. As usual we take the temperature of the maximum of the dielectric constant as the critical temperature.

Fig. 6 shows a plot of ln P_s versus $\ln|t|$, with $t = (T - T_c) / T_c < 0$. From the slope of the straight line drawn in the figure ($0.01 < |t| < 0.6$) we have determined a critical

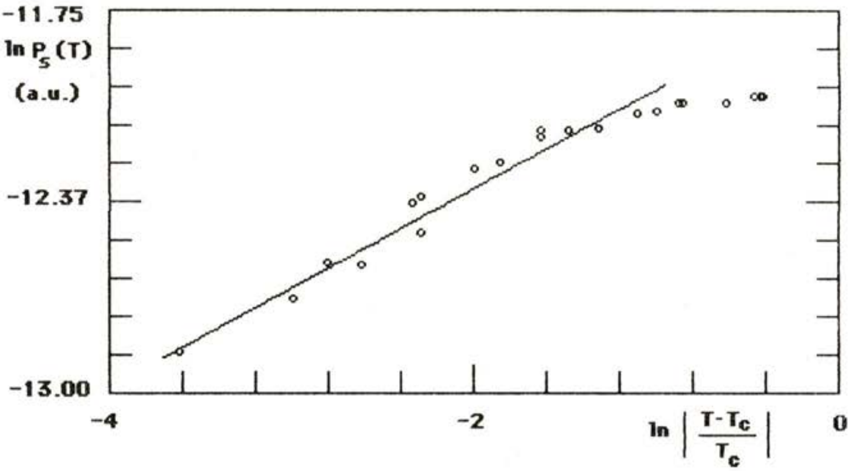

Fig. 6 — Logarithmic plot of the spontaneous polarization (P_s) versus reduced temperature (t).

exponent $\beta = 0.31$. This value closely agrees with $\beta = 0.30 \pm 0.05$, obtained from Raman scattering in SbSBr [4]; it is also of the same order of magnitude as the value $\beta = 0.26$ reported in [8], obtained from a birefringence study. Fig. 7 shows the logarithm of the applied a. c. field (E) versus ln P, for several temperatures near T_c; the data are fitted by lines $\ln E = \tilde{\delta}(T) \ln P + \text{const.}$ A plot of $\tilde{\delta}$ versus T can be seen in Fig. 8: $\tilde{\delta}$ (T) is a function with a rapid variation and so it is difficult to determine precisely the critical exponent δ ($E \sim P^{\delta}$ for $T = T_c$ [10]). The value of $\tilde{\delta}$ for $T_c = 23.8K$ is 4.1.

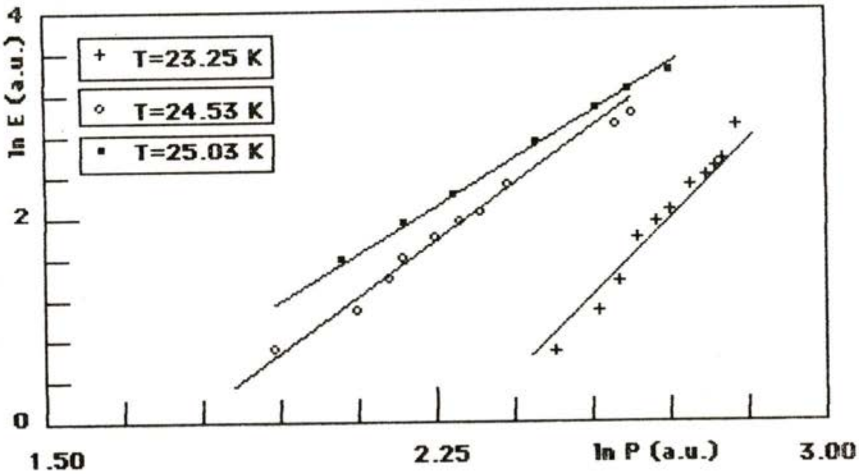

Fig. 7 — Logarithmic plot of electric polarization (P) versus electric field (E), at different temperatures: + 23.25 K, o 24.53 K, ▪ 25.03 K.

