CRITICAL BEHAVIOUR OF DARK CURRENT IN FERROELECTRIC $Bi_{0.08}Sb_{0.92}SI$ (*)

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ABSTRACT — Dark current as a function of temperature has been used to study the ferro-paraelectric phase transition in $Bi_{0.08}Sb_{0.92}SI$.

A simple model is proposed to account for the correlation between the temperature dependence of the activation energy of the impurity levels and the temperature dependence of the intrinsic absorption edge in a one-dimensional structure which $Bi_{0.08}Sb_{0.92}SI$ closely resembles.

1 — INTRODUCTION

Some $A_V B_{VI} C_{VII}$ compounds exhibit a ferro-paraelectric phase transition of displacive nature, accompanied by a change in the coefficient of the temperature dependence of the width of the forbidden gap (E_g) at the critical temperature (T_c); if the transition is of first order there is also a discontinuity in the intrinsic absorption edge at T_c [1]. In SbSI, for instance, this discontinuity is about 0.03 eV ; also $(\partial E_g^+ / \partial T) \simeq -9 \times 10^{-4}$ eV K^{-1} and $(\partial E_g^- / \partial T) \simeq -2.2 \times 10^{-3}$ eV K^{-1}

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in the paraelectric and ferroelectric regions, respectively [2]. A similar behaviour is also observed in SbSBr and BiSBr [2].

These effects should lead to anomalies in the temperature dependence of dark current in the critical region due to the change in the activation energy of the impurity levels, as it was in fact observed in SbSI [3,4].

In the following we have studied the critical behaviour of dark current in ferroelectric mixed compound $Bi_{0.08}Sb_{0.92}SI$ and a simple model is proposed to account for the correlation between the temperature dependence of the activation energy of the impurity levels and the temperature dependence of E_g in a one-dimensional structure which $Bi_{0.08}Sb_{0.92}SI$ closely resembles.

2 — EXPERIMENTAL PROCEDURE

Experimental results were obtained by using needle-shaped crystals, 10-15 mm in length and about 0.2 mm^2 in cross section, as determined by microscope measurements. Silver or gold paste contacts were used. The crystals were polarised with a d.c. field (200-400 V cm^{-1}) while being cooled down slowly to a temperature well below the critical temperature ; care was taken never to subject them to thermal shock. The samples were then heated at constant rates of approximately 1 mK s^{-1} far from the transition while, near the critical temperature, this rate was less than 0.5 mK s^{-1}. Dark current along the c-axis was measured with a Keithley 610 C electrometer under d.c. fields over a range 200-400 V cm^{-1}. The entire apparatus system was shielded from external electric fields.

3 — EXPERIMENTAL RESULTS AND DISCUSSION

In figure 1 we plotted dark current (I) versus inverse temperature for $Bi_{0.08}Sb_{0.92}SI$; this figure clearly shows a different behaviour of I above and below critical temperature. Temperature dependence of dark current and its temperature derivative near T_c are shown in

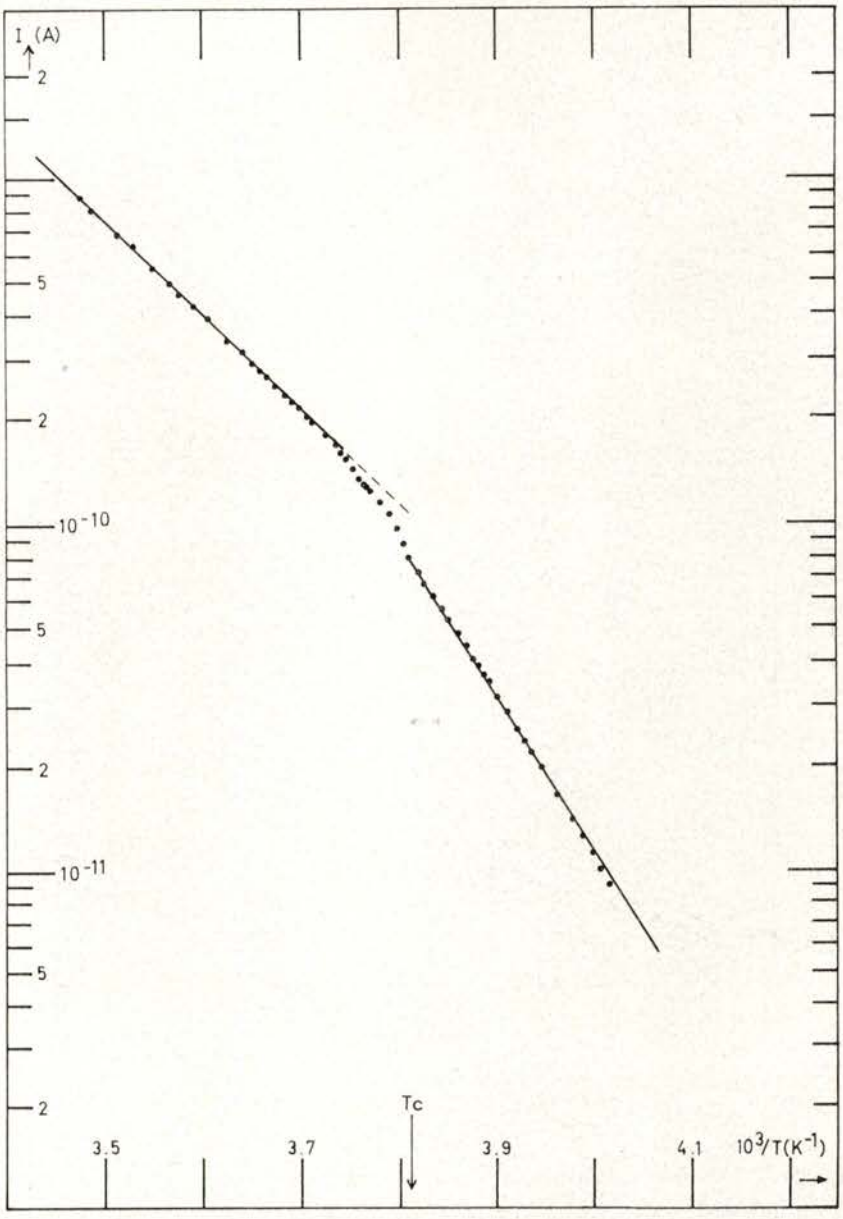

Fig. 1 — Dependence of dark current (I) (logarithmic scale) on the inverse temperature near the critical point.