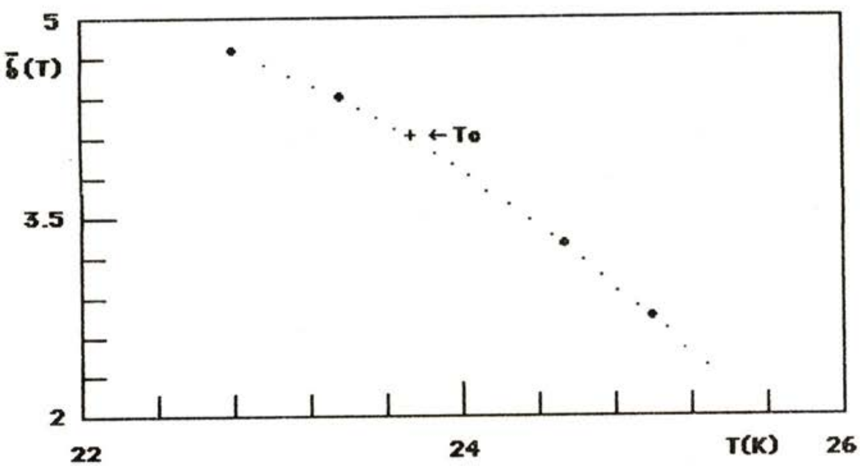

Fig. 8 — $\tilde{\delta}$ (see text) versus temperature (T).

Fig. 9 shows ln ε_r versus ln $|t|$. We can see a flattening of the electric permittivity close to T_c. This situation is commonly encountered in ferroelectrics with low T_c [9]. Well below

T_c the experimental data can be fitted to the expression $\ln \varepsilon_r = -1.38 \ln |t| + 6.99$ $(0.3 < |t| < 0.8)$, and the exponent associated with the electrical susceptibility is $\gamma' = 1.38$.

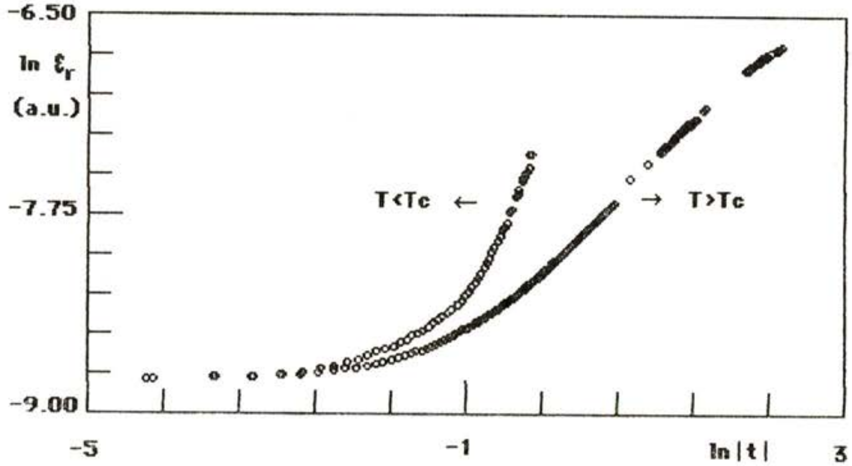

Fig. 9 — Logarithmic plot of electrical permittivity (ε_r) versus reduced temperature (t), for $T < T_c$ and $T > T_c$.

The critical exponents we found for $T < T_c$ clear deviate from those predicted by a mean field theory and can be associated with the role played by fluctuations in the phase transition. In particular, fluctuations can be enhanced by defects of the asymmetric type and it seems plausible that critical exponents in defective systems deviate more from the mean field exponents than those in the pure system [12]. The theoretical values of critical exponents in a 3-dimension short range model with just one order parameter component are $\beta = 0.325$ and $\gamma = \gamma' = 1.241$ [13].

In the paraelectric region the plot of ε_r^{-1} versus T (Fig. 9) allows us to distinguish three regions. Above T ~ 50K the experimental data can be fitted to a modified Curie-Weiss law [11] $\varepsilon_r^{-1} = A_0 (T - T_0) / (T - T_0 + \tilde{T})$, with $T_0 \sim 22.5 \pm 0.5$K, $A_0 \sim (1.96 \pm 0.01) \times 10^{-3}$ and $\tilde{T} = 147.4$K. A similar behaviour is reported in [14]. This law is predicted by a quasi-one dimension shell model which takes into account interactions between two sublattices (rigid cations and polarisable anions) [11]. A single exponent law is verified between 36 K and 50 K and in that region data can be fitted to $\ln \varepsilon_r = -0.59 \ln |t| + 8.02$; which leads to the exponent 0.59. Near T_c there is a considerable roundness in ε_r. A behaviour similar to this one was observed in KH_2PO_4 under a pressure of 15.4 kbar ($T_c = 32K$), as can be seen in Fig. 4c of reference [9].

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