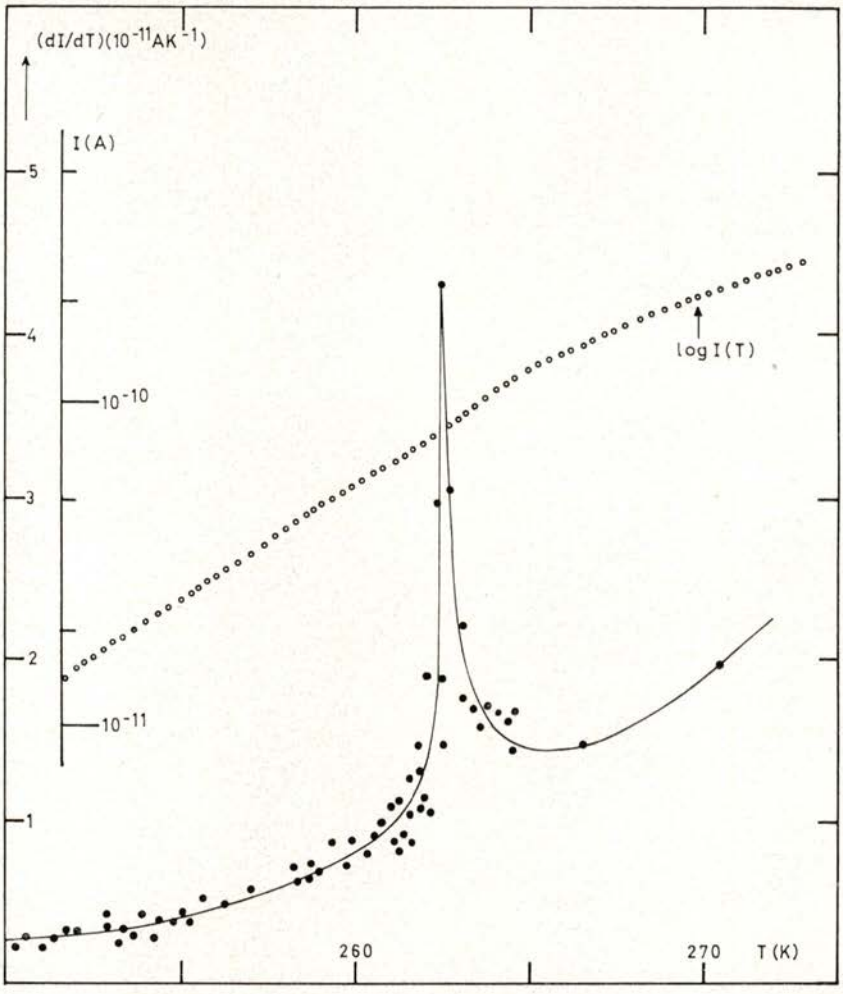

Fig. 2 — Temperature dependences of the dark current (I) (logarithmic scale) and of the temperature derivative of dark current near the critical temperature, $T_c = 262.4$ K.

figure 2. A method of sliding averages was used to calculate the first derivative of I [5]. We take, as usual, the relative maximum of (dI/dT) as the critical temperature (T_c) and for $Bi_{0.08}Sb_{0.92}SI$ we find $T_c \simeq 262.4$ K, lower than the values reported for SbSI, as expected [6,7].

From figure 1 we can see that the dark current above (I_+) and below (I_-) T_c obeys the relations

$$I_{\pm} = A_{\pm} \exp(-E^*_{\pm}/kT) \qquad (1)$$

where $A_{\pm}$ are constants, $E^*_{\pm}$ are the effective activation energies of the impurity levels and k is the Boltzmann constant. We determined:

$$E^*_+ \simeq 0.54 \pm 0.01 \text{ eV} \; ; \; A_+ \simeq 2.670 \text{ A} \; ;$$

$$E^*_- \simeq 0.90 \pm 0.01 \text{ eV} \; ; \; A_- \simeq 1.789 \times 10^7 \text{ A}$$

If the changes in mobility and effective mass of free carriers can be taken as relatively small, the anomalous variation of dark current at the critical region will be mainly associated with the free carrier concentration. Then for a semiconductor with an impurity level of activation energy E, we have $I(T) = A \exp(-E/kT)$.

It seems plausible, as we have assumed for SbSI [4] that the activation energies of impurity levels vary with temperature accompanying a width variation of the forbidden band. Taking into account the experimental results concerning the temperature dependence of dark current, E must be a linear function of temperature in both phases, at least in the range of temperatures we have studied. So

$$E_+ = E_{0+} - a_+(T - T_c) \qquad \text{for } T > T_c$$
$$E_- = E_{0-} - a_-(T - T_c) \qquad \text{for } T < T_c$$

where E_{0+} and E_{0-} are the activation energies of the impurity levels at T_c in the paraelectric and ferroelectric phases, respectively, and a_+, a_- are constants, Accordingly,

$$I_{\pm} = A \exp(a_{\pm}/k) \cdot \exp[-(E_{0\pm} + a_{\pm} T_c)/kT]$$

and by comparison with (1)

$$E^*_{\pm} = E_{0\pm} + a_{\pm} T_c \; ; \; A_{\pm} = A \exp(a_{\pm}/k)$$

The shift of the activation energy (ΔE_c) at the critical temperature is given by

$$I_+ (T_c) / I_- (T_c) = \exp (\Delta E_c / k T_c)$$

From our data we obtain:

$$I_+ (T_c) = 1.16 \times 10^{-10} \text{ A} \; ; \; I_- (T_c) = 9.60 \times 10^{-11} \text{ A} \; ;$$

$$\Delta E_c = |E_{0+} - E_{0-}| = 0.0041 \text{ eV} \; ; \; |a_+ - a_-| = 13.6 \times 10^{-4} \text{ eV K}^{-1} .$$

The relation $|a_+ - a_-| = k \ln (A_- / A_+)$ would, naturally, lead to the same value, 13.6×10^{-4} eV K^{-1}.

These results show that the change in the effective activation energy of the impurity levels at T_c is approximately 0.36 eV whereas the actual shift of the activation energy ΔE_c has a much lower value, about 0.0041 eV. This difference seems to support our assumption that 0.54 and 0.90 eV are not the actual values for the activation energies of the impurity levels.

Experimental results reported for $Bi_xSb_{1-x}SI$ suggest that one of the effects of the atomic substitution of Sb by Bi is the existence of a tricritical point in the (x, T) plane, localized around $x \simeq 0.17$ and $T_t \simeq 211$ K [8,9]. Therefore, as long as the phase transition remains of first order, a decreasing shift of the intrinsic absorption edge at T_c with increasing x is expected. We have found $\Delta E_c = 0.011$ eV for Sb S I which is a higher value than that observed for $Bi_{0.08}Sb_{0.92}SI$ (0.0041 eV).

4 — THEORETICAL MODEL

$A_V B_{VI} C_{VII}$ crystals are generally thin needles, indicating highly anisotropic properties and its structure consists of chains formed by the charged groups $(V-VI)^+$ and $(VII)^-$ running parallel to the c-axis [10]. Bonding between neighbouring chains is weak, probably Van der Waals type, and so if interactions between chains can be

neglected, those compounds may approximately be represented by a linear chain of alternating groups of ions regularly spaced by a distance b as in figure 3. We represent the state in which an extra

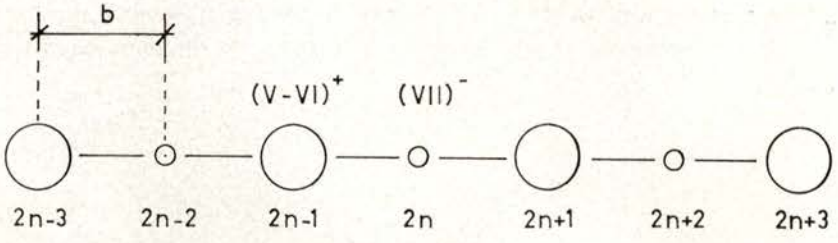

Fig. 3 — Schematic representation of one-dimensional lattice.

electron occupies the 2n site of the linear chain by the ket $|2n>$ and we assume that $\{|2n>\}$ form a complete set of orthonormal eigenfunctions of the Hamiltonian $\hat{H}$ (n positive or negative integer) [11]. For the sake of simplicity we take the Hamiltonian of the system to satisfy:

$$<2n\,|\hat{H}|\,2n> = E_1$$

$$<2n+1\,|\hat{H}|\,2n+1> = E_2$$

$$<2n\,|\hat{H}|\,2n+m> = -A \quad \text{if } m = \pm 1$$

$$<2n\,|\hat{H}|\,2n+m> = 0 \quad \text{otherwise}$$

where E_1, E_2, A are real quantities and $E_1 < E_2$.

With these assumptions, we have two energy bands for the electronic states separated by an energy gap $E_g = E_2 - E_1$. If there is an electronic defect in the chain, e.g. an imperfection in the site 0, one matrix element becomes different, $<0\,|\,\hat{H}\,|\,0> = E_1 + \Delta E$ ($\Delta E > 0$), the other elements remainig unchanged.

We look for solutions of Schrödinger equation of the form

$$|\phi> = \exp(-i E t/\hbar)\,\Sigma_n\, a_n\,|n>,$$

with

$$a_n \text{ (for } n<0,\ n \text{ even)} = \alpha e^{n\chi b};\ a_n \text{ (for } n>0,\ n \text{ even)} = \alpha e^{-n\chi b}$$

$$a_n \text{ (for } n<0,\ n \text{ odd)} = \beta e^{n\chi b};\ a_n \text{ (for } n>0,\ n \text{ odd)} = \beta e^{-n\chi b}$$

where α and β are constants and χ a real positive number.

If we substitute this trial solution into Schrödinger's equation, we have:

$$\begin{aligned}
&\vdots \qquad\qquad\qquad\qquad \vdots \\
E\alpha e^{-2\chi b} &= E_1 \alpha e^{-2\chi b} - A\beta e^{-\chi b} - A\beta e^{-3\chi b} \\
E\beta e^{-\chi b} &= E_2 \beta e^{-\chi b} - A\alpha e^{-2\chi b} - A\alpha \\
E\alpha &= (E_1 + \Delta E)\alpha - A\beta e^{-\chi b} - A\beta e^{-\chi b} \\
E\beta e^{-\chi b} &= E_2 \beta e^{-\chi b} - A\alpha - A\alpha e^{-2\chi b} \\
E\alpha e^{-2\chi b} &= E_1 \alpha e^{-2\chi b} - A\beta e^{-3\chi b} - A\beta e^{-\chi b} \\
&\vdots \qquad\qquad\qquad\qquad \vdots
\end{aligned}$$

The middle five equations are satisfied provided that

$$\begin{aligned}
\beta^2 (E - E_2) &= \alpha^2 (E - E_1) \\
e^{-\chi b} &= -\alpha (E - E_1 - \Delta E)/(2A\beta) \\
e^{+\chi b} &= \alpha (E_1 - E - \Delta E)/(2A\beta).
\end{aligned}$$

These equations are consistent only if,

$$[(E - E_1)^2 - (\Delta E)^2](E - E_2) = 4A^2 (E - E_1).$$

The energy of the trapped electron is given by E in this expression if $0<(E-E_1)<E_g$. Taking $E_2 - E_1 = E_g$ and $E - E_1 = x$, we have,

$$(x - E_g)[x^2 - (\Delta E)^2] = 4A^2 x \qquad (2)$$

We now suppose ΔE and A to be very slow varying functions of temperature as compared with E_g and x. This seems to be the

situation for $A_V\ B_{VI}\ C_{VII}$ compounds. Taking the temperature derivative of the last equation, we find.

$$dx/dT = (dE_g/dT) \cdot [x^2 - (\Delta E)^2]/[3x^2 - 2E_g x - (\Delta E)^2 - 4A^2].$$

So the temperature derivative of the activation energy (x) depends on the temperature derivative of E_g, on the energy of the trapped electron in the lattice defect and on the probability amplitude, per unit time, for the electron to jump from one atom to the next one. If ΔE , $A >> x$, then

$$dx/dT \simeq (dE_g/dT) \cdot (\Delta E)^2/[(\Delta E)^2 + 4A^2].$$

Therefore the thermal derivative of the impurity activation energy is smaller than the thermal derivative of the gap width E_g.

We have collected in table I values of x $(0 < x < E_g)$ and dx/dT calculated for different values of $(\Delta E)^2$ and A^2 . We have taken $E_g = 1.9 - 0.003\ \Delta T$ eV, where $\Delta T = T - T_c$ was assumed to be 1 K; these values are suggested by the experimental data for SbS_4I [2].

TABLE I

$(\Delta E)^2$ [(eV)^2]	$4A^2$ [(eV)^2]	x [eV]	dx/dT [eV K^{-1}]
0.05	0.01	0.221	0.059×10^{-4}
0.1	1	0.141	1.5
0.5	0.5	0.546	2.8
0.5	1	0.442	3.6
0.75	0.75	0.621	4.1
1.85	1	0.936	7.7
1.85	10	0.285	4.1
1.85	100	0.034	0.55
1.88	0.1	1.29	3.4
1.899	0.01	1.37	0.49
1.899	1	0.948	7.9
1.899	1.7	0.804	8.0
1.899	8	0.345	4.9
3	0.1	1.581	9.4
5	0.1	1.796	24

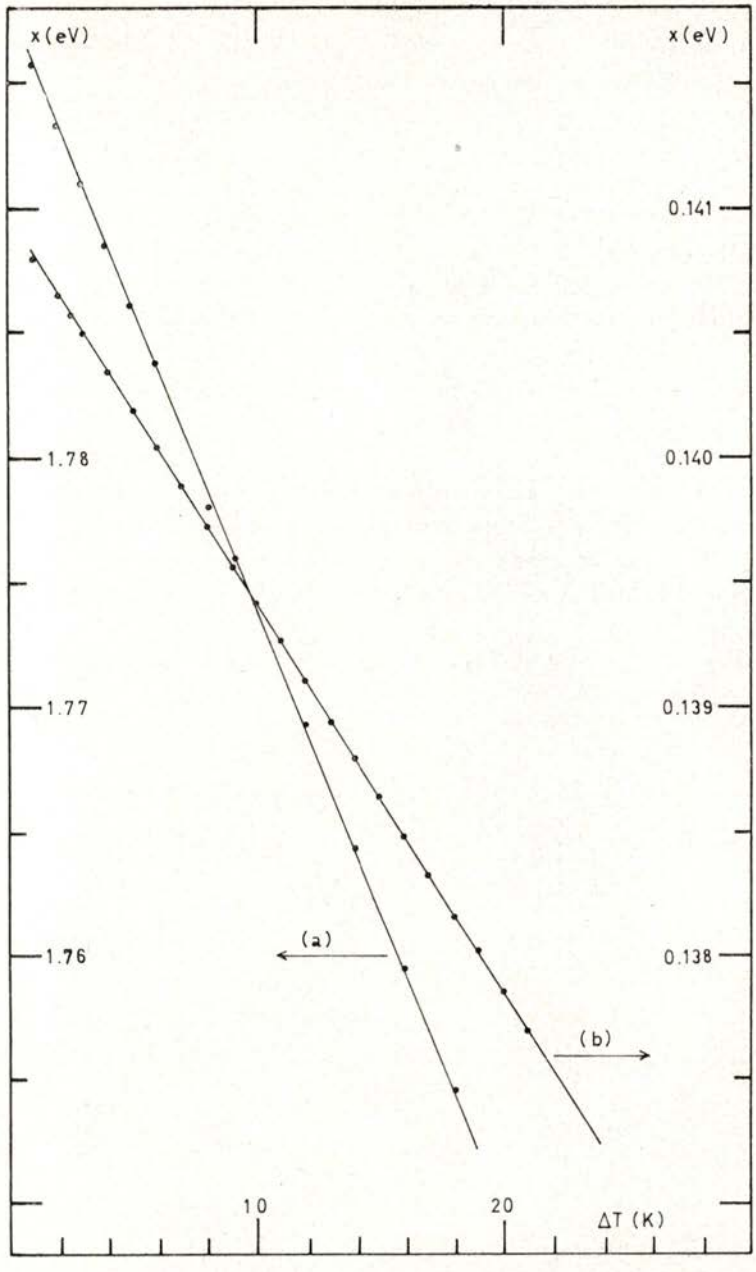

Fig. 4 — Theoretical values of x versus $\Delta T = T - T_c$ taken from eq. (2), with $E_g = 1.9 - 0.003\ \Delta T$ eV
curve a) $(\Delta E)^2 = 0.1$ (eV)^2; $4A^2 = 1$ (eV)^2.
curve b) $(\Delta E)^2 = 5$ (eV)^2; $4A^2 = 0.1$ (eV)^2.

In a range of $\Delta T = 20$ K, x varies linearly with temperature as can be seen in fig. 4. Hence our simple model seems to account for the main results concerning dark current behaviour in SbSI and $Bi_{0.08}\,Sb_{0.92}\,S\,I$ near the critical region.

